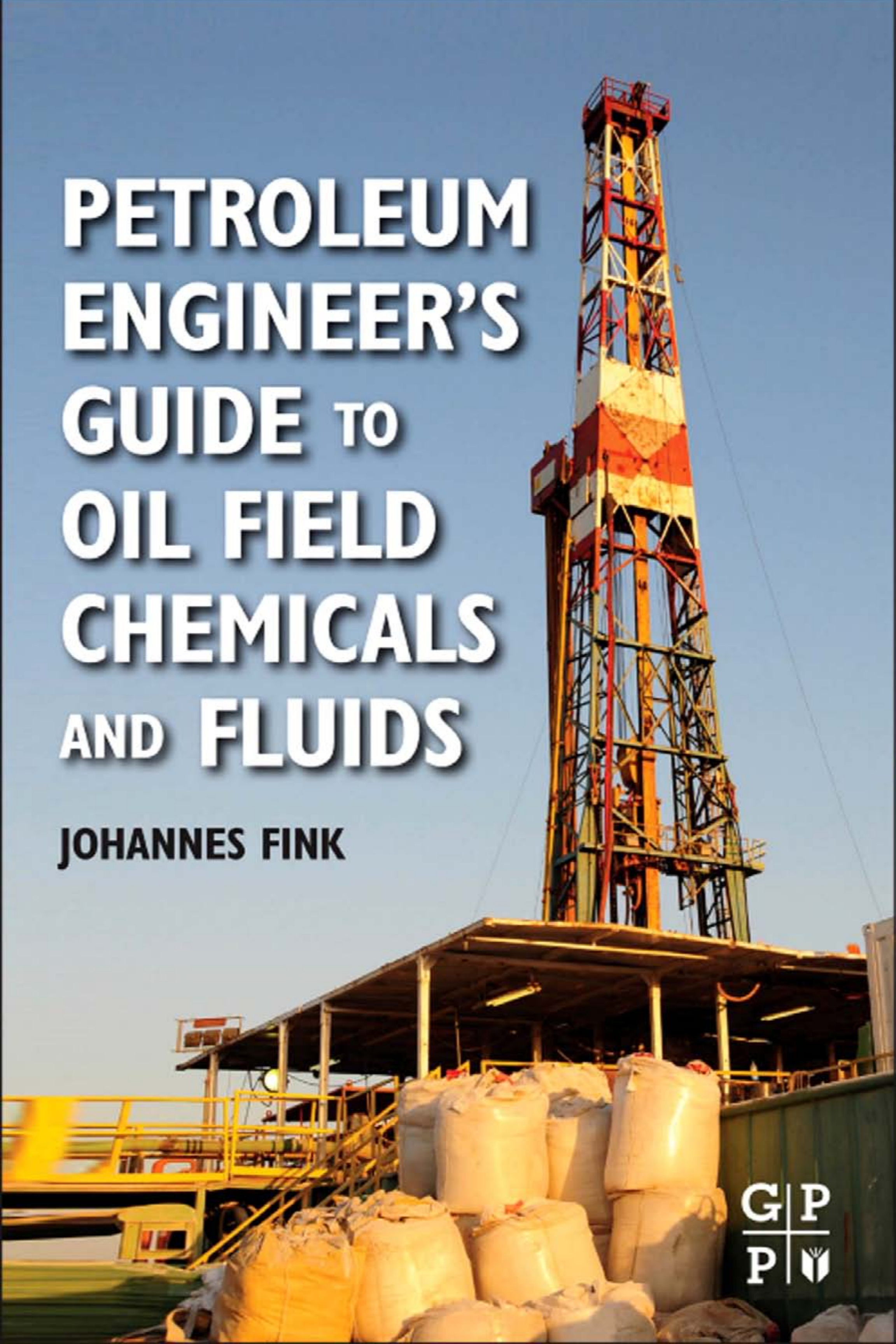

PETROLEUM ENGINEER'S GUIDE TO OIL FIELD CHEMICALS AND FLUIDS

JOHANNES FINK

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Petroleum Engineer's Guide to Oil Field Chemicals and Fluids

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Johannes Karl Fink

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Preface

This manuscript is an extension and update of *Oil Field Chemicals*, which appeared in 2003. The text focuses mainly on the organic chemistry of oil field chemicals. As indicated by the title, engineers with less background in organic chemistry are likely to use this text, so various sketches of the chemicals and additional explanations and comments are included in the text with which an educated organic chemist will certainly be familiar.

The material presented here is a compilation from the literature, including patents, arranged in the order needed by a typical job. It starts with drilling fluids and related classes of compounds, such as fluid loss, bit lubricants, etc. Then it crosses over to the next major topics: cementing, fracturing, enhanced recovery, and it ends with pipelines and spill.

Some of the chemicals are used in more than one main field; for example, surfactants are used in nearly all applications. To these chemicals the last three chapters are devoted. As environmental aspects are gaining increasing importance, this issue is dealt with carefully.

HOW TO USE THIS BOOK

Index

There are four indices: an index of tradenames, an index of acronyms, an index of chemicals, and a general index.

If an acronym occurs for the first time in a chapter, it is expanded to its long form, e.g., acrylic acid (AA) and placed in the index. Subsequent occurrences only show the short form, i.e., AA. If the term occurs only once in a specific chapter, it is given exclusively in the long form.

In the chemical index, bold faced page numbers refer to the sketches of structural formulas or to reaction equations.

Bibliography

A bibliography is given for each chapter and is sorted in the order of occurrence. After the bibliography, a list of tradenames that are found in the references and which chemicals are behind these names, as far is known, is added.

ACKNOWLEDGMENTS

I am indebted to our local library, Dr. C. Hasenhüttl, Dr. J. Delanoy, and Mr. C. Slamenik for support in literature acquisition. Thanks are given to Professor I. Lakatos, University of Miskolc, who directed my interest to this topic, and to my wife Margit who encouraged me to finalize the material when I felt exhausted. Last but not least, I want to thank the publisher for kind support, in particular Ken McCombs and Jill Leonard.

J.K.F.

Chapter 1

Drilling Muds

According to the American Petroleum Institute (API), a drilling fluid is defined as a circulating fluid, used in rotary drilling to perform any or all of the various functions required in drilling operations.

Drilling fluids are mixtures of natural and synthetic chemical compounds used to cool and lubricate the drill bit, clean the hole bottom, carry cuttings to the surface, control formation pressures, and improve the function of the drill string and tools in the hole. They are divided into two general types: water-based drilling muds (WBMs) and oil-based drilling muds (OBMs). The type of fluid base that is used depends on drilling and formation needs, as well as the requirements for disposing of the fluid after it is no longer needed. Drilling muds are a special class of drilling fluids used to drill most deep wells. The term *mud* is used because of the thick consistency of the formulation.

Drilling fluids serve several fundamental functions (Brazzel, 2009; Melbouci and Sau, 2008):

- Control of downhole formation pressures,
- Overcoming the fluid pressure of the formation,
- Avoiding damage to the producing formation,
- Removal of cuttings generated by the drill bit from the borehole, and
- Cooling and lubricating the drill bit.

In order to perform their fundamental functions, drilling fluids should possess several desirable characteristics, which greatly enhance the efficiency of the drilling operation.

These include desired rheological properties (plastic viscosity, yield value, low-end rheology, and gel strengths), fluid loss prevention, stability under various temperature and pressure operating conditions, stability against contaminating fluids, such as salt water, calcium sulfate, cement, and potassium contaminated fluids (Melbouci and Sau, 2008).

The drilling fluid should also have penetration enhancement characteristics that wet the drill string and keep the cutting surfaces of the drill bit clean (whether it is a roller cone or other configuration).

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Wetting ability is at least in part a function of the surface tension of the fluid. The fluid should also have a high degree of lubricity and to minimize friction between the drill string and the wall of the borehole to minimize of differential sticking. In this situation, the hydrostatic pressure of the drilling fluid column must be sufficiently higher than the formation pressure so that the drill string is forced against the wall of the borehole and stuck.

It should also prevent the solids of the formation, primarily shales and clays, from swelling, so reducing the incidence of drill sticking, undergauge holes etc.

CLASSIFICATION OF MUDS

The classification of drilling muds is based on their fluid phase alkalinity, dispersion, and the type of chemicals used in their formulation. The classification according to (Lyons, 1996) is reproduced in Table 1.1.

Drilling muds are usually classified as either WBMs or OBMs, depending upon the continuous phase of the mud. However, WBMs may contain oil and OBMs may contain water (Guichard et al., 2008).

OBMs generally use hydrocarbon oil as the main liquid component, with other materials such as clays or colloidal asphalts being added to provide the desired viscosity together with emulsifiers, polymers, and other additives including weighting agents. Water may also be present, but in an amount not usually greater than 50% by volume of the entire composition. If more than

TABLE 1.1 Classification of Drilling Muds

Class	Description
Fresh water muds[d]	pH from 7–9.5, include spud muds, bentonite-containing muds, phosphate-containing muds, organic thinned muds (red muds, lignite muds, lignosulfonate muds), organic colloid muds
Inhibited muds[d]	Water-based drilling muds that repress hydration of clays (lime muds, gypsum muds, sea water muds, saturated salt water muds)
Low-solids muds[n]	Contain less than 3–6% of solids. Most contain an organic polymer
Emulsions	Oil in water and water in oil (reversed phase, with more than 5% water)
OBMs	Contain less than 5% water; mixture of diesel fuel and asphalt

d) Dispersed systems
n) Nondispersed systems

about 5% of water is present, the mud is often referred to as an invert emulsion, i.e., a water-in-oil emulsion.

WBMs conventionally contain viscosifiers, fluid loss control agents, weighting agents, lubricants, emulsifiers, corrosion inhibitors, salts, and pH control agents. Water makes up the continuous phase of the mud, and is usually present as at least 50 volume percent of the entire composition. Oil is also usually present in small amounts, but will typically not exceed the amount of the water, so that the mud will retain its character as a water-continuous-phase material.

Potassium muds are the most widely accepted water mud system for drilling water sensitive shales. K^+ ions attach to clay surfaces and lend stability to the shale that is exposed to drilling fluids by the bit. The ions also help to hold the cuttings together, minimizing its dispersion into finer particles. Potassium chloride, KCl is the most widely used source of potassium, with others being potassium acetate, potassium carbonate, potassium lignite, potassium hydroxide, and potassium salt of partially hydrolyzed polyacrylamide (PHPA).

For rheological control, different types of polymers are used, such as xanthan gum and PHPA. For fluid loss control, mixtures of starch and polyanionic cellulose (PAC) are often used. Carboxymethyl starch, hydroxypropyl starch, carboxymethyl cellulose (CMC), and sodium polyacrylate are also used. PHPA is widely used for shale encapsulation.

Salt water muds contain varying amounts of dissolved sodium chloride (NaCl) as a major component. Undissolved salt may also be present in saturated salt muds to increase density or to act as a bridging agent over permeable zones. Starch and its derivatives for fluid loss control, and xanthan gums for hole cleaning are among the few additives that are effective for salt water muds.

Sea water mud is a WBM designed for offshore drilling whose make-up water is taken from the ocean. Sea water has relatively low salinity, containing about 3–4% of NaCl, but has a high hardness because of the presence of Mg^{+2} and Ca^{+2} ions. This hardness is removed from sea water by adding NaOH (sodium hydroxide), which precipitates Mg^{+2} as $Mg(OH)_2$ (magnesium hydroxide) and by adding Na_2CO_3 (sodium carbonate), which removes Ca^{+2} as $CaCO_3$ (calcium carbonate). The additives are the same as those used in fresh water muds (Guichard et al., 2008), namely

- Bentonite clay,
- Lignosulfonate,
- Lignite,
- CMC, or
- PAC, and
- Caustic soda.

Xanthan gum may be used in place of bentonite. Silicate-mud is a type of shale-inhibitive water mud that contains sodium or potassium silicate as the inhibitive component. If this material is used, then a high pH is a necessary characteristic of silicate muds in order to control the amount and type of polysilicates that are formed. This is achieved by the addition of NaOH (or KOH) and the appropriate silicate solution. Silicate anions and colloidal silica gel combine to stabilize the wellbore by sealing microfractures, forming a silica layer on shales and possibly acting as an osmotic membrane, which can produce in-gauge holes through troublesome shale sections that otherwise might require an oil mud.

Lime mud is a type of WBM that is saturated with lime ($Ca(OH)_2$), and has excess, undissolved lime solids maintained in reserve. Fluid loss additives include starch, hydroxypropyl starch, CMC, or PAC (Guichard et al., 2008).

Dispersed Noninhibited Systems

Drilling fluids used in the upper hole sections are referred to as *dispersed noninhibited systems*. They are formulated from fresh water and may contain bentonite. The classification of bentonite-based muds is shown in Table 1.2. The flow properties are controlled by a flocculant or thinner, and the fluid loss is controlled with bentonite and CMC.

Phosphate-treated Muds

Phosphates are only effective in small concentrations, and the mud temperature must be less than 55°C. The salt contamination must be less than 500 ppm sodium chloride. The concentration of calcium ions should be kept as low as possible. The pH should be between 8 and 9.5. Some phosphates may decrease the pH, so more NaOH must be added.

Lignite Muds

Lignite muds are temperature resistant up to 230°C. Lignite can control viscosity, gel strength, and fluid loss. The total hardness must be lower than 20 ppm.

TABLE 1.2 Classification of Bentonite Fluid Systems

Solid–solid Interactions	Inhibition Level	Drilling Fluid Type
Dispersed	Noninhibited	Fresh water clay NaCl $< 1\%$, $CaCl_2$, < 120 ppm
Dispersed	Inhibited	Saline fluids, Na^+, Ca^{2+} salt, saturated salt, gypsum, lime)
Nondispersed	Noninhibited	Fresh water low-solids muds
Nondispersed	Inhibited	Salt and polymer fluids

Quebracho Muds

Quebracho is a natural product extracted from the heartwood of the Schinopsis trees that grow in Argentina and Paraguay. It is a well-characterized polyphenolic, readily extracted from the wood by treatment with hot water, and is widely used as a tanning agent. It is also used as a mineral dressing, as a dispersant in drilling muds, and in wood glues. Quebracho is commercially available as a crude hot water extract, either in lump, ground, or spray-dried form, or as a bisulfite-treated, spray-dried product that is completely soluble in cold water. It is also available in a bleached form, which can be used in applications where the dark color of unbleached quebracho is undesirable (Shuey and Custer, 1995).

Quebracho-treated fresh water muds were originally used at shallow depths. It is also referred to as *red mud* because of the deep red color. Quebracho acts as a thinner. Polyphosphates are also added when Quebracho is used. Quebracho is active at low concentrations and consists of tannates.

Lignosulfonate Muds

Lignosulfonate fresh water muds contain ferrochrome lignosulfonate for viscosity and gel strength control. These muds are resistant to most types of drilling contamination because of the thinning efficiency of the lignosulfonate in the presence of large amounts of salt and at extreme hardnesses.

Lime Muds

Lime muds contain caustic soda, an organic thinner, hydrated lime, and a colloid for filtrate loss. From this a pH of 11.8 can result, with calcium ions at a concentration of 3–20 ppm in the filtrate. Lime muds exhibit low viscosity, low gel strength, and good suspension of weighting agents. They can carry a larger concentration of clay solids at lower viscosities than other types of mud. At high temperatures, lime muds present a danger of gelation.

Sea Water Muds

The average composition of sea water is shown in Table 1.3. Most of the hardness in sea water is caused by magnesium. Sea water muds have sodium chloride concentrations above 10,000 ppm. They also contain bentonite, thinner (lignosulfonate or lignosulfonate with lignite), and an organic filtration control agent.

Nondispersed Noninhibited Systems

In nondispersed systems no special agents are added to deflocculate the solids in the fluid. The main advantages of these systems are the higher viscosities and the higher yield point-to-plastics viscosity ratio. These alterated flow properties

TABLE 1.3 Composition of Sea Water

Component	Concentration/[ppm]
Sodium	10,500
Potassium	400
Magnesium	300
Calcium	400
Chloride	19,000
Sulfate	3,000

provide a better cleaning of the borehole, allow a lower annular circulating rate, and minimize the washout of the borehole.

Low-solids Fresh Water Muds

Clear fresh water is the best drilling fluid in terms of penetration rate. Therefore, it is desirable to achieve a maximal drilling rate using a minimal amount of solid additives. Originally, low-solids mud formulations were used in hard formations, but they now also tend to be used in other formations. Several types of flocculants are used to promote the settling of drilled solids by flocculation.

Variable Density Fluids

Variable density fluids are those that have a density which varies as a function of the pressure in the subterranean formation. Such a fluid comprises a base fluid and a proportion of elastic particles.

These elastic particles allow the density of the variable density fluid to vary as a function of pressure. For instance, as the elastic particles encounter higher downhole pressures, they become compressed, thereby decreasing the volume and in turn increasing the density of the fluid that contains them. When the elastic particles are fully compressed, the density increases considerably.

The increase in volume of the elastic particles in turn reduces the overall density of the variable density drilling fluid. The resulting change in density may be sufficient to permit the return of the variable density fluid through the riser to the surface without the need for any additional pumps or subsurface additives (Ravi et al., 2009).

The elastic particles are usually either a copolymer of styrene and divinylbenzene, a copolymer of styrene and acrylonitrile, or a terpolymer of styrene, vinylidene chloride, and acrylonitrile (Ravi et al., 2009).

Gas-based Muds

Although natural gas (methane) exhaust or other combustion gases can be used, air is the most common gas to be used in such drilling fluids. It is used to produce so-called foam muds, in which air bubbles are surrounded by a film of water containing a foam-stabilizing substance or film-strengthening material, such as an organic polymer or bentonite.

This type of mud is not recirculated and is often used for reduced-pressure drilling to improve the hole stability in caving formations. However, this type of mud has some limitations, since the drilling water produces wet formations, and it has a limited salt tolerance.

Drill-in Fluids

After drilling a well to the total depth, it is a normal practice to replace the drilling mud with a completion fluid. This fluid is a clean, solids-free, or acid soluble, non-damaging formulation, intended to minimize reductions in permeability of the producing zone. Prior to producing from the formation, it is usually necessary to clean up what is left by the original mud and the completion fluid, by breaking and degrading the filter cake with an oxidizer, enzyme, or an acid solution.

Nowadays, many wells exploit the pay-zone formations for long distances horizontally. It is no longer practical in these wells to drill the pay-zone with conventional, solids-laden muds, as the extended clean-up process afterwards is much more difficult. Consequently, the current generation of drill-in fluids was developed.

Drill-in fluids are completion fluids, but they also act as drilling muds. As the pay-zone is penetrated horizontally, these fluids must provide the multifunctional requirements of drilling fluids in addition to the non-damaging attributes of completion fluids. In practice, the normal drilling mud is replaced with a drill-in fluid just before the pay-zone is penetrated, and used until the end of the operation.

MUD COMPOSITIONS

Commercial products are listed in the literature. The additional components include bactericides, corrosion inhibitors, defoamers, emulsifiers, fluid loss and viscosity control agents, and shale control additives (Anonymous, 1991a,b,c, 1992, 1996).

Inhibitive Water-based Muds

Minimizing the environmental impact of the drilling process is a highly important part of drilling operations, in order to comply with environmental regulations which have become stricter throughout the world. In fact, this is a mandatory requirement for the North Sea sector. The drilling fluids industry has made significant progress in developing new fluids and ancillary additives to fulfill the increasing technical demands for drilling oil wells. Additives now have very little or no adverse effects on the environment or on drilling economics.

New drilling fluid technologies have been developed to allow the continuation of oil-based performance with regard to formation damage, lubricity, and wellbore stability aspects and thus penetration rates. These aspects were greatly improved by incorporating polyols or silicates as shale inhibitors in the fluid systems.

Polyol-based fluids contain a glycol or glycerol as a shale inhibitor, commonly used in conjunction with conventional anionic and cationic fluids to provide additional inhibition of swelling and dispersing of shales. They also provide some lubrication properties.

Sodium or potassium silicates are known to provide levels of shale inhibition comparable to that of OBMs. This type of fluid is characterized by a high pH (>12), for optimum stability of the mud system. The inhibition properties of such fluids are due to the precipitation or gelation of silicates that occurs on contact with divalent ions and lower pH in the formulation, providing an effective water barrier that prevents hydration and dispersion of the shales.

Water-based Muds

These muds have water as the continuous phase, which may contain several dissolved substances such as alkalies, salts and surfactants, organic polymers in colloidal state, droplets of emulsified oil, and various insoluble substances, such as barite, clay, and cuttings in suspension.

The mud composition that is selected for use often depends on the dissolved substances present in the most economically available make-up water, or on the soluble or dispersive materials in the formations to be drilled. Several mud types or systems are recognized and described in the literature such as:

- Spud muds,
- Dispersed/deflocculated muds,
- Lime muds,
- Gypsum muds,
- Salt water muds,
- Nondispersed polymer muds,
- Inhibitive potassium muds,
- Cationic muds, and
- Mixed metal hydroxide muds.

Despite their environmental acceptability, conventional WBMs exhibit major deficiencies relative to OBMs/pseudo oil-based drilling muds (POBMs)

TABLE 1.4 Water-based Drilling Muds

Compound	References
Glycol-based	Lee et al. (1997)
Alkali silicates	Mullen and Gabrysch (2001), Urquhart (1997)
Polyacrylamide, carboxymethyl cellulose	Kotelnikov et al. (1996)
Carboxymethyl cellulose, zinc oxide	Gajdarov and Tankibaev (1996)
Acrylamide copolymer, polypropylene glycol (PPG) (water-based mud)	Patel and Muller (1996)

because of their relatively poor shale inhibition, lubricity, and thermal stability characteristics. To overcome these deficiencies, specific additives may be added to the WBM compositions to bring their properties close to that of OBMs/POBMs while minimizing their environmental impact.

Components of WBMs are shown in Table 1.4. Various methods for the modification of lignosulfonates have been described in the literature, for example, condensation with formaldehyde (Martyanova et al., 1997) or modification with iron salts (Ibragimov et al., 1998). It has been found that chromium-modified lignosulfonates, as well as mixed metal lignosulfonates of chromium and iron, are highly effective as dispersants. They are therefore useful for controlling the viscosity of drilling fluids and reducing their yield point and gel strength. Because chromium is potentially toxic, its release into the natural environment is continuously being reviewed by various government agencies around the world.

Therefore, less toxic substitutes are desirable. These can be prepared by combining tin or cerium sulfate with an aqueous solution of calcium lignosulfonate, thereby producing a solution of tin or cerium sulfonate and a calcium sulfate precipitate (Patel, 1994b).

Compositions with Improved Thermal Stability

To avoid the problems associated with viscosity reduction in polymer-based aqueous fluids, formates, such as potassium formate and sodium formate, are commonly added to enhance their thermal stability, but this is very expensive, and thermal stabilities of polymer-based aqueous fluids can be improved by other means (Maresh, 2009).

The stability of a wellbore treatment fluid may be maintained up to temperatures of 135–160°C (275–325°F) by introducing various polysaccharides into the fluid. The apparent viscosities of some drilling fluids containing xanthan gum and polyacrylamide (PAM) before and after rolling at 120°C are shown in Table 1.5.

TABLE 1.5 Apparent Viscosity Before and After Rolling (Maresh, 2009)

Composition	Before η/[cP]	After η/[cP]
Brine/XC	13	3
Brin/PA	8.5	6
Brine/Filtercheck	4	4
Brine/FLC/XC	16	10.5
Brine/FLC/PA	14.6	9
Brine/XC/CLAYSEAL	12.5	3
XC/PA	30	28.5
XC/PA/FLC	38.5	16.5
XC/PA/FLC/CLAYSEAL	34	28
XC/PA/FLC/CLAYSEAL/Barite	38.5	38.5

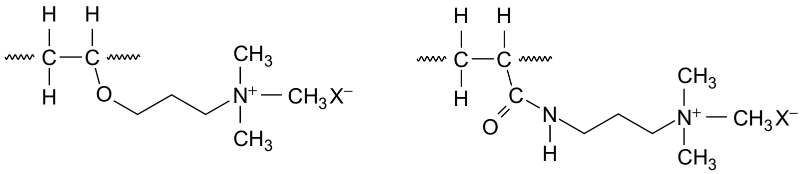


FIGURE 1.1 Quaternized etherified polyvinyl alcohol and quaternized polyacrylamide (Patel et al., 2009).

Shale Encapsulator

A shale encapsulator is added to a WBM in order to reduce the swelling of the subterranean formation in the presence of water. It must be at least partially soluble in the aqueous continuous phase in order to be effective.

A conventional encapsulator is a quaternary PAM, preferably a quaternized polyvinyl alcohol. Useful anions include halogen, sulfate, nitrate, and formate (Patel et al., 2009).

By varying the molecular weight and the degree of amination, a wide variety of products can be produced. It is possible to create shale encapsulators for use in low salinity conditions, including fresh water (Patel et al., 2009). The repeating units of quaternized, etherified polyvinyl alcohol and quaternized PAM are shown in Figure 1.1.

Membrane Formation

In order to increase wellbore stability, formulations for water-based drilling fluids can be provided that form a semi-permeable osmotic membrane over a specific shale formation (Schlemmer, 2007). This membrane allows the comparatively free movement of water through the shale, but significantly restricts the movement of ions across the membrane and thus into the shale.

Membrane formation involves the application of two reactants to form a relatively insoluble Schiff base in situ, which deposits the shale as a polymer film. This Schiff base coats the clay surfaces as a polymer membrane.

The first reactant is a soluble monomer, oligomer, or polymer with ketone, aldehyde, aldol functionalities, or precursors to those. Examples are carbohydrates, such as dextrin and linear or branched starch. The second reactant is a primary amine. These compounds react via a condensation reaction to form an insoluble crosslinked polymer. The formation of a Schiff base is shown in Figure 1.2.

Figure 1.2 shows the reaction of a dextrine with a diamine, but other primary amines and polyamines will of course react in the same way. Long chain

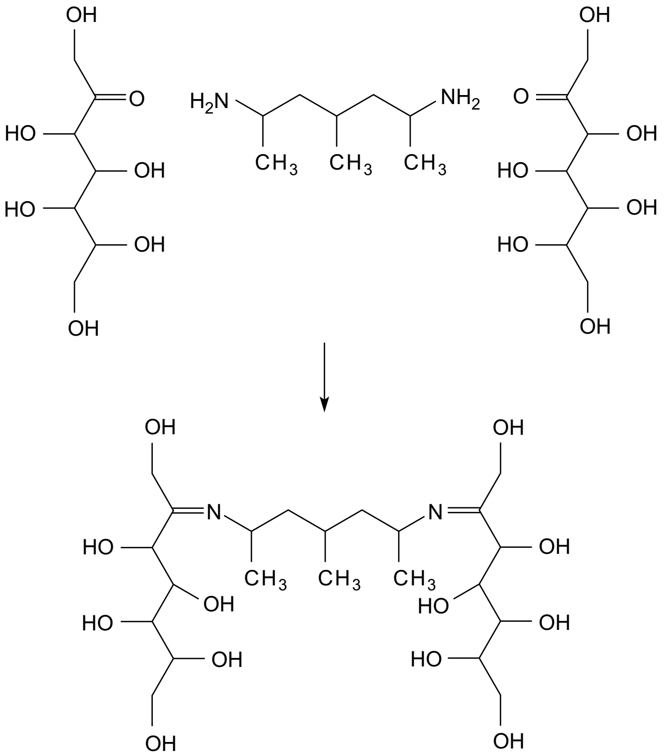


FIGURE 1.2 Formation of a Schiff base (Schlemmer, 2007).

amines, diamines, or polyamines with a relatively low amine ratio may require pH adjustment, using materials such as sodium hydroxide, potassium hydroxide, sodium carbonate, potassium carbonate, or calcium hydroxide (Schlemmer, 2007). The Schiff base formed in this way must be essentially insoluble in the carrier brine in order to deposit a sealing membrane on the shale during the drilling of a well.

By carefully selecting the primary polymer and the crosslinking amine, their relative concentrations, and the pH, the required degree of crosslinking, polymerization, and precipitation of components occurs, effectively forming an osmotically effective membrane on or within the face of the exposed rock.

Oil-based Drilling Muds

These materials have oil as their continuous phase, usually diesel oil, mineral oil or low toxicity mineral oil. Because some water will always be present, the OBM must contain water-emulsifying agents. Various thickening and suspending agents as well as barite are added. The emulsified water may contain alkalies and salts. If water is purposely added (for economical reasons), the OBM is called an invert emulsion mud.

Due to the character of their continuous phase, OBMs provide unequaled performance attributes with respect to the rate of penetration, shale inhibition, wellbore stability, high lubricity, high thermal stability, and high salt tolerance. However, they are subjected to strict environmental regulation regarding their discharge and recycling.

OBMs are now being replaced by synthetic muds. Diesel oil is harmful to the environment, particularly the marine environment in offshore applications. The use of palm oil derivatives could be considered as a harmless alternative (Yassin and Kamis, 1990), or hydrated castor oil can be used as a viscosity promoter instead of organophilic quaternized clays (Mueller et al., 1991).

An OBM can be made more viscous with maleated ethylene-propylene elastomers (Jones and Acker, 1999). The elastomers are ethylene-propylene copolymers or ethylene-propylene-diene terpolymers. These compounds are far more effective oil mud viscosifiers than the organophilic clays orginally used. However, specific organophilic clays can provide a drilling fluid composition that is less sensitive to high temperatures (Dino and Thompson, 2001).

Poly-α-olefins (PAOs) are biodegradable and non-toxic to marine organisms. They also meet viscosity and pour point specifications for OBM formulations (Ashjian et al., 1995). The hydrogenated dimer of 1-decene (Mercer and Nesbit, 1992) can be used instead of conventional organic fluids, as can *n*-1-octene (Lin, 1996).

Polyethercyclicpolyols

Polyethercyclicpolyols possess molecular properties and characteristics that permit the preparation of enhanced drilling fluids, which inhibit the formation of gas hydrates, prevent shale dispersion, and reduce the swelling of the formation to enhance wellbore stability, reduce fluid loss, and reduce filter cake thickness.

Drilling muds that incorporate these compounds are substitutes for OBMs in many applications (Blytas and Frank, 1995; Blytas et al., 1992; Blytas et al., 1992; Zuzich and Blytas, 1994; Zuzich et al., 1995). Polyethercyclicpolyols are prepared by thermally condensing a polyol, for example glycerol, to oligomers and cyclic ethers.

Emulsifier for Deep Drilling

Two major problems are encountered when using OBMs for drilling very deep wells (Dalmazzone, 2007). The first is a problem with the stability of the emulsions at elevated temperatures. The emulsion must be stable up to temperatures of 200°C. If the emulsion coalesces, the fluid loses its rheological properties.

The second problem is their environmental impact. The emulsification agents must not only be effective, but also as non-toxic as possible.

Fatty acid amides consisting of *N*-alkylated polyether chains are used as emulsifiers. For those the term ‘polyalkoxylated superamides’ has been coined (Le Helloco et al., 2004). As a cosurfactant, tall oil fatty acids or their salts can be used.

Biodegradable Composition

Some oil-based drilling fluids are biodegradable. The main oil phase component of these materials is a mixture of methyl esters from biodegradable fatty acids. A typical formulation of a biodegradable drilling fluid is shown in Table 1.6.

Electric Conductive Nonaqueous Mud

A wellbore fluid has been developed that has a nonaqueous continuous liquid phase and exhibits an electrical conductivity that is a factor of 10^4 to 10^7 greater than a conventional invert emulsion. 0.2–10% by volume of carbon black particles and emulsifying surfactants are used as additives. Information from electrical logging tools, including measurements while drilling, can be obtained (Sawdon et al., 2000).

Water Removal

Water can be removed from OBMs by the action of magnesium sulfate (Smith and Jeanson, 2001).

Synthetic Muds

Synthetic muds are expensive. Two factors influence the direct cost, namely the costs per barrel and mud losses. Synthetic muds are the technical equivalent of OBMs when drilling intermediate hole sections. They are technically superior to all water-based systems when drilling reactive shales in directional wells.

TABLE 1.6 Biodegradable Drilling Fluid (Goncalves et al., 2007)

Compound	Amount/[%]			Function
Soybean methylate	55	to	70	Oil component
D-Limonene	1	to	5	Pour point depressant
2,6-Di-*tert*-butyl-*p*-cresol	0.1	to	0.5	Antioxidant
Hydrogenated castor oil	0.3	to	1	Oil component
Fatty acid salts	3	to	6	Puffer
Magnesium oxide	1	to	3	In situ soap former
NaCl Brine	26	to	30	Aqueous component
Organophilic clay	0.5	to	1	Viscosifier
Succinimide copolymer	0.1	to	0.5	Fluid loss agent
Sodium polyacrylate	0.1	to	0.5	Fluid loss agent
Citric acid	0.1	to	1.5	Puffer
Barium sulfate	0.1	to	25	Weighting agent

With efficient solids-control equipment, optimized drilling, and good housekeeping practices, the cost of the synthetic mud can be brought to a level that is comparable to OBM (Munro et al., 1993).

POBMs or synthetic oil-based drilling muds are made on the same principle as OBMs. They have been developed to maintain the performance characteristics of OBMs while reducing their environmental impact. The objective behind the design of these drilling fluids is to exchange the diesel oil or mineral oil base with an organic fluid that has a lower environmental impact. The organic fluids used are esters, polyolefins, acetal, ether, and linear alkyl benzenes. As with OBMs, POBMs may contain various ingredients, such as thickening and suspending agents and emulsifying agents as well as weighting agents.

POBMs were developed to maintain the technical performance characteristics of OBMs and reduce their environmental impact. They are, however, not as stable as OBMs depending upon the continuous phase present. From an environmental perspective, legislation is becoming as strict for POBMs as for OBMs. The mud selection process is based on the mud's technical performance and environmental and financial impact.

Skeletally isomerized linear olefins exhibited a better high-temperature stability in comparison to a drilling fluid prepared from a conventional PAO. Fluid loss properties are good, even in the absence of fluid loss additives (Gee et al., 1992, 1998, 2000; Williamson et al., 1995). Although normal α-olefins are not generally useful, mixtures of mostly linear olefins are minimally toxic and are highly effective as the continuous phase of drilling fluids (Gee et al., 1995, 1992).

Acetals as mineral oil substitutes exhibit good biodegradability and are less toxic than mineral oils (Hille et al., 1992, 1998). Acrylic acid (AA) salts are formed by the neutralization reaction of AA in aqueous solution (Shimomura et al., 1990).

Alginates are hydrocolloids, which are extracted from brown marine microalgae. Water-soluble alginates are prepared as highly concentrated, pumpable suspensions in mixtures of propylene glycol and water by using hydroxypropylated guar gum in combination with carboxymethylated cellulose, which is used as a suspending agent (Kehoe and Joyce, 1993).

Inverted Emulsion Drilling Muds

Inverted emulsion muds are used in 10–20% of all drilling jobs. Historically, first of all crude oils, then diesel oils and mineral oils were used to formulate invert drilling fluids. Considerable environmental damage may occur when the mud gets into the sea. Drilling sludge and the heavy mud sink to the seabed and partly flow with the tides and sea currents to the coasts. All of these hydrocarbons contain no oxygen and are not readily biodegraded (Hille et al., 1998).

Because of problems of toxicity and persistence, alternative drilling oils have been developed. Examples of such oils are fatty acid esters and branched chain synthetic hydrocarbons such as PAOs. Fatty acid ester-based oils have excellent environmental properties, but drilling fluids made with these esters tend to have lower densities and are prone to hydrolytic instability.

PAO-based drilling fluids can be formulated to high densities with good hydrolytic stability and low toxicity. They are, however, somewhat less biodegradable than esters and they are expensive. The fully weighted, high-density fluids tend to be too viscous (Lin, 1996).

Esters

Esters of C_6 to C_{11} monocarboxylic acids (Müller et al., 1990; Mueller et al., 1990a,b, 1994), acid-methyl esters (Mueller et al., 1990a), and polycarboxylic acid esters (Mueller et al., 1991), as well as oleophilic monomeric and oligomeric diesters (Mueller et al., 1991), have all been proposed as basic materials for inverted emulsion muds. Natural oils are triglyceride ester oils (Wilkinson et al., 1995) and are similar to synthetic esters. Diesters also have been proposed (Mueller et al., 1991, 1992, 1993, 1995; Muller et al., 1993).

Acetals

Acetals and oleophilic alcohols or oleophilic esters are suitable for the preparation of inverted emulsion drilling muds and emulsion drilling muds. They may replace the base oils, diesel oil, purified diesel oil, white oil, olefins, and alkyl benzenes (Hille et al., 1996, 1998). Examples are isobutyraldehyde, di-2-ethylhexyl acetal, dihexyl formal. Also mixtures with coconut alcohol, soya oil, and α-methyldecanol are suitable. Some aldehydes are shown in Figure 1.3.

Inverted emulsion muds are more useful in stable, water sensitive formations and in inclined boreholes. They are stable up to very high temperatures and provide excellent corrosion protection. Their disadvantages are their higher price, the greater risk if gas reservoirs are bored through, the more difficult handling for the team at the tower, and their greater environmental problems.

The high setting point of linear alcohols and the poor biodegradability of branched alcohols limit their use as an environment-friendly mineral oil substitute. Higher alcohols, which are slightly water-soluble, are eliminated for use in offshore muds because of their high toxicity to fish.

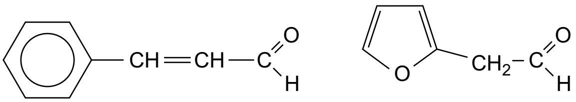
Esters and acetals can be degraded anaerobically on the seabed. This possibility minimizes the environmentally damaging effect on the seabed. When such products are used, rapid recovery of the ecology of the seabed takes place after the end of drilling. Acetals, which have a relatively low viscosity and in particular a relatively low setting point, can be prepared by combining various aldehydes and alcohols (Hille et al., 1998; Young and Young, 1994).

Anti-settling Properties

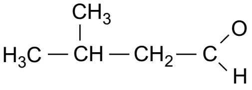
Ethylene-AA copolymer, neutralized with amines such as triethanol amine or *N*-methyl diethanol amine, enhances anti-settling properties (McNally et al., 1999; Santhanam and MacNally, 2001).

Glycosides

If glycosides are used in the internal phase, then much of the concern over the ionic character of the internal phase is not necessary. If water is limited in the system, then the hydration of the shales is greatly reduced.



Cinnamaldehyde 2-Furaldehyde



Isobutyraldehyde

FIGURE 1.3 Aldehydes.

The reduced water activity of the internal phase of the mud and the improved efficiency of the shale is an osmotic barrier if the glycoside interacts directly with the shale. This helps to lower the water content of the shale, thus increasing rock strength, lowering effective mean stress, and stabilizing the wellbore (Hale and Loftin, 1996).

Methyl glucosides also could find applications in water-based drilling fluids and have the potential to replace OBMs (Headley et al., 1995). The use of such a drilling fluid could reduce the need for the disposal of oil-contaminated drilling cuttings, minimize health and safety concerns, and minimize adverse environmental effects.

Miscellaneous

Other proposed base materials are listed in Table 1.7. Quaternary oleophilic esters of alkylolamines and carboxylic acids improve the wettability of clay (Ponsati et al., 1992, 1994). Nitrates and nitrites can replace calcium chloride in inverted emulsion drilling muds (Fleming and Fleming, 1995).

Reversible Phase Inversion

Invert emulsion fluids, in which the emulsion can be readily and reversibly converted from a water-in-oil type emulsion to an oil-in-water type emulsion, have been developed. The essential ingredient is an amine-based surfactant, which

TABLE 1.7 Other Materials for Inverted Emulsion Drilling Fluids

Base material	References
Ethers of monofunctional alcohols	Mueller et al. (1990)
Branched didecyl ethers	Godwin and Mathys (1993), Godwin and Sollie (1993)
α-Sulfofatty acids	Mueller et al. (1996)
Oleophilic alcohols	Mueller et al. (1990b), Muller et al. (1990)
Oleophilic amides	Mueller et al. (1990c)
Hydrophobic side chain polyamide from *N*,*N*-didodecylamine and sodium polyacrylate or polyacrylic acid	Monfreux et al. (2000)
Polyether amine	Wall et al. (1995)
Phosphate ester of a hydroxy polymer	Brankling (1994)

may be diethoxylated tallow amine, diethoxylated soya amine, or *N*-tallow-1,3-diaminopropane (Patel, 2008).

The invert emulsion is admixed with an acid that can protonate the amine surfactant. When sufficient quantities of the acid are present, the invert emulsion is converted so that the oleaginous fluid becomes the discontinuous phase and the non-oleaginous fluid becomes the continuous phase.

The phase inversion is reversible, so that on addition of a base capable of deprotonating the protonated amine surfactant, a stable invert emulsion is formed, where the oleaginous liquid becomes the continuous phase and the non-oleaginous fluid become the discontinuous phase (Patel, 2008).

In other words, when the drilling fluid is converted into an oil-in-water type emulsion, solids, now substantially water-wet, may now be separated from the fluid, by gravity or mechanical means, for further processing or disposal. The fluid may then be mixed with a base, which can deprotonate the protonated amine surfactant, and so converts the oil-in-water type emulsion back to a water-in-oil emulsion. The resulting water-in-oil emulsion may then be used as it is, or may be reformulated into a drilling fluid that is suitable for use in another well (Patel, 2008).

Foam Drilling

Drilling low-pressure reservoirs with nonconventional methods can use low-density dispersed systems, such as foams, to achieve underbalanced conditions. Selection of an adequate foam formulation, requires not only the reservoir characteristics but also the foam properties to be taken into account.

Parameters such as stability of foam, and the interactions between rock-fluid and drilling fluid-formation fluid are among the properties to consider when designing the drilling fluid (Aguilar et al., 2000).

A composition with a specific pH, an ionic surfactant, and a polyampholytic polymer whose charge depends on the pH, is circulated in a well. By varying the pH, it is possible to destabilize the foam in such a way as to more easily break it back at the surface, and potentially to recycle the foaming solution (Argillier and Roche, 2000).

Chemically Enhanced Drilling

Chemically enhanced drilling offers substantial advantages over conventional methods in carbonate reservoirs. Coiled tubing provides the perfect conduit for chemical fluids that can accelerate the drilling process and provide stimulation while drilling (Rae and Di Lullo, 2001). The chemical fluids are mainly acidic in order to dissolve or disintegrate the carbonate rock.

Supercritical Carbon Dioxide Drilling

The efficiency of drilling operations can be increased using a drilling fluid material that exists as supercritical fluid, or a dense gas at temperature and pressure conditions occurring in the drill site, such as carbon dioxide.

A supercritical fluid exhibits physiochemical properties intermediate between those of liquids and gases. Mass transfer is rapid with supercritical fluids, and their dynamic viscosities are nearer to those of normal gaseous states.

In the vicinity of the critical point, the diffusion coefficient is more than 10 times that of a liquid. Carbon dioxide can be compressed readily to form a liquid, and under typical borehole conditions, it is a supercritical fluid.

The viscosity of carbon dioxide at its critical point is only 0.02 cP. This value increases with pressure to about 0.1 cP at 70 MPa (about 10,000 psi). Because the diffusivity of carbon dioxide is so high, and the rock associated with petroleum-containing formations is generally porous, the carbon dioxide is effective in penetrating the formation.

Carbon dioxide therefore is often used to stimulate the production of oil wells, because it tends to dissolve in the oil, reducing the oil viscosity while providing a pressure gradient that drives the oil from the formation.

Carbon dioxide can be used to reduce mechanical drilling forces, to remove cuttings, or to jet erode a substrate. Supercritical carbon dioxide is used with coiled-tube drilling equipment. The very low viscosity of supercritical carbon dioxide provides efficient cooling of the drill head and efficient cuttings removal.

Furthermore, the diffusivity of supercritical carbon dioxide within the pores of petroleum formations is significantly higher than that of water, making jet erosion much more effective than water. Supercritical carbon dioxide jets can be used to assist mechanical drilling, for erosion drilling, or for scale removal. Spent carbon dioxide can be vented to the atmosphere, collected for reuse, or directed into the formation to aid in the recovery of petroleum (Kolle, 2002).

ADDITIVES

Thickeners

A variety of compounds that are useful as thickeners is shown in Table 1.8 and the individual compounds are explained in detail in the following sections.

Polymers

Thickener polymers include polyurethanes (PUs), polyesters, PAMs, natural polymers, and modified natural polymers (Doolan and Cody, 1995).

TABLE 1.8 Thickeners

Compound	References
A water-soluble copolymer of hydrophilic and hydrophobic monomers, acrylamide (AAm)-acrylate of silane or siloxane	Meyer et al. (1999)
Carboxymethyl cellulose, polyethylene glycol	Lundan et al. (1993), Lundan and Lahteenmaki (1996)
Combination of a cellulose ether with clay	Rangus et al. (1993)
Amide-modified carboxyl-containing polysaccharide	Batelaan and van der Horts (1994)
Sodium aluminate and magnesium oxide	Patel (1994a)
Thermally stable hydroxyethyl cellulose (HEC) 30% ammonium or sodium thiosulfate and 20% HEC	Lukach and Zapico (1994)
AA copolymer and oxyalkylene with hydrophobic group	Egraz et al. (1994)
Copolymers acrylamide-acrylate and vinylsulfonate–vinylamide	Waehner (1990)
Cationic polygalactomannans and anionic xanthan gum	Yeh (1995)
Copolymer from vinyl urethanes and AA or alkyl acrylates	Wilkerson et al. (1995)
2-Nitroalkyl ether–modified starch	Gotlieb (1996)
Polymer of glucuronic acid	Courtois-Sambourg et al. (1993)
Ferrochrome lignosulfonate and carboxymethyl cellulose	Kotelnikov et al. (1992)
Cellulose nanofibrils[a]	Langlois (1998, 1999)
Quaternary alkyl amido ammonium salts	Subramanian et al. (2001)
Chitosan[b]	House and Cowan (2001)

a) Stable up to temperatures of about 180°C
b) Solubilized in acidic solution

pH Responsive Thickeners

The viscosity of ionic polymers is dependent on their pH. In particular, pH responsive thickeners can be prepared by copolymerization of acrylic or methacrylic acid ethyl acrylate or other vinyl monomers and tristyrylpoly(ethyleneoxy)$_x$ methyl acrylate. Such a copolymer provides a stable, aqueous, colloidal dispersion at a pH lower than 5.0, but becomes an effective thickener for aqueous systems on adjustment to a pH of 5.5 to 10.5 or higher (Robinson, 1996, 1999).

Mixed Metal Hydroxides

By addition of mixed metal hydroxides, typical bentonite muds are transformed to an extremely shear-thinning fluid (Lange and Plank, 1999). At rest, these fluids exhibit a very high viscosity but are thinned to an almost water-like consistency when shear stress is applied.

The shear thinning rheology of mixed metal hydroxides and bentonite fluids is due to the formation of a three-dimensional, fragile network of mixed metal hydroxides and bentonite.

The positively charged, mixed metal hydroxide particles attach themselves to the surface of negatively charged bentonite platelets. Typically, magnesium aluminum hydroxide salts are used as mixed metal hydroxides.

Mixed metal hydroxides demonstrate the following advantages in drilling (Felixberger, 1996):

- High cuttings removal,
- Suspension of solids during shutdown,
- Lower pump resistance,
- Stabilization of the borehole,
- High drilling rates, and
- Protection of the producing formation.

Mixed metal hydroxide drilling muds have been used successfully in horizontal wells; in tunneling under rivers, roads, and bays; for drilling in fluids; for drilling large-diameter holes; with coiled tubing; and to ream out cemented pipe.

Mixed metal hydroxides can be prepared from the corresponding chlorides by treatment with ammonia (Burba and Strother, 1991). Experiments with various drilling fluids showed that the mixed metal hydroxides system, coupled with propylene glycol (Deem et al., 1991), caused the least skin damage of the drilling fluids tested.

Thermally activated mixed metal hydroxides, made from naturally occurring minerals, especially hydrotalcites, may contain small or trace amounts of metal impurities besides the magnesium and aluminum components, which are particularly useful for activation (Keilhofer and Plank, 2000).

Mixed hydroxides of bivalent and trivalent metals with a three-dimensional spaced-lattice structure of the garnet type ($Ca_3Al_2[OH]_{12}$) have been described (Burba et al., 1992; Mueller et al., 1997).

Lubricants

Bit lubricants are dealt with in detail in Chapter 4. During drilling, the drill string may develop an unacceptable rotational torque or, in the worst case, become stuck. When this happens, the drill string cannot be raised, lowered, or rotated. Common factors leading to this situation include:

- Cuttings or slough build-up in the borehole,
- An undergauge borehole,
- Irregular borehole development embedding a section of the drill pipe into the drilling mud wall cake, or
- Unexpected differential formation pressure.

Differential pressure sticking occurs when the drill pipe becomes embedded in the mud wall cake opposite a permeable zone.

The difference between the hydrostatic pressure in the drill pipe and the formation pressure holds the pipe in place, resulting in a sticking pipe. Differential sticking may be prevented, and a stuck drill bit may be freed by using an OBM, or an oil-based, or water-based surfactant composition.

Such a composition reduces friction, permeates drilling mud wall cake, destroys binding wall cake, and reduces the differential pressure. Unfortunately, many such compositions are toxic to marine life.

Bacteria

Bacterial contamination of drilling fluids contributes to a number of problems. Many of the muds contain sugar-based polymers in their formulation that provide an effective food source for bacterial populations. This can lead to direct degradation of the mud.

In addition, the bacterial metabolism can generate deleterious products. Most notable among these is hydrogen sulfide, which can lead to the decomposition of mud polymers, the formation of problematic solids such as iron sulfide, and corrosive action on drilling tubes and drilling hardware (Elphingstone and Woodworth, 1999). Moreover, hydrogen sulfide is a toxic gas.

Many polymers are used in drilling fluids as fluid loss control agents or viscosifiers. Because of the degradation of these polymers by bacteria in drilling fluids, an increase in fluid loss can occur. All naturally occurring polymers are capable of being degraded by bacterial action, but some are more susceptible than others. One solution, besides using bactericides, is to replace the starch with low viscosity PAC, polyanionic lignin, or other enzyme-resistant polymer (Hodder et al., 1992).

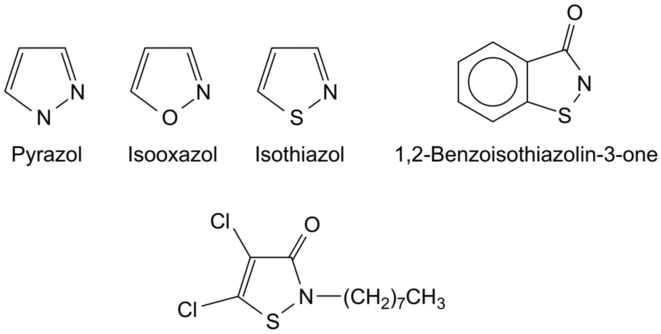
Certain additives are protected from biodegradation while drilling deep wells by quaternary ammonium salts (Rastegaev et al., 1999), which considerably reduces consumption of the additives needed.

Bacterial control is important not only in drilling fluids, but also for other oil and gas operations. The topic is treated more extensively in Chapter 5. Some bactericides especially recommended for drilling fluids are summarized in Table 1.9 and sketched out in Figure 1.4.

TABLE 1.9 Bactericides for Drilling Fluids

Bactericide	References
Bis[tetrakis(hydroxymethyl) phosphonium] sulfate[a]	Elphingstone and Woodworth (1999)
Dimethyl-tetrahydro-thiadiazine-thione	Karaseva et al. (1995)
2-Bromo-4-hydroxyacetophenone[b]	Oppong and King (1995)
Thiocyanomethylthio-benzothiazole[c]	Oppong and Hollis (1995)
Dithiocarbamic acid,	Austin and Morpeth (1992)
Hydroxamic acid[c]	Austin and Morpeth (1992)
1,2-Benzoisothiazolin-3-one	Morpeth and Greenhalgh (1990)
3-(3,4-Dichlorophenyl)-1,1-dimethylurea	Morpeth and Greenhalgh (1990)
Di-iodomethyl-4-methylphenyl sulfone[d]	Morpeth and Greenhalgh (1990)
Isothiazolinones	Downey et al. (1995), Hsu (1990, 1995), Morpeth (1993)

a) Absorbed on solid
b) Synergistically effective with organic acids
c) Synergistically effective with organic acids
d) Algicide



Pyrazol

Isooxazol

Isothiazol

1,2-Benzoisothiazolin-3-one

4,5-Dichloro-2-*N*-octyl-isothiazolin-3-one

FIGURE 1.4 Components for biozides.

Corrosion Inhibitors

Corrosion inhibitors are the subject of several topics in petroleum industries, such as transport and completion. They are detailed in Chapter 6.

Viscosity Control

Bentonites are highly colloidal and swell in water to form thixotropic gels. This property results from their micaceous sheet structure. Because of these viscosity-building characteristics, bentonites are used as viscosity enhancers or builders in such areas as drilling muds and fluids, concrete and mortar additives, foundry and molding sands, and compacting agents for gravel and sand, as well as cosmetics. Most bentonites that are found in nature are in their sodium or calcium form.

The performance of a calcium bentonite as a viscosity builder can often be enhanced by conversion to the sodium form. Crude bentonite can be upgraded to a range of solutions with unusually high aqueous viscosities (Bauer et al., 1993). The crude material is sheared and dried. Sodium carbonate is then dry-blended with the material and pulverized. The resulting bentonite clays are self-suspending, self-swelling, and self-gelatinizing when mixed with water.

The modification of bentonite with alkylsilanes also improves their dispersing properties (Kondo and Sawada, 1996). Incorporation of phosphonate-type compounds in bentonites for drilling mud permits the removal of free calcium ions in the form of soluble and stable complexes, and the preservation or restoration of the initial fluidity of the mud (Michelson and Vattement, 1999). The phosphonates also have dispersing and fluidizing effects on the mud.

Clay Stabilization

Selected clay stabilizers are shown in Table 1.10. Thermally treated carbohydrates are suitable as shale stabilizers (Sheu and Bland, 1992). They may be formed by heating an alkaline solution of the carbohydrate, and the reaction product may be reacted with a cationic base. The inversion of non-reducing sugars may be first effected on selected carbohydrates, with the inversion catalyzing the browning reaction.

Formation Damage

Polyacrylates are often added to drilling fluids to increase their viscosity and limit formation damage. The filter cake is critical to preventing reservoir invasion by mud filtrate. Polymer invasion of the reservoir has been shown to have a great impact on permeability reduction (Audibert et al., 1999). The invasion of filtrate and solids in drilling in fluid can cause serious reservoir damage.

Shale Stabilizer

Swelling due to shale hydration is one of the most important causes of borehole instability. Three processes are known to contribute to shale instability (Bailey et al., 1994):

1. Movement of fluid from the wellbore into the shale,
2. Changes in stress and strain, which occur during the interaction of shale and filtrate, and
3. Softening and erosion, caused by invasion of mud filtrate and consequent chemical changes in the shale.

Adding a shale stabilizer to drilling fluids is an effective way to control clay swelling (Fu and Hu, 1997). A copolymer of AAm and acrylonitrile has been found to be effective in this regard. Experimental results show that the inhibitors are effective in inhibiting shale hydration swelling, especially their quaternized product. 2-Hydroxybutyl ether and polyalkyl ether modified polygalactomannans have been described as useful shale hydration inhibitors (Dino, 1997).

TABLE 1.10 Clay Stabilizers for Drilling Fluids

Additive	References
Modified poly-amino acid[a]	Bruton and McLaurine (1993)
Polyacrylamide	Ballard et al. (1994)
Amphoteric acetates and glycinates	Jarrett (1997a)
Capryloamphoglycinate	Alonso-Debolt and Jarrett (1995)
Cocoamphodiacetate	Alonso-Debolt and Jarrett (1995)
Disodium cocoamphodiacetate	Alonso-Debolt and Jarrett (1995)
Lauroamphoacetate	Alonso-Debolt and Jarrett (1995)
Sodium capryloamphohydroxypropyl sulfonate	Alonso-Debolt and Jarrett (1995)
Sodium mixed C_8 amphocarboxylate	Alonso-Debolt and Jarrett (1995)
Alkylamphohydroxypropyl sulfonate	Alonso-Debolt and Jarrett (1995)
Polyvinylpyrrolidone	
Polyvinyl alcohol	
Starches	
Cellulosic material	Patel et al. (1995)
Partially hydrolyzed polyacrylamide and PPG, or a betaine	Patel et al. (1995)
Quaternized trihydroxyalkyl amine	Patel et al. (1995)
Polyfunctional polyamine	McGlothlin and Woodworth (1996)

a) Water sensitive smectite or illite shale formations

TABLE 1.11 Surface Active Agents for Drilling Muds

Compound	References
Alkylpolyglycosides	Lecocumichel and Amalric (1995)
Amphoteric surfactants	Dahanayake et al. (1996)
Acetal or ketal adduct hydroxy polyoxyalkylene ether[a]	Felix (1996)
Amphoteric anion ethoxy and propoxy units	Hatchman (1999)
Alkanolamine	Hatchman (1999)

a) Controlling foam formation, drilling muds

A copolymer of styrene and maleic anhydride (MA) with alkylene oxide based side chains is effective as a shale stabilizer (Smith and Balson, 2000), as are a variety of polyoxyalkylene amines. It was found that polyoxypropylene-diamine $H_2N{-}CH(CH_3)CH_2[{-}OCH_2CH(CH_3)]_x{-}NH_2$ (Patel et al., 2001) is the best, with $x < 15$. Surfactants are used to change the interfacial properties. Suitable surfactants are given in Table 1.11.

Fluid Loss Additives

Filtration control is an important property of a drilling fluid, particularly when drilling through permeable formations, where the hydrostatic pressure exceeds the formation pressure. It is important for a drilling fluid to quickly form a filter cake to effectively minimize fluid loss, but which also is thin and erodable enough to allow product to flow into the wellbore during production (Jarrett and Clapper, 2010). Fluid loss additives are detailed in Chapter 2. Here a few fluid loss additives are summarized for quick reference.

There are a number of methods that have been proposed to help prevent the loss of circulation fluid (Messenger, 1981). Some of these methods use fibrous, flaky, or granular materials to plug the pores as the particulate material settles out of the slurry.

Other methods use materials that interact in the fissures of the formation to form a plug of increased strength. Lost circulation additives are summarized in Table 1.12.

Water Swellable Polymers

Certain organic polymers absorb comparatively large quantities of water, for example, alkali metal polyacrylate or crosslinked polyacrylates (Green, 2001). Such water-absorbent polymers, insoluble in water and in hydrocarbons, can be

TABLE 1.12 Lost Circulation Additives

Material	References
Encapsulated lime	Walker (1986)
Encapsulated oil-absorbent polymers	Delhommer and Walker (1987a)
Hydrolyzed polyacrylonitrile	Yakovlev and Konovalov (1987)
Divinylsulfone, crosslinked	
Poly(galactomannan) gum	Kohn (1988)
PU foam	Glowka et al. (1989)
Partially hydrolyzed polyacrylamide 30% hydrolyzed, crosslinked with Cr^{3+}	Sydansk (1990)
Compound	**References**
Oat hulls	House et al. (1991)
Rice products	Burts Jr (1992, 1997)
Waste olive pulp	Duhon (1998)
Nut cork	Fuh et al. (1993), Rose (1996)
Pulp residue waste	Gullett and Head (1993)
Petroleum coke	Whitfill et al. (1990)
Shredded cellophane	Burts Jr (2001)

injected into the well so that they encounter naturally occurring or added water at the entrance to and within an opening in the formation. The resultant swelling of the polymer forms a barrier to the continued passage of the circulation fluid through that opening into the formation.

The hydrocarbon carrier fluid initially prevents water from contacting the water-absorbent polymer until such water contact is desired. Once the hydrocarbon slug containing the polymer is properly placed at the lost circulation zone, water is mixed with it so that the polymer will absorb the water and substantially increase in size to close off the lost circulation zone (Bloys and Wilton, 1991; Delhommer and Walker, 1987b; Walker, 1989). The situation is similar to an oil-based cement. The opposite mechanism is used by a hydrocarbon-swellable elastomer (Wood, 2001).

Anionic Association Polymer

Another type of lost circulation agent is a combination of an organic phosphate ester and an aluminum compound, for example, aluminum isopropoxide.

The alkyl phosphate ester becomes crosslinked by the aluminum compound to form an anionic association polymer, which serves as a gelling agent (Reid and Grichuk, 1991), hence preventing fluid loss.

Fragile Gels

A fragile gel is one that can be easily disrupted or thinned under shear stress, etc, but can quickly return to a gel when the stress is alleviated or removed, such as when the circulation of the fluid is stopped. Fragile gels may be disrupted simply by a pressure or a compression wave during drilling. They break instantaneously when disturbed, turning from a gel back into a liquid with minimum pressure, force, and time.

Metal crosslinked phosphate esters impart a fragile progressive gel structure to a variety of oil and invert emulsion-based drilling fluids, both at neutral or acidic pH.

The amount of phosphate ester and metal crosslinker that is used in a drilling fluid depends on the oil type and the desired viscosity of the product. Generally, however, more phosphate ester and metal crosslinker is used for gelling or enhancing the viscosity of the fluid for transport than is used for imparting fragile progressive gel structure to the drilling fluid (Bell and Shumway, 2009).

Aphrons

Other lost-circulation additives can be present in an encapsulated form. The encapsulation is then dissolved and the material swells to close fissures. Microbubbles in a drilling fluid can be generated by certain surfactants, and polymers known as *aphrons* are a different approach to reduce the fluid loss (Ivan et al., 2001).

An aphron drilling fluid is similar to a conventional drilling fluid, but the drilling fluid system is converted to an energized air-bubble mud system before drilling (Kinchen et al., 2001).

Permanent Grouting

Lost circulation also can be suppressed by grouting permanently, either with cement or with organic polymers that cure in situ (Allan and Kukacka, 1995; Cowan and Hale, 1994).

Scavengers

Oxygen Scavengers

Oxygen corrosion is often underestimated, but studies have shown that the corrosion can be limited when proper oxygen scavengers are used. Hydrazine leads the group of chemicals that are used for oxygen removal. Because of its special properties, it is used for corrosion control in heating systems and in drilling operations, well workover, and cementing (Sikora, 1994).

Hydrogen Sulfide Removal

It is sometimes necessary to remove hydrogen sulfide from a drilling mud. Techniques using iron compounds that form sparingly soluble sulfides have been developed, for example, the use of iron (II) oxalate (Sunde and Olsen, 2000) and iron sulfate (Prokhorov et al., 1993), where the sulfur is precipitated out as FeS. Alternatively, ferrous gluconate is an organic iron-chelating agent, stable at pH levels as high as 11.5 (Davidson, 2001).

Zinc compounds have a high reactivity with regard to H_2S and therefore are suitable for the quantitative removal of even small amounts of hydrogen sulfide (Wegner and Reichert, 1990). However, at high temperatures they may negatively affect the rheology of drilling fluids.

Surfactants

Surfactant in Hydrocarbon Solvent

Methyl-diethyl-alkoxymethyl ammonium methyl sulfate has high foam extinguishing properties (Fabrichnaya et al., 1997).

Biodegradable Surfactants

Alkylpolyglucosides (APGs) are highly biodegradable surfactants (Nicora and McGregor, 1998). The addition of APGs, even at very low concentrations, to a polymer mud can drastically reduce fluid loss even at high temperatures. Moreover, both fluid rheology and temperature resistance are improved.

Deflocculants and Dispersants

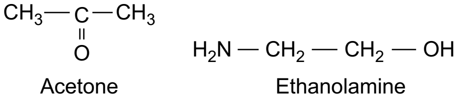
Deflocculants have a relatively low molecular weight. Complexes of tetravalent zirconium with organic acids, such as citric, tartaric, malic, and lactic acids, and a complex of aluminum and citric acid have been claimed to be active as dispersants.

Polymers composed of sodium styrene sulfonate, MA, and a zwitterionic functionalized MA (Grey, 1993; Peiffer et al., 1991, 1992, 1993) are also suitable. The dispersant is especially useful in dispersing bentonite suspensions (Burrafato and Carminati, 1994).

Polymers with amine sulfide terminal moieties are synthesized by using aminethiols as chain transfer agents in aqueous addition polymerization reactions. The polymers are useful as mineral dispersants (McCallum and Weinstein, 1994).

Shale Stabilizing Surfactants

There are special shale stabilizing surfactants consisting of non-ionic alkanolamides (Jarrett, 1997b), for example, acetamide monoethanolamines and diethanol amines. Acetone and ethanolamine are shown in Figure 1.5.



$CH_3-C(=O)-CH_3$ $\quad H_2N-CH_2-CH_2-OH$

FIGURE 1.5 Acetone, ethanolamine.

Toxicity

Alkyl phenol ethoxylates are a class of surfactants that have been used widely in the drilling fluid industry. The popularity of these surfactants is based on their cost effectiveness, availability, and range of obtainable hydrophilic-lipophilic balance values (Getliff and James, 1996).

However, studies have shown that alkyl phenol ethoxylates exhibit oestrogenic effects and can cause sterility in some male aquatic species. This may have subsequent human consequences, and such possibilities have led to their use being banned in some countries, and agreements to phase out their use have been drawn up. Alternatives are available, and in some cases they show an even better technical performance.

Defoamers

Defoamers are covered in Chapter 22.

Hydrate Inhibitors

Hydrate inhibitors for drilling fluids are summarized in Chapter 13.

Weighting Materials

There are many weighting materials, including barite and iron oxides, which are used to increase the specific weight of a slurry. Conversely, the specific weight can be reduced by foaming or by the addition of hollow glass particles.

Barite

Barite has been used as a weighting agent in drilling fluids since the 1920s. It is preferred over other materials because of its high density, low production costs, low abrasiveness, and ease of handling. Other weighting materials have been used, but they are problematic or costly. Finished barite producers sometimes blend ores from different sources to obtain the desired average density to meet API specifications.

Some barite ores contain alkaline-soluble carbonate minerals that can be detrimental to a drilling fluid, such as iron carbonate (siderite), lead carbonate (cerussite), and zinc carbonate (smithsonite) (Kulpa et al., 1992). Details of how to characterize barite have been worked out (Recommended practice for chemical analysis of barite, 1996). Barite can be modified to become oleophilic (Shen et al., 1998, 1999).

To recover barite from drilling muds, a direct flotation without prior dewatering and washing of the drilling muds has been described (Heinrich, 1992). An alkyl phosphate is used as a collecting and frothing reagent.

Ilmenite

Environmental considerations suggest replacing barite with ilmenite. However, the use of this as weighting material can cause severe erosion problems. Using ilmenite with a narrow particle size distribution around $10\,\mu$ can reduce the erosion to a level experienced with barite (Saasen et al., 2001).

Carbonate

It is possible to replace barite and iron-based weighting material with carbonate if a high degree of weighting is not required. Besides being cheaper than barite, such materials are less abrasive, which is especially important when drilling is performed in producing formations. It is also readily soluble in hydrochloric acid. The main shortcomings of carbonate powders are due to the presence of a coarsely divided fraction, and also of noncarbonate impurities (Lipkes et al., 1996).

Zinc Oxide, Zirconium Oxide, and Manganese Tetroxide

Zinc oxide (ZnO), is a particularly suitable material for weighting because it has a high density; $5.6\,\mathrm{g\,ml^{-1}}$ versus $4.5\,\mathrm{g\,ml^{-1}}$for barite. It is soluble in acids (e.g., HCl), and its particle size can be set so that it does not invade the formation. Acid solubility is particularly useful because dissolved ZnO can be pass through a production screen without plugging it. A high density means less weighting material is needed per unit mud volume to achieve a desired density.

The particle size, around $10\,\mu$, is such that the ZnO particles do not invade the formation core with the filtrate. On the other hand, the particle size is not large enough to settle out of suspension.

Zirconium oxide possesses similar properties to ZnO. It has a density of $5.7\,\mathrm{g\,ml^{-1}}$ and is soluble in nitric acid and hot concentrated hydrochloric, hydrofluoric, and sulfuric acids. Therefore, a filter cake formed from zinc or zirconium oxide can be dissolved. The high solubility of ZnO in acids makes it particularly suitable as weighting material (Lau et al., 1997). On the other hand, manganese tetroxide (Mn_3O_4) is so fine that it invades the formation with the filtrate.

Hollow Glass Microspheres

Initially, glass microspheres were used in the 1970s to overcome severe lost circulation problems in the Ural Mountains. The technology has subsequently been used in other sites (McDonald et al., 1999). Hollow glass beads reduce the density of a drilling fluid and can be used for underbalanced drilling (Medley Jr. et al., 1997, 1995). Field applications have been reported (Arco et al., 2000).

Organoclay Compositions

It has long been known that organophilic clays can be used to thicken a variety of organic compositions. Such clays are prepared by the reaction of an organic cation with a clay. If this cation contains at least one alkyl group of at least 8–10 carbon atoms, then the clays produced have the property of increasing the viscosity of organic liquids and thus imparting desired rheological properties to a wide variety of such liquids, including paints, coatings, adhesives, and similar products.

It is also well known that such organoclays may function to thicken polar or nonpolar solvents, depending on the organic salt. Their efficiency in nonaqueous systems can be further improved by adding a polar organic material of low molecular weight to the composition. Such materials have been called *dispersants*, *dispersion aids*, and *solvating agents*. Low molecular weight alcohols and ketones, particularly methanol and acetone, have been found to be the most efficient.

Organophilic clays are generally prepared by reacting a hydrophilic clay with an organic cation, usually a quaternary ammonium salt compound produced from a fatty nitrile. Examples of hydrophilic clays include bentonite, attapulgite, and hectorite.

Native clay surfaces have negatively charged sites and cationic counter ions such as sodium and calcium cations. Thus, they may be treated with a cationic surfactant to displace the cations that are naturally present at the clay surfaces. The cationic surfactant becomes tightly held to the surfaces through electrostatic charges. In this manner, the hydrophilic nature of the clay is reversed, making it more soluble in oil. Bentonite, when treated with sodium cations, is known as sodium bentonite. Those monovalent sodium cations may be easily displaced from the clay, making a large number of anionic sites available (Miller, 2009).

Quaternary ammonium compounds contain nitrogen moieties in which one or more of the hydrogen atoms attached to the nitrogen are substituted by organic radicals. One of the most popular quaternary ammonium compounds for organophilic clays is dimethyl dihydrogenated tallow ammonium chloride. Tallow contains unsaturated and saturated fatty acids, including oleic acid, palmitic acid, stearic acid, and other minor fatty acids.

The hydrocarbon structure of this compound and the two long chain alkyl groups makes it very oil-soluble. Further, the presence of two methyl groups prevent steric interference, thus allowing close packing of the ammonium cation at the clay surface.

The dimethyl dihydrogenated tallow ammonium chloride surfactant, however, cannot be activated efficiently at relatively low temperatures. Improved cationic surfactants have been developed in which the ammonium compounds have greater numbers of alkyl groups. Inclusion of a benzyl group greatly enhances the performance of organophilic clays at low temperatures (Miller, 2009).

Two or more types of organic salts in the presence of an organic anion act synergistically. The combination of hydrophobic and hydrophilic organic salts and an organic anion produces an organophilic clay gellant, which exhibits improved gelling properties in nonaqueous systems (Nae et al., 1995).

Examples are dimethyl dihydrogenated tallow quaternary ammonium chloride and methyl bis-polyoxyethylene (15 units) cocoalkyl quaternary ammonium chloride, and the salts stearic, succinic, and tartaric acids (Mardis et al., 1997; Nae et al., 1993, 1999).

Biodegradable Organophilic Clay

Organophilic clays are treated with a quaternary ammonium surfactant having an amide linkage. Examples of such surfactants are shown in Figure 1.6.

The surfactants are based on stearamides. The benzyl group greatly enhances the performance of organophilic clays at temperatures near 7°C.

This type of cationic surfactant is substantially biodegradable, meaning that it is capable of being decomposed by natural biological processes. In particular, it undergoes aerobic biodegradation, which is the breakdown of organic chemicals by microorganisms when oxygen is present.

In this process, aerobic bacteria use oxygen as an electron acceptor and degrade organic chemicals into smaller compounds, producing carbon dioxide and water as the final product (Miller, 2009).

Clays treated in this way may therefore be used in drilling fluids without concern that the surfactant could accumulate in the environment. The surfactant will usually not reach toxic levels that could harm the surrounding environment and the life supported by it (Miller, 2009). The organophilic clay is suitable for both oil-based fluids and invert emulsions.

Polyvinyl neodecanoate

Organophilic clays have been considered as necessary for the suspension of drill cuttings. However, formulations have been developed recently that have

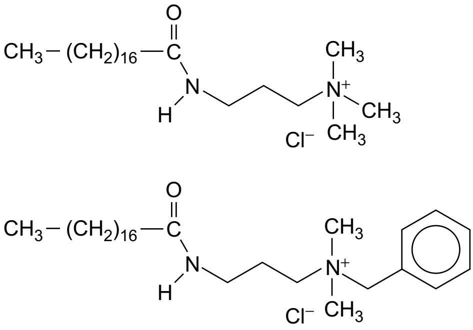


FIGURE 1.6 Quaternary ammonium surfactants (Miller, 2009).

improved suspension properties, without organophilic clays (Miller and Kirsner, 2009).

Additives for clayless formulations are emulsified copolymers of 2-ethylhexyl acrylate (EHA) and AA. However, at elevated temperatures it is likely that some acrylate will hydrolyze to AA, thus raising the level of AA moieties in the copolymer. For certain applications, vinyl neodecanoate may be substituted for EHA (Miller and Kirsner, 2009).

These drilling fluids do not need viscosifiers or additional suspension agents and generally do not need fluid loss control agents or filtration control additives. Their rheological properties remain stable over a broad temperature range, even after exposure to high temperatures (Miller and Kirsner, 2009).

Since space is limited at some well sites, such as offshore platforms, it may be advantageous to use efficient drilling fluid additives, which can be formulated using as few additives as possible.

Miscellaneous

Reticulated Bacterial Cellulose

Reticulated bacterial cellulose may be used in place of a conventional gellant, or in combination with conventional gellants to produce enhanced drilling muds (Westland et al., 1992). Only relatively small quantities of this material is needed to enhance their rheologic properties.

Scleroglucan

Scleroglucan is a polysaccharide secreted by the mycelia of certain microorganisms, produced by aerobic fermentation of D-glucose. It has been proposed as a better alternative to xanthan gum for drilling fluid compositions (Gallino et al., 1996).

For drilling fluid applications, scleroglucan can be used in unrefined form. It is an effective thickener for water (Vaussard et al., 1997) and enhances the lubricating and cleaning power of WBMs. In the drilling of deviated wells, scleroglucan permits better cleaning of the well (Donche et al., 1994; Vaussard et al., 1991). It can also be used in drilling jobs with large-diameter wells (Lacret and Donche, 1991; Ladret and Donche, 1991, 1996).

Uintaite

Uintaite is a naturally occurring, hydrocarbon mineral that is classified as an asphaltite. It is a natural product whose chemical and physical properties vary and depend strongly on the uintaite source. It is also called Gilsonite, which is a registered trademark of American Gilsonite Co., Salt Lake City, Utah.

General purpose Gilsonite brand resin has a softening point of about 175°C, Gilsonite HM has a softening point of about 190°C, and Gilsonite Select 300 and Select 325 have softening points of about 150°C and 160°C, respectively. The softening points of these natural uintaites depend primarily on the source vein that is mined when the mineral is produced.

Uintaite is described by Kirk-Othmer (Neel, 1980). The typical material used in drilling fluids is mined from an area around Bonanza, Utah, and has a specific gravity of 1.05 with a softening point ranging from 190–205°C, although a lower softening point (165°C) material is sometimes used. It has a low acid value, a zero iodine number, and is soluble or partially soluble in aromatic and aliphatic hydrocarbons, respectively.

For many years uintaite and other asphaltic-type products have been used in water-based drilling fluids as additives to assist in borehole stabilization. These additives can minimize hole collapse in formations that contain water sensitive, sloughing shales. Uintaite and asphalt-type materials have been used for many years to stabilize sloughing shales and to reduce borehole erosion. Other benefits derived from these products include borehole lubrication and reduction in the need for filtration.

Uintaite is not easily water-wet with most surfactants. Thus, stable dispersions of uintaite are often difficult to achieve, particularly in the presence of salts, calcium, solids, and other drilling fluid contaminants and in the presence of diesel oil. The uintaite must be readily dispersible and must remain water-wet; otherwise it will coalesce and be separated from the drilling fluid, along with cuttings at the shale shaker or in the circulating pits. Surfactants and emulsifiers are often used with uintaite drilling mud additives.

Loose or poor bonding of the surfactant to the uintaite will lead to it being washed off during use, possible agglomeration, and the removal of uintaite from the mud system with the drilling wastes. Thus, the importance of the wettability, rewettability, and storage stability criteria is evident.

A preferred product comprises about 2 parts Gilsonite HM, about 1 part Gilsonite Select, about 1 part causticized lignite, and about 0.1–0.15 part of a non-ionic surfactant (Christensen et al., 1991, 1993).

Sodium Asphalt Sulfonate

Neutralized sulfonated asphalt (i.e., salts of sulfonated asphalt and their blends with materials such as Gilsonite, blown asphalt, lignite, and mixtures of the latter compounds) are commonly used as additives in drilling fluids. These additives, however, cause some foaming in water or water-based fluids, and they are only partially soluble in the fluids.

Liquid additives have therefore been developed to overcome some of the problems associated with the use of dry additives. However, liquid compositions containing polyglycols can give rise to stability problems. Stable compositions can be obtained by special methods of preparation (Patel, 1996). In particular first the viscosifier is mixed with water, then the polyglycol, and finally the sulfonated asphalt is added.

Formation Damage by Gilsonite and Sulfonated Asphalt

Laboratory experiments have been conducted with a chromium lignite/ chromium lignosulfonate mud system both without and with solid lubricants. These studies looked at filtration loss, cake quality, and their impact on the formation.

A comparative evaluation has led to the conclusion that Gilsonite is a better additive compared with sulfonated asphalt, as it results in less filtration loss and compact cake formation, thereby reducing formation damage. Flow studies have indicated that the addition of these solid lubricants can be used in drilling fluids without adversely impacting the producing zones (Garg et al., 1995).

Multicomponent Additives

Multi-component additives for drilling fluids have been proposed, containing three primary components, namely a (Brazzel, 2009)

1. Rate of penetration enhancer,
2. Lubricant, and
3. Clay inhibitor or stabilizer.

Penetration enhancers are ester-based oils, which are potential carriers for other additives, such as surfactants. The lubricant is a chlorinated wax. The clay stabilizer is a polyglycol. The three components are premixed in a single container, for ease of use in adding to a drilling fluid system.

The pre-blended additive has significant advantages. Once a desired specific ratio is blended, then adding it at that ratio to a drilling fluid system is very much simplified and maintaining the desired volumetric concentrations in the system is much easier. Adding it to the overall system, is much quicker than adding each component singly (Brazzel, 2009).

CLEANING OPERATIONS

Cuttings Removal

When drilling deviated and horizontal wells, gravity causes deposits of drill cuttings and especially fines, or smaller sized cuttings, to build up along the lower side or bottom of the wellbore. Such deposits are commonly called *cuttings beds*. Buildup of cuttings beds can lead to undesirable friction, and possibly to sticking of the drill string.

Removing the drill cuttings from a deviated well, in particular when drilled at a high angle, can be difficult. Limited pump rate, eccentricity of the drill pipe, sharp build rates, high bottom hole temperatures, and oval-shaped wellbores can all contribute to inadequate hole cleaning.

Well treatments by circulating fluids that have been specially formulated to remove such cuttings beds are periodically necessary to prevent buildup to the point that the cuttings or fines interfere with the drilling apparatus.

Usually, the drilling operation must be stopped while such treatment fluids are swept through the wellbore to remove the fines. Alternatively, special viscosifier drilling fluid additives have been proposed to enhance the ability of the drilling fluid to transport cuttings, but such additives at best merely delay the buildup of cuttings beds and they can be problematic in themselves if they change the density of the drilling fluid. Removal of cutting beds has also performed mechanically wherein the drill string is pulled back along the well, pulling the bit through the horizontal or deviated section of the well.

Barium sulfate can be used as a sweep material. It should be ground and sieved to a size range that is sufficiently small to enable it to be suspended in the drilling fluid. After adding it to the drilling fluid, the fluid is circulated in the wellbore, where it removes the small cuttings or cuttings beds from the borehole and delivers them to the well surface.

The composition and the cuttings are then removed from the drilling fluid in a manner that prevents a significant change in its density. This is done by sieving or screening, preferably by the principal shale shaker of the drilling operation (West et al., 2001).

Junk Removal

Drilling equipment that is broken or stuck in the hole can be dissolved by means of nitric and hydrochloric acids mixed in a proportion of 1:3. To accelerate the dissolving of the metal, a mixture containing 1.1 parts of sodium nitrate and 1.0 part of monoethanolamine is added initially to the acids in the amount of 0.05–13.0 parts per 100 parts of acid mixture. The acidic residue in the hole is neutralized by addition of alkali and converted into drilling fluid by addition of polymer solution (Dolganskaya and Sharipov, 1992).

Filter Cake Removal

As the drilling fluid is circulated, a layer of solids, referred to as a filter cake, is usually formed on the walls of the wellbore. A certain degree of cake buildup usually is desirable to isolate formations from drilling fluids. Once the wellbore has been drilled to the desired depth, the drill string and bit are removed, and a pipe string, e.g., casing, liners, etc., are introduced into the wellbore.

Eventually, the wellbore may be conditioned by circulating the drilling fluid. The purpose of this conditioning is to remove as much of the filter cake and the gelled drilling fluid from the walls of the wellbore as possible. However, sometimes this is not enough to remove the undesired material completely. Problems with subsequent processing, e.g., in primary cementing operations may also arise, because in general, cement compositions are not compatible with the drilling fluid and the filter cake.

To mitigate these problems, a special chemical wash composition containing surfactants can be introduced, sometimes known as preflushes.

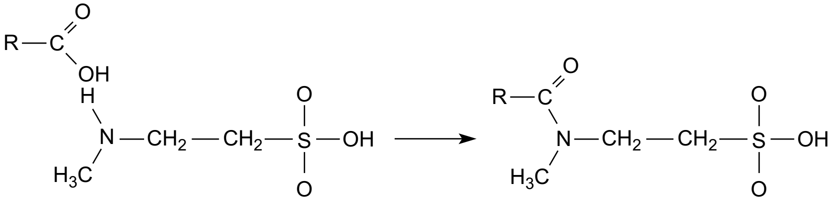


FIGURE 1.7 Acylation of *N*-Methyl-taurine.

An aqueous chemical wash solution contains sulfonated bisulfite lignin, and a taurate, present in amounts of 0.1– 5% (Dealy and Chatterji, 2010). The sulfonated lignin is produced by the bisulfite process, or by sulfomethylation of a lignosulfonate with formaldehyde.

Taurates, or taurides, are generally based on taurine, or 2-aminoethanesulfonic acid. Taurine occurs naturally in food, being first isolated from ox bile in 1827. Taurine derivates have biological and medial roles (Azuma et al., 2009), and are used in cosmetics and as surfactants.

Examples of taurates useful for preflushes are *N*-methyl-*N*-cocoyl taurate, *N*-methyl-*N*-palmitoyl taurate, and *N*-methyl-*N*-oleyl taurate and their metal salts. They are obtained by the acylation of *N*-methyl taurine with the corresponding long chain acids (Walele and Syed, 1995), c.f., Figure 1.7.

Additional additives may be included in the chemical wash compositions, such as (Dealy and Chatterji, 2010):

- Viscosifying agents,
- Defoamers,
- Curing agents,
- Corrosion inhibitors,
- Scale inhibitors, and
- Formation conditioning agents.

Viscosifying agents may be clays, diatomaceous earth, starches, or polymers.

DRILLING FLUID DISPOSAL

Toxicity

Drilling fluids are known to be potentially toxic and are therefore environmentally damaging. They are composed, unlike other most toxic agents, of a wide variety of chemicals, thus making it difficult to predict the actual risk of a specific drilling mud, but methods for assessing this toxicity have been developed (Kanz and Cravey, 1985).

Studies under laboratory conditions revealed that in 9% of cases, drilling muds were acutely toxic at concentrations of 1,000–10,000 ppm. However, in the natural environment, concentrations drop rapidly to background levels of around 200–1,000 ppm, hence low levels may be tolerated in the environment.

In a more recent study, soil samples from oil and gas drilling and production sites were analyzed for contaminating substances associated with drilling fluids and petroleum products. The results revealed that contamination of the soil was widespread and persistent. However, it is generally localized in the immediate vicinity of drilling and production activity. Most prominently, heavy metals, such as barium, chromium, lead, and zinc were detected. Further problems may be caused by salinity, pH, and petroleum hydrocarbons.

No discernible pattern of contamination between well sites was observed due to the variability of methods and materials used in the drilling of individual wells. It was considered that the levels of contaminating agents that were found do not represent an immediate environmental threat. However, the long-term cumulative effects are largely unknown (Carls et al., 1995).

The most consistently toxic bioassay phase is the suspended solid phase. This phase consists of bentonite, cuttings, and soluble components. The toxicity has been explained by specific chemical toxicity of a given mud component, or by physical toxicity generated by abrading or clogging epithelial tissue, i.e., respiratory or digestive body surfaces. In addition, the danger to marine animals from exposure to waste drilling muds may also originate from chemical toxicity. Further details are beyond the scope of this text and the reader is referred to the literature for more information (Kanz and Cravey, 1985, p. 329).

In a long-term study, the influence of increased levels of petroleum hydrocarbons upon soil and plants has been studied. Different doses of drilling fluids and crude oil were applied to clean soil, and the changes in some chemical parameters of the soil, plant density, and crop yields were measured. Drilling fluids showed a stronger impact on the chemical properties of the studied soil, while the plant density and yield were more strongly affected by the levels of crude oil. The soil levels of petroleum hydrocarbons, mineral oils, and polycyclic aromatic hydrocarbons were significantly reduced after the first trial year (Kisic et al., 2009).

For the reasons illustrated above, there is a need to take care in the waste management of drilling muds. Selected solutions for the waste management of these materials will now be discussed.

Conversion Into Cements

Water-based drilling fluids may be converted into cements using hydraulic blast furnace slag (Bell, 1993; Cowan and Hale, 1995; Cowan et al., 1994; Cowan and Smith, 1993; Zhao et al., 1996), a unique material that has low impact on the rheological and fluid loss properties of drilling fluids. It can be activated to set in drilling fluids that are difficult to convert to cements by other solidification technologies.

Hydraulic blast furnace slag has a more uniform and consistent quality than Portland well cements, and it is available in large quantities from multiple sources. Fluid and hardened solid properties of blast furnace slag and drilling fluids mixtures used for cementing operations are comparable with the properties of conventional Portland cement compositions.

Environmental Regulations

In response to effluent limitation guidelines promulgated by the Environmental Protection Agency for the discharge of drilling wastes offshore, alternatives to WBMs and OBMs have been developed. Thus, synthetic-based muds are more efficient than WBMs for drilling difficult and complex formation intervals, and they have lower toxicity and lower environmental impacts than diesel or conventional mineral OBMs.

Synthetic drilling fluids may present a significant pollution prevention opportunity, because they are recycled, and smaller volumes of metals are discharged with the cuttings. A framework for a comparative risk assessment for the discharge of synthetic drilling fluids has been developed that will help to identify potential impacts and benefits associated with the use of specific drilling muds (Meinhold, 1998).

CHARACTERIZATION OF DRILLING MUDS

Important parameters for characterizing the properties of a drilling mud are viscosity, specific weight, gel strength, and filtration performance.

Viscosity

Viscosity is measured by means of a Marsh funnel. The funnel is dimensioned so that the outflow time of 1 qt (926 ml) fresh water at 70°F (21°C) is 26 s.

Viscosity is also measured with a rotational viscometer. The mud is placed between two concentric cylinders. One cylinder rotates with constant velocity, while the other is connected by a spring. The torque on this cylinder results in a deviation of its position from rest, which may serve as a measure of viscosity.

Gel strength is measured by a rotational viscometer, if the maximal deflection of the pointer is monitored when the motor is turned on with low speed, the liquid being at rest for a prolonged time before, for example, for 10 min. This maximal deflection measurement is referred to as a 10-minute gel.

API Filtration

A filter press is used to determine the wall-building characteristics of a mud. This press consists of a cylindrical chamber, which is resistant to alkaline media. A filter paper is placed on the bottom of the chamber. The mud is placed into the chamber and a pressure of 0.7 MPa is applied. After 30 min the volume of filtrate is reported. The filter cake is inspected visually and the consistency is noted as hard, soft, tough, rubbery, or firm.

There is another procedure suitable for OBMs under high-pressure and high-temperature conditions. Here, filtration is performed at 100 psi (7 MPa) and at temperatures of 200°F (93°C). It should be noted that research has shown that there may be significant differences between static and dynamic filtering.

Alkalinity and pH

Alkalinity is measured by acid-base titration, with methylorange or phenolphthalein as an indicator. Phenolphthalein changes color at pH 8.3, whereas methylorange changes color at pH 4.3. At pH 8 the neutralization of the strongly alkaline components such as NaOH is essentially complete.

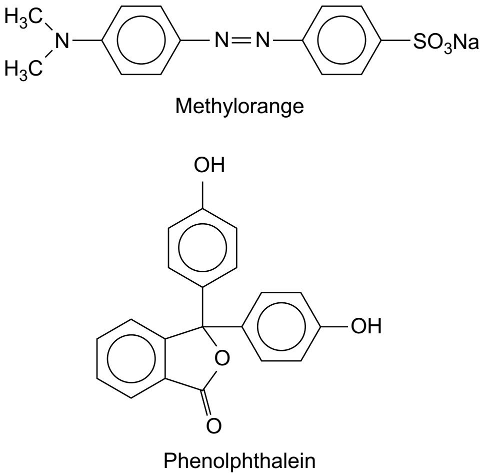
Further reduction of the pH to 4 will also measure the levels of carbonates and bicarbonates that are present. Colorimetric tests and glass electrode systems are used to determine pH. Some indicators are shown in Figure 1.8.

Total Hardness

The sum of calcium and magnesium ions in the mud determines its total hardness. These ions are analyzed by complexometric titrations using ethylene diamine tetraacetic acid.

Roller Oven

The effects of temperature and various chemical additives on the rheological, filtration, and chemical properties of fluids and muds under simulated circulating conditions can be elucidated in a roller oven (Schroeder, 1987, 1992).



Methylorange

Phenolphthalein

FIGURE 1.8 pH Indicators.

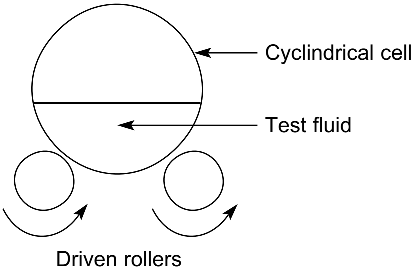


FIGURE 1.9 Construction of a roller cell (schematically).

Its basic construction is shown in Figure 1.9. A more detailed view can be found in the literature (Schroeder, 1987).

In this oven, motorized rollers rotate a cylindrical cell, which contains the sample under investigation. A heating element is situated beneath the rollers, which heats the chamber to a predetermined temperature. A timer may be preset to start and end the test automatically without having an operator in constant attendance (Schroeder, 1987). The roller oven is a versatile tool to monitor ageing, and the change in properties of fluids used in the petroleum industry, as a function of temperature (Mueller et al., 2003).

REFERENCES

Aguilar, K., Colina, R., B.M., A.A., Rojas, Y., 2000. Evaluation criteria to formulate foam as underbalanced drilling fluid. In: Proceedings Volume on CD ROM, Iadc et al Underbalanced Drilling Conf. (Houston, TX, 8/28–29/2000).

Allan, M.L., Kukacka, L.E., 1995. Calcium phosphate cements for lost circulation control in geothermal. Geothermics 24 (2), 269–282.

Alonso-Debolt, M., Jarrett, M.A., 1995. Drilling fluid additive for water-sensitive shales and clays, and method of drilling using the same. EP Patent 668 339, assigned to Baker Hughes Inc., August 23, 1995.

Anonymous, 1991a. Drilling fluids product directory, Offshore Incorporating Oilman (Int. Ed.) 51 (9), 43–44, 46.

Anonymous, 1991b. Drilling fluids product directory, Offshore Incorporating Oilman (Int. Ed.) 51 (10), 62, 64–65, 67–68, 70, 72–73.

Anonymous, 1991c. World oil's 1991 guide to drilling, completion and workover fluids. World Oil 212 (6), 75–112.

Anonymous, 1992. 1992-93 environmental drilling and completion fluids directory, Offshore Incorporating Oilman (Int. Ed.) 52 (9), 41–42, 45–46, 48, 50–56.

Anonymous, 1996. World oil's 1996 drilling, completion and workover fluids. World Oil 217 (6), 85–126.

Arco, M.J., Blanco, J.G., Marquez, R.L., Garavito, S.M., Tovar, J.G., Farias, A.F., Capo, J.A., 2000. Field application of glass bubbles as a density-reducing agent. In: Proceedings Volume, Annu. SPE Tech. Conf. (Dallas, TX, 10/1–4/2000), pp. 115–126.

Argillier, J.F., Roche, P., 2000. Drilling method using a reversible foaming composition (procede de forage utilisant une composition moussante reversible). EP Patent 1 013 739, assigned to Inst. Francais Du Petrole, June 28, 2000.

Ashjian, H., Peel, L.C., Sheerin, T.J., Williamson, R.S., 1995. Non toxic, biodegradable well fluids. WO Patent 9 509 215, assigned to Mobil Oil Corp., April 06, 1995.

Audibert, A., Argillier, J.F., Ladva, H.K.J., Way, P.W., Hove, A.O., 1999. Role of polymers on formation damage. In: Proceedings Volume, SPE Europe Formation Damage Conf. (The Hague, Neth, 5/31/1999-6/1/1999), pp. 505–516.

Austin, P.W., Morpeth, F.F., 1992. Composition and use. EP Patent 500 352, assigned to Imperial Chemical Inds Pl, August 26, 1992.

Azuma, J., Schaffer, S.W., Ito, T. (Eds.), 2009. Taurine 7, Vol. 643 of Advances in Experimental Medicine and Biology, Springer Verlag, Heidelberg.

Bailey, L., Reid, P.I., Sherwood, J.D., 1994. Mechanisms and solutions for chemical inhibition of shale swelling and failure. In: Proceedings Volume, Recent Advances in Oilfield Chemistry, 5th Royal Soc. Chem. Int. Symp. (Ambleside, Engl, 4/13–15/94), pp. 13–27.

Ballard, T.J., Beare, S.P., Lawless, T.A., 1994. Shale inhibition with water-based muds: The influence of polymers on water transport through shales. In: Proceedings Volume, Recent Advances in Oilfield Chemistry, 5th Royal Soc. Chem. Int. Symp. (Ambleside, Engl, 4/13–15/94), pp. 38–55.

Batelaan, J.G., van der Horts, P.M., 1994. Method of making amide modified carboxyl-containing polysaccharide and fatty amide-modified polysaccharide so obtainable. WO Patent 9 424 169, assigned to Akzo Nobel NV, October 27, 1994.

Bauer, P.M., Hanlon, D.J., Menking, W.R., 1993. Process for producing bentonite clays exhibiting enhanced solution viscosity properties. US Patent 5 248 641, assigned to Southern Clay Products In, September 28, 1993.

Bell, S., 1993. Mud-to-cement technology converts industry practices. Pet. Eng. Int. 65 (9), 51–52, 54–55.

Bell, S.A., Shumway, W.W., 2009. Additives for imparting fragile progressive gel structure and controlled temporary viscosity to oil based drilling fluids. US Patent 7 560 418, assigned to Halliburton Energy Services, Inc. (Duncan, OK), July 14, 2009.

Bloys, J.B., Wilton, B.S., 1991. Control of lost circulation in wells. US Patent 5 065 820, assigned to Atlantic Richfield Co., November 19, 1991.

Blytas, G.C., Frank, H., 1995. Copolymerization of polyethercyclicpolyols with epoxy resins. US Patent 5 401 860, assigned to Shell Oil Co., March 28, 1995.

Blytas, G.C., Frank, H., Zuzich, A.H., Holloway, E.L., 1992. Method of preparing polyethercyclicpolyols. EP Patent 505 000, assigned to Shell Internat. Res. Mij BV, September 23, 1992.

Blytas, G.C., Zuzich, A.H., Holloway, E.L., Frank, H., 1992. Method of preparing polyethercyclicpolyols. EP Patent 505 002, assigned to Shell Internat. Res. Mij BV, September 23, 1992.

Brankling, D., 1994. Drilling fluid. WO Patent 9 402 565, assigned to Oilfield Chem. Technol. Ltd., February 03, 1994.

Brazzel, R.L., 2009. Multi-component drilling fluid additive, and drilling fluid system incorporating the additive. US Patent 7 635 667, assigned to Ambar Lonestar Fluid Services, LLC (Layfayette, LA), December 22, 2009.

Bruton, J.R., McLaurine, H.C., 1993. Modified poly-amino acid hydration suppressant proves successful in controlling reactive shales. In: Proceedings Volume, 68th Annu. SPE Tech. Conf. (Houston, 10/3–6/93), pp. 127–135.

Burba, J.L.I., Hoy, E.F., Read Jr., A.E., 1992. Adducts of clay and activated mixed metal oxides. WO Patent 9 218 238, assigned to Dow Chemical Co., October 29, 1992.

Burba, J.L.I., Strother, G.W., 1991. Mixed metal hydroxides for thickening water or hydrophilic fluids. US Patent 4 990 268, assigned to Dow Chemical Co., February 05, 1991.

Burrafato, G., Carminati, S., 1994. Aqueous drilling muds fluidified by means of zirconium and aluminium complexes. EP Patent 623 663, assigned to Eniricerche SPA and Agip SPA, November 09, 1994.

Burts Jr., B.D., 1992. Lost circulation material with rice fraction. US Patent 5 118 664, assigned to Bottom Line Industries In, June 02, 1992.

Burts Jr., B.D., 1997. Lost circulation material with rice fraction. US Patent 5 599 776, assigned to M & D Inds Louisiana Inc., February 04, 1997.

Burts Jr., B.D., 2001. Well fluid additive, well fluid made therefrom, method of treating a well fluid, method of circulating a well fluid. US Patent 6 323 158, assigned to Bottom Line Industries In, November 27, 2001.

Carls, E.G., Fenn, D.B., Chaffey, S.A., 1995. Soil contamination by oil and gas drilling and production operations in Padre Island National Seashore, Texas, U.S.A. Environ. J. Manage. 45 (3), 273–286.

Christensen, K.C., Davis, N.I., Nuzzolo, M., 1991. Water-wettable drilling mud additives containing uintaite. US Patent 5 030 365, assigned to Chevron Research Co., July 09, 1991.

Christensen, K.C., Davis, N.I., Nuzzolo, M., 1993. Water-wettable drilling mud additives containing uintaite. AU Patent 636 334, assigned to American Gilsonite Co., April 29, 1993.

Courtois-Sambourg, J., Courtois, B., Heyraud, A., Colin-Morel, P., Rinaudo-Duhem, M., 1993. Polymer compounds of the glycuronic acid, method of preparation and utilization particularly as gelifying, thickening, hydrating, stabilizing, chelating or flocculating means. WO Patent 9 318 174, assigned to Picardie Univ., September 16, 1993.

Cowan, K.M., Hale, A.H., 1995. High temperature well cementing with low grade blast furnace slag. US Patent 5 379 840, assigned to Shell Oil Co., January 10, 1995.

Cowan, M.K., Hale, A.H., 1994. Restoring lost circulation. US Patent 5 325 922, assigned to Shell Oil Co., July 05, 1994.

Cowan, K.M., Hale, A.H., Nahm, J.J.W., 1994. Dilution of drilling fluid in forming cement slurries. US Patent 5 314 022, assigned to Shell Oil Co., May 24, 1994.

Cowan, K.M., Smith, T.R., 1993. Application of drilling fluids to cement conversion with blast furnace slag in Canada. In: Proceedings Volume, no. 93-601, Cade/caodc Spring Drilling Conf. (Calgary, Can, 4/14–16/93) Proc.

Dahanayake, M., Li, J., Reierson, R.L., Tracy, D.J., 1996. Amphoteric surfactants having multiple hydrophobic and hydrophilic groups. EP Patent 697 244, assigned to Rhone Poulenc Inc., February 21, 1996.

Dalmazzone, C., Audibert-Hayet, A., Langlois, B., Touzet, S., 2007. Oil-based drilling fluid comprising a temperature-stable and non-polluting emulsifying system. US Patent 7 247 604, assigned to Institut Francais du Petrole (Rueil Malmaison Cedex, FR) and Rhodia Chimie (Aubervilliers Cedex, FR), July 24, 2007.

Davidson, E., 2001. Method and composition for scavenging sulphide in drilling fluids. WO Patent 0 109 039, assigned to Halliburton Energy Serv., February 08, 2001.

Dealy, S.T., Chatterji, J., 2010. Chemical wash compositions for removing drilling fluids. US Patent 7 662 752, assigned to Halliburton Energy Services, Inc. (Duncan, OK), February 16, 2010.

Deem, C.K., Schmidt, D.D., Molner, R.A., 1991. Use of mmh (mixed metal hydroxide)/propylene glycol mud for minimization of formation damage in a horizontal well. In: Proceedings Volume, no. 91-29, 4th Cade/caodc Spring Drilling Conf. (Calgary, Can, 4/10–12/91) Proc.

Delhommer, H.J., Walker, C.O., 1987a. Encapsulated oil absorbent polymers as lost circulation additives for oil based drilling fluids. US Patent 4 704 213, November 03, 1987.

Delhommer, H.J., Walker, C.O., 1987b. Method for controlling lost circulation of drilling fluids with hydrocarbon absorbent polymers. US Patent 4 633 950, January 06, 1987.

Dino, D.J., 1997. Modified polygalactomannans as oil field shale inhibitors. US Patent 5 646 093, assigned to Rhone Poulenc Inc., July 08, 1997.

Dino, D., Thompson, J., 2001. Organophilic clay additives and oil well drilling fluids with less temperature dependent rheological properties containing said additives. EP Patent 1 138 740, assigned to Elementis Specialties Inc., October 04, 2001.

Dolganskaya, S.I., Sharipov, A.U., 1992. Removal from hole of junk and stuck drilling equipment – by dissolving latter with mixture of nitric and hydrochloric acids with added sodium nitrate and ethanolamine. SU Patent 1 782 271, assigned to W Sibe Deep Pros Dril Des., December 15, 1992.

Donche, A., Vaussard, A., Isambourg, P., 1994. Application of scleroglucan muds to drilling deviated wells. US Patent 5 330 015, assigned to Soc. Natl. Elf Aquitaine, July 19, 1994.

Doolan, J.G., Cody, C.A., 1995. Pourable water dispersible thickening composition for aqueous systems and a method of thickening said aqueous systems. US Patent 5 425 806, assigned to Rheox Inc., June 20, 1995.

Downey, A.B., Willingham, G.L., Frazier, V.S., 1995. Compositions comprising 4,5-dichloro-2-*n*octyl-3-isothiazolone and certain commercial biocides. EP Patent 680 695, assigned to Rohm & Haas Co., November 08, 1995.

Duhon, J.J.S., 1998. Olive pulp additive in drilling operations. US Patent 5 801 127, September 01, 1998.

Egraz, J.B., Grondin, H., Suau, J.M., 1994. Acrylic copolymer partially or fully soluble in water, cured or not and its use (copolymere acrylique partiellement ou totalement hydrosoluble, reticule ou non et son utilisation). EP Patent 577 526, assigned to Coatex SA, January 05, 1994.

Elphingstone, E.A., Woodworth, F.B., 1999. Dry biocide. US Patent 6 001 158, assigned to Baker Hughes Inc., December 14, 1999.

Fabrichnaya, A.L., Shamraj, Y.V., Shakirzyanov, R.G., Sadriev, Z.K., Koshelev, V.N., Vakhrushev, L.P., Tavrin, A.E., 1997. Additive for drilling solutions with high foam extinguishing properties – containing specified surfactant in hydrocarbon solvent with methyl-diethyl-alkoxymethyl ammonium methyl sulphate. RU Patent 2 091 420, assigned to Etn Co. Ltd., September 27, 1997.

Felix, M.S., 1996. A surface active composition containing an acetal or ketal adduct. WO Patent 9 600 253, assigned to Dow Chemical Co., January 04, 1996.

Felixberger, J., 1996. Mixed metal hydroxides (MMH) – an inorganic thickener for water-based drilling muds (Mixed Metal Hydroxide (MMH) – Ein anorganisches Verdickungsmittel für wasserbasierte Bohrspülungen). In: Proceedings Volume, DMGK Spring Conf. (Celle, Ger, 4/25–26/96), pp. 339–351.

Fleming, J.K., Fleming, H.C., 1995. Invert emulsion drilling mud. WO Patent 9 504 788, assigned to J K F Investments Ltd. and Hour Holdings Ltd., February 16, 1995.

Fu, M., Hu, X., 1997. An investigation into shale stability by utilizing copolymer of acrylamide and acrylonitrile and its derivatives. Jianghan, J., Pet. Inst. 19 (1), 70–73.

Fuh, G.F., Morita, N., Whitfill, D.L., Strah, D.A., 1993. Method for inhibiting the initiation and propagation of formation fractures while drilling. US Patent 5 180 020, assigned to Conoco Inc., January 19, 1993.

Gajdarov, M.M., Tankibaev, M.A., 1996. Non-clayey drilling solution – contains organic stabiliser, caustic soda, water and mineral additive in form of zinc oxide, to improve its thermal stability. RU Patent 2 051 946, assigned to Aktyubinsk Oil Gas Inst., January 10, 1996.

Gallino, G., Guarneri, A., Poli, G., Xiao, L., 1996. Scleroglucan biopolymer enhances wbm (water-base mud) performances. In: Proceedings Volume, Annu. SPE Tech. Conf. (Denver, 10/6–9/96), pp. 105–119.

Garg, V., Ralhan, M., Tewari, H.C., Srivastava, A., Nanda, S.K., Rawat, H.S., 1995. Impact assessment of solid lubricants used in drilling fluids on the producing zone. In: Proceedings Volume, Vol. 3, 1st India Oil & Natur Gas Corp Ltd et al Int. Petrol. Conf. (Petrotech 95) (New Delhi, India, 1/9–12/95), pp. 55–60.

Gee, J.C., Lawrie, C.J., Williamson, R.C., 1995. Drilling fluids comprising mostly linear olefins. WO Patent 9 521 226, assigned to Chevron Chemical Co., August 10, 1995.

Gee, J.C., Williamson, R.C., Lawrie, C.J., 1992. Drilling fluids comprising mostly linear olefins. US Patent 6 057 272, assigned to Chevron Chem. Co., November 19, 1992.

Gee, J.C., Williamson, R.C., Lawrie, C.J., Miller, S.J., 1998. Skeletally isomerized linear olefins. US Patent 5 741 759, assigned to Chevron Chemical Co., April 21, 1998.

Gee, J.C., Williamson, R.C., Lawrie, C.J., Miller, S.J., 2000. Skeletally isomerized linear olefins. US Patent 6 054 415, assigned to Chevron Chem. Co., April 25, 2000.

Getliff, J.M., James, S.G., 1996. The replacement of alkyl-phenol ethoxylates to improve the environmental acceptability of drilling fluid additives. In: Proceedings Volume, Vol. 2, 3rd SPE et al Health, Safety & Environ. Int. Conf. (New Orleans, 6/9–12/96), pp. 713–719.

Glowka, D.A., Loeppke, G.E., Rand, P.B., Wright, E.K., 1989. Laboratory and Field Evaluation of Polyurethane Foam for Lost Circulation Control, Vol. 13 of The Geysers – Three Decades of Achievement: A Window on the Future, Geothermal Resources Council, Davis, Calif, pp. 517–524.

Godwin, A.D., Mathys, G.M.K., 1993. Ester-free ethers. WO Patent 9 304 028, assigned to Exxon Chemical Patents In, March 04, 1993.

Godwin, A.D., Sollie, T., 1993. Load bearing fluid. EP Patent 532 128, assigned to Exxon Chemical Patents In, March 17, 1993.

Goncalves, J., De Oliveira, M.F., Aragäo, t.F.L., 2007. Compositions of oil-based biodegradable drilling fluids and process for drilling oil and gas wells. US Patent 7 285 515, assigned to Petroleo Brasileiro S.A. – Petrobras (BR), October 23, 2007.

Gotlieb, K.F., Bleeker, I.P., van Doren, H.A., Heeres, A., 1996. 2-nitroalkyl ethers of native or modified starch, method for the preparation thereof, and ethers derived therefrom. EP Patent 710 671, assigned to Coop Verkoop Prod. Aard De, May 08, 1996.

Green, B.D., 2001. Method for creating dense drilling fluid additive and composition therefor. WO Patent 0 168 787, assigned to Grinding & Sizing Co. Inc., September 20, 2001.

Grey, R.A., 1993. Process for preparing alternating copolymers of olefinically unsaturated sulfonate salts and unsaturated dicarboxylic acid anhydrides. US Patent 5 210 163, assigned to Arco Chemical Technol. Inc., May 11, 1993.

Guichard, B., Wood, B., Vongphouthone, P., 2008. Fluid loss reducer for high temperature high pressure water based-mud application. US Patent 7 449 430, assigned to Eliokem S.A.S. (Villejust, FR), November 11, 2008.

Gullett, P.D., Head, P.F., 1993. Materials incorporating cellulose fibres, methods for their production and products incorporating such materials. WO Patent 9 318 111, assigned to Stirling Design Intl Ltd., September 16, 1993.

Hale, A.H., Loftin, R.E., 1996. Glycoside-in-oil drilling fluid system. US Patent 5 494 120, assigned to Shell Oil Co., February 27, 1996.

Hatchman, K., 1999. Drilling fluid concentrates. EP Patent 903 390, assigned to Albright & Wilson Ltd., March 24, 1999.

Headley, J.A., Walker, T.O., Jenkins, R.W., 1995. Environmentally safe water-based drilling fluid to replace oil-based muds for shale stabilization. In: Proceedings Volume, SPE/IADC Drilling Conf. (Amsterdam, Neth, 2/28/95–3/2/95), pp. 605–612.

Heinrich, G., 1992. Process for recovering barite from drilling muds. CA Patent 1 310 144, November 10, 1992.

Hille, M., Wittkus, H., Weinelt, F., 1996. Application of acetal-containing mixtures (verwendung von acetal enthaltenden mischungen). EP Patent 702 074, assigned to Hoechst AG, March 20, 1996.

Hille, M., Wittkus, H., Weinelt, F., 1998. Use of acetal-containing mixtures. US Patent 5 830 830, assigned to Clariant GmbH, November 03, 1998.

Hille, M., Wittkus, H., Windhausen, B., Scholz, H.J., Weinelt, F., 1992. Application of acetals (verwendung von acetalen). EP Patent 512 501, assigned to Hoechst AG, November 11, 1992.

Hille, M., Wittkus, H., Windhausen, B., Scholz, H.J., Weinelt, F., 1998. Use of acetals. US Patent 5 759 963, assigned to Hoechst AG, June 02, 1998.

Hodder, M.H., Ballard, D.A., Gammack, G., 1992. Controlling drilling fluid enzyme activity. Pet. Eng. Int. 64 (11), 31, 33, 35.

House, R.F., Cowan, J.C., 2001. Chitosan-containing well drilling and servicing fluids. US Patent 6 258 755, assigned to Venture Innovations Inc., July 10, 2001.

House, R.F., Wilkinson, A.H., Cowan, C., 1991. Well working compositions, method of decreasing the seepage loss from such compositions, and additive therefor. US Patent 5 004 553, assigned to Venture Innovations Inc., April 02, 1991.

Hsu, J.C., 1990. Synergistic microbicidal combinations containing 3- isothiazolone and commercial biocides. US Patent 4 906 651, assigned to Rohm & Haas Co., March 06, 1990.

Hsu, J.C., 1995. Biocidal compositions. EP Patent 685 158, assigned to Rohm & Haas Co., December 06, 1995.

Ibragimov, F.B., Kolesov, A.I., Konovalov, E.A., Rud, N.T., Gavrilov, B.M., Mojsa, J.N., Rjabokon, A.A., Shcherbaeva, O.M., 1998. Preparation of lignosulphonate reagent – for drilling solutions, involves additional introduction of water-soluble salt of iron, and anti-foaming agent. RU Patent 2 106 383, March 10, 1998.

Ivan, C.D., Blake, L.D., Quintana, J.L., 2001. Aphron-base drilling fluid: Evolving technologies for lost circulation control. In: Proceedings Volume, Annu. SPE Tech. Conf. (New Orleans, LA, 9/30/2001-10/3/2001).

Jarrett, M., 1997a. Amphoteric acetates and glycinates as shale stabilizing surfactants for aqueous well fluids. US Patent 5 593 952, assigned to Baker Hughes Inc., January 14, 1997.

Jarrett, M., 1997b. Nonionic alkanolamides as shale stabilizing surfactants for aqueous well fluids. US Patent 5 607 904, assigned to Baker Hughes Inc., March 04, 1997.

Jarrett, M., Clapper, D., 2010. High temperature filtration control using water based drilling fluid systems comprising water soluble polymers. US Patent 7 651 980, assigned to Baker Hughes Incorporated (Houston, TX), January 26, 2010.

Jones, C.K., Acker, D.B., 1999. Oil-based drilling muds with increased viscosity. EP Patent 922 743, assigned to Nalco Exxon Energy Chem. L, June 16, 1999.

Kanz, J.E., Cravey, M.J., 1985. Oil well drilling fluids: Their physical and chemical properties and biological impact. In: Saxena, J., Fisher, F. (Eds.), Hazard Assessment of Chemicals, vol. 5. Elsevier, New York, pp. 291–421.

Karaseva, E.V., Dedyukhina, S.N., Dedyukhin, A.A., 1995. Treatment of water-based drilling solution to prevent microbial attack – by addition of dimethyl- tetrahydro-thiadiazine-thione bactericide. RU Patent 2 036 216, May 27, 1995.

Kehoe, J.D., Joyce, M.K., 1993. Water soluble liquid alginate dispersions. US Patent 5 246 490, assigned to Syn Chem. Inc., September 21, 1993.

Keilhofer, G., Plank, J., 2000. Solids composition based on clay minerals and use thereof. US Patent 6 025 303, assigned to Skw Trostberg AG, February 15, 2000.

Kinchen, D., Peavy, M.A., Brookey, T., Rhodes, D., 2001. Case history: Drilling techniques used in successful redevelopment of low pressure H_2S gas carbonate formation. In: Proceedings Volume, Vol. 1, SPE/IADC Drilling Conf. (Amsterdam, Netherlands, 2/27/2001-3/1/2001), pp. 392–403.

Kisic, I., Mesic, S., Basic, F., Brkic, V., Mesic, M., Durn, G., Zgorelec, Z., Bertovic, L., 2009. The effect of drilling fluids and crude oil on some chemical characteristics of soil and crops. Geoderma 149 (3–4), 209–216.

Kohn, R.S., 1988. Thixotropic aqueous solutions containing a divinylsulfone-crosslinked polygalactomannan gum. US Patent 4 752 339, June 21, 1988.

Kolle, J.J., 2002. Coiled tubing drilling with supercritical carbon dioxide. US Patent 6 347 675, assigned to Tempress Technologies Inc., February 19, 2002.

Kondo, M., Sawada, T., 1996. Readily dispersible bentonite. US Patent 5 491 248, assigned to Hojun Kogyo Co. Ltd., February 13, 1996.

Kotelnikov, V.S., Demochko, S.N., Fil, V.G., Marchuk, I.S., 1996. Drilling mud composition - contains carboxymethyl cellulose, acrylic polymer, ferrochrome lignosulphonate, cement and water. SU Patent 1 829 381, assigned to Ukr. Natural Gas Res. Inst., April 20, 1996.

Kotelnikov, V.S., Demochko, S.N., Melnik, M.P., Mikitchak, V.P., 1992. Improving properties of drilling solution - by addition of ferrochrome- lignosulphonate and aqueous solution of cement and carboxymethyl cellulose. SU Patent 1 730 118, assigned to Ukr. Natural Gas Res. Inst., April 30, 1992.

Kulpa, K., Adkins, R., Walker, N.S., 1992. New testing vindicates use of barite. Am. Oil Gas Report. 35 (4), 52–54.

Lacret, A., Donche, A., 1991. Use of scleroglucan muds for the drilling of large diameter holes (application des boues au scleroglucane au forage des puits a gros diametre). FR Patent 2 662 447, assigned to Soc. Natl. Elf Aquitaine, November 29, 1991.

Ladret, A., Donche, A., 1991. Use of scleroglucan muds for the drilling of large diameter holes (application des boues au scleroglucane au forage des puits a gros diametre). EP Patent 459 881, assigned to Soc. Natl. Elf Aquitaine, December 04, 1991.

Ladret, A., Donche, A., 1996. Application of muds containing scleroglucan to drilling large diameter wells. US Patent 5 525 587, assigned to Soc. Natl. Elf Aquitaine, June 11, 1996.

Lange, P., Plank, J., 1999. Mixed metal hydroxide (MMH) viscosifier for drilling fluids: Properties and mode of action (Mixed Metal Hydroxide (MMH) – Eigenschaften undWirkmechanismus als Verdickungsmittel in Bohrspülungen). Erdöl Erdgas Kohle 115 (7–8), 349–353.

Langlois, B., 1998. Fluid comprising cellulose nanofibrils and its use for oil mining. WO Patent 9 802 499, assigned to Rhone Poulenc Chimie, January 22, 1998.

Langlois, B., Guerin, G., Senechal, A., Cantiani, R., Vincent, I., Benchimol, J., 1999. Fluid comprising cellulose nanofibrils and its use for oil mining (fluide comprenant des nanofibrilles de cellulose et son application pour l'exploitation de gisements petroliers). EP Patent 912 653, assigned to Rhodia Chimie, May 06, 1999.

Lau, H.C., Hale, A.H., Bernardi Jr., L.A., 1997. Drilling fluid. US Patent H168, assigned to Shell Oil Comp., October 7, 1997.

Le Helloco, J.-G., Joye, J.-L., Taverna, C.C., 2004. Polyalkoxylated superamides optionally functionalized, use as emulsifiers. US Patent 6 689 908, assigned to Rhodia Chimie (Courbevoie Cedex, FR), February 10, 2004.

Lecocumichel, N., Amalric, C., 1995. Concentrated aqueous compositions of alkylpolyglycosides, and applications thereof. WO Patent 9 504 592, assigned to Seppic SA, February 16, 1995.

Lee, L.J., Patel, A., Stamatakis, E., 1997. Glycol based drilling fluid. WO Patent 9 710 313, assigned to M I Drilling Fluids Llc., March 20, 1997.

Lin, K.-F., 1996. Synthetic paraffinic hydrocarbon drilling fluid. US Patent 5 569 642, assigned to Albemarle Corp., October 29, 1996.

Lipkes, M.I., Mezhlumov, A.O., Shits, L.A., Avdeev, G.E., Fomenko, V.I., Shvetsov, A.M., 1996. Carbonate weighting material for drilling-in producing formations and well overhaul. Stroit Neft Gaz Skvazhin Sushe More (5–6), 34–41.

Lukach, C.A., Zapico, J., 1994. Thermally stable hydroxyethylcellulose suspension. EP Patent 619 340, assigned to Aqualon Co., October 12, 1994.

Lundan, A.O., Anas, P.H., Lahteenmaki, M.J., 1993. Stable cmc (carboxymethyl cellulose) slurry. WO Patent 9 320 139, assigned to Metsa Serla Chemicals Oy, October 14, 1993.

Lundan, A.O., Lahteenmaki, M.J., 1996. Stable cmc (carboxymethyl cellulose) slurry. US Patent 5 487 777, assigned to Metsa Serla Chemicals Oy, January 30, 1996.

Lyons, W.C., 1996. Standard Handbook of Petroleum and Natural Gas Engineering, vol. 1–2. Gulf Publishing Co., Burlington.

Müller, H., Herold, C.P., von Tapavicza, S., Neuss, M., Zöllner, W., Burbach, F., 1990. Invert drilling muds. WO Patent 9 010 681, assigned to Henkel KG Auf Aktien, September 20, 1990.

Mardis, W., Sanchaz, J., Basson, H., 1997. Organoclay compositions manufactured with organic acid ester-derived quaternary ammonium compounds, their preparation and non-aqueous fluid systems containing such compositions. EP Patent 798 267, assigned to Rheox International Inc., October 01, 1997.

Maresh, J.L., 2009. Wellbore treatment fluids having improved thermal stability. US Patent 7 541 316, assigned to Halliburton Energy Services, Inc. (Duncan, OK), June 2, 2009.

Martyanova, S.V., Chezlov, A.A., Nigmatullina, A.G., Piskareva, L.A., Shamsutdinov, R.D., 1997. Production of lignosulphonate reagent for drilling muds – by initial heating with sulphuric acid, condensation with formaldehyde, and neutralisation of mixture with sodium hydroxide. RU Patent 2 098 447, assigned to Azimut Res. Prod. Assoc., December 10, 1997.

McCallum, T.F.I., Weinstein, B., 1994. Amine-thiol chain transfer agents. US Patent 5 298 585, assigned to Rohm & Haas Co., March 29, 1994.

McDonald, W.J., Cohen, J.H., Hightower, C.M., 1999. New lightweight fluids for underbalanced drilling, DOE/FETC Rep 99-1103, Maurer Engineering Inc.

McGlothlin, R.E., Woodworth, F.B., 1996. Well drilling process and clay stabilizing agent. US Patent 5 558 171, assigned to M I Drilling Fluids Llc., September 24, 1996.

McNally, K., Nae, H., Gambino, J., 1999. Oil well drilling fluids with improved anti-settling properties and methods of preparing them. EP Patent 906 946, assigned to Rheox Inc., April 07, 1999.

Medley Jr., G.H., Haston, J.E., Montgomery, R.L., Martindale, I.D., Duda, J.R., 1997. Field application of lightweight, hollow-glass-sphere drilling fluid. Pet. J. Technol. 49 (11), 1209–1211.

Medley Jr., G.H., Maurer, W.C., Garkasi, A.Y., 1995. Use of hollow glass spheres for underbalanced drilling fluids. In: Proceedings Volume, Annu. SPE Tech. Conf. (Dallas, 10/22–25/95), pp. 511–520.

Meinhold, A.F., 1998. Framework for a comparative environmental assessment of drilling fluids, Brookhaven Nat Lab Rep BNL-66108, Brookhaven Nat Lab (November 1998).

Melbouci, M., Sau, A.C., 2008. Water-based drilling fluids. US Patent 7 384 892, assigned to Hercules Incorporated (Wilmington, DE), June 10, 2008.

Mercer, J.D., Nesbit, L.L., 1992. Oil-base drilling fluid comprising branched chain paraffins such as the dimer of 1-decene. US Patent 5 096 883, assigned to Union Oil Co. California, March 17, 1992.

Messenger, J.U., 1981. Lost Circulation. PennWell Publishing Co., Tulsa, OK, pp. 44–56.

Meyer, V., Audibert-Hayet, A., Gateau, J.P., Durand, J.P., Argillier, J.F., 1999. Water-soluble copolymers containing silicon. GB Patent 2 327 946, assigned to Inst. Francais Du Petrole, February 10, 1999.

Michelson, A., Vattement, H., 1999. Bentonite-based drilling mud and drilling method making use thereof (boue de forage a base de bentonite et procede de forage la mettant en oeuvre). EP Patent 936 263, assigned to Cie Du Sol, August 18, 1999.

Miller, J.J., 2009. Drilling fluids containing biodegradable organophilic clay. US Patent 7 521 399, assigned to Halliburton Energy Services, Inc. (Duncan, OK), April 21, 2009.

Miller, J., Kirsner, J., 2009. Drilling fluid comprising a vinyl neodecanoate polymer and method for enhanced suspension. US Patent 7 572 755, assigned to Halliburton Energy Services, Inc. (Ducan, OK), August 11, 2009.

Monfreux, N., Perrin, P., Lafuma, F., Sawdon, C., 2000. Invertible emulsions stabilised by amphiphilic polymers and application to bore fluids (emulsions inversables stabilisees par des polymers amphiphiles. application a des fluides de forage). WO Patent 0 031 154, assigned to Sofitech NV, Schlumberger Canada Ltd., and Dowell Schlumberger SA, June 02, 2000.

Morpeth, F.F., 1993. Biocide composition and its use. EP Patent 542 721, assigned to Imperial Chemical Inds Pl, May 19, 1993.

Morpeth, F.F., Greenhalgh, M., 1990. Composition and use. EP Patent 390 394, assigned to Imperial Chemical Inds Pl, October 03, 1990.

Mueller, H., Breuer, W., Herold, C.P., Kuhm, P., von Tapavicza, S. 1997. Mineral additives for setting and/or controlling the rheological properties and gel structure of aqueous liquid phases and the use of such additives. US Patent 5 663 122, assigned to Henkel KG Auf Aktien, September 02, 1997.

Mueller, H., Herold, C.-P., Fues, J.F., 1996. Use of surface-active alpha-sulfo-fatty acid di-salts in water and oil based drilling fluids and other drill-hole treatment agents. US Patent 5 508 258, assigned to Henkel KG, April 16, 1996.

Mueller, H., Herold, C.P., von Tapavicza, S., 1990a. Monocarboxylic acid-methyl esters in invertemulsion muds (monocarbonsaeure-methylester in invert-bohrspuelschlaemmen). EP Patent 382 071, assigned to Henkel KG Auf Aktien, August 16, 1990.

Mueller, H., Herold, C.P., von Tapavicza, S., 1990b. Oleophilic alcohols as components of invert emulsion drilling fluids (oleophile alkohole als bestandteil von invert-bohrspuelungen). EP Patent 391 252, assigned to Henkel KG Auf Aktien, October 10, 1990.

Mueller, H., Herold, C.P., von Tapavicza, S., 1990c. Oleophilic basic amine derivatives as additives in invert emulsion muds (oleophile basische aminverbindungen als additiv in invert-bohrspuelschlaemmen). EP Patent 382 070, assigned to Henkel KG Auf Aktien, August 16, 1990.

Mueller, H., Herold, C.P., von Tapavicza, S., 1991. Use of hydrated castor oil as a viscosity promoter in oil-based drilling muds. WO Patent 9 116 391, assigned to Henkel KG Auf Aktien, October 31, 1991.

Mueller, H., Herold, C.P., von Tapavicza, S., Fues, J.F., 1991. Fluid borehole-conditioning agent based on polycarboxylic acid esters. WO Patent 9 119 771, assigned to Henkel KG Auf Aktien, December 26, 1991.

Mueller, H., Herold, C.P., von Tapavicza, S., Grimes, D.J., Braun, J.M., Smith, S.P.T., 1990a. Use of selected ester oils in drilling muds, especially for offshore oil or gas recovery (verwendung ausgewaehlter esteroele in bohrspuelungen insbesondere zur off-shore- erschliessung von erdoel- bzw. erdgasvorkommen (i)). EP Patent 374 671, assigned to Henkel KG Auf Aktien and Baroid Ltd., June 27, 1990.

Mueller, H., Herold, C.P., von Tapavicza, S., Grimes, D.J., Braun, J.M., Smith, S.P.T., 1990b. Use of selected ester oils in drilling muds, especially for offshore oil or gas recovery (verwendung ausgewaehlter esteroele in bohrspuelungen insbesondere zur off-shore- erschliessung von erdoel- bzw. erdgasvorkommen (ii)). EP Patent 374 672, assigned to Henkel KG Auf Aktien and Baroid Ltd., June 27, 1990.

Mueller, H., Herold, C.P., von Tapavicza, S., Neuss, M., Burbach, F., 1994. Use of selected ester oils of low carboxylic acids in drilling fluids. US Patent 5 318 954, assigned to Henkel KG Auf Aktien, June 07, 1994.

Mueller, H., Herold, C.-P., von Tapavicza, S., Stoll, G., Jeschke, R., Fues, J.F., 2003. Use of selected oleophilic ethers in water-based drilling fluids of the o/w emulsion type and corresponding drilling fluids with improved ecological acceptability. US Patent 6 596 670, assigned to Cognis Deutschland GmbH & Co. KG, Duesseldorf and Baroid Limited, London, July 22, 2003.

Mueller, H., Herold, C.P., Westfechtel, A., von Tapavicza, S., 1991. Free-flowing drill hole treatment agents based on carbonic acid diesters. WO Patent 9 118 958, assigned to Henkel KG Auf Aktien, December 12, 1991.

Mueller, H., Herold, C.P., Westfechtel, A., von Tapavicza, S., 1992. Fluid drill-hole treatment agents based on carbonic acid diesters. ZA Patent 9 104 341, assigned to Henkel KG Auf Aktien, January 20, 1992.

Mueller, H., Herold, C.P., Westfechtel, A., von Tapavicza, S., 1993. Free-flowing drill hole treatment agents based on carbonic acid diesters (fliessfaehige bohrlochbehandlungsmittel auf basis von kohlensaeurediestern). EP Patent 532 570, assigned to Henkel KG Auf Aktien, March 24, 1993.

Mueller, H., Herold, C.P., Westfechtel, A., von Tapavicza, S., 1995. Fluid-drill-hole treatment agents based on carbonic acid diesters. US Patent 5 461 028, assigned to Henkel KG Auf Aktien, October 24, 1995.

Mueller, H., Stoll, G., Herold, C.P., von Tapavicza, S., 1990. Application of selected ethers of monofunctional alcohols in drilling fluids (verwendung ausgewaehlter ether monofunktioneller alkohole in bohrspuelungen). EP Patent 391 251, assigned to Henkel KG Auf Aktien, October 10, 1990.

Mullen, G.A., Gabrysch, A., 2001. Synergistic mineral blends for control of filtration and rheology in silicate drilling fluids. US Patent 6 248 698, assigned to Baker Hughes Inc., June 19, 2001.

Muller, H., Herold, C.P., von Tapavicza, S., 1990. Drilling fluids. ZA Patent 9 002 669, assigned to Henkel KG Auf Aktien, October 08, 1990.

Muller, H., Herold, C.P., Westfechtel, A., von Tapavicza, S., 1993. Free-flowing drill hole treatment agents based on carbonic acid diesters. AU Patent 643 299, assigned to Henkel KG Auf Aktien, November 11, 1993.

Muller, H., Stoll, G., Herold, C.P., von Tapavicza, S., 1990. Drilling fluids. ZA Patent 9 002 665, assigned to Henkel KG Auf Aktien, October 08, 1990.

Munro, R., Hanni, G., Young, A., 1993. The economics of a synthetic drilling fluid for exploration drilling in the UK sector of the North Sea. In: Proceedings Volume, IBC Tech. Serv. Ltd Prev. Oil Discharge from Drilling Oper. – The Options Conf. (Aberdeen, Scot, 6/23–24/93).

Nae, H., Reichert, W.W., Eng, A.C., 1993. Organoclay compositions prepared with a mixture of two organic cations and their use in non-aqueous systems. EP Patent 542 266, assigned to Rheox International Inc., May 19, 1993.

Nae, H.N., Reichert, W.W., Eng, A.C., 1995. Organoclay compositions containing two or more cations and one or more organic anions, their preparation and use in non-aqueous systems. US Patent 5 429 999, assigned to Rheox Inc., July 04, 1995.

Nae, H., Reichert, W., Eng, A.C., 1999. Organoclay compositions containing two or more cations and one or more organic anions, their preparation and use in non-aqueous systems. EP Patent 681 990, assigned to Rheox International Inc., November 24, 1999.

Neel, K.R., 1980. Gilsonite. In: Kirk-Othmer Encyclopedia of Chemical Technology, third ed., vol. 11. J. Wiley & Sons, New York, pp. 802–806.

Nicora, L.F., McGregor, W.M., 1998. Biodegradable surfactants for cosmetics find application in drilling fluids. In: Proceedings Volume, Iadc/SPE Drilling Conf. (Dallas, 3/3–6/98), pp. 723–730.

Oppong, D., Hollis, C.G., 1995. Synergistic antimicrobial compositions containing (thiocyanomethylthio) benzothiazole and an organic acid. WO Patent 9 508 267, assigned to Buckman Labs Internat. Inc., March 30, 1995.

Oppong, D., King, V.M., 1995. Synergistic antimicrobial compositions containing a halogenated acetophenone and an organic acid. WO Patent 9 520 319, assigned to Buckman Labs Internat. Inc., August 03, 1995.

Patel, B.B., 1994a. Fluid composition comprising a metal aluminate or a viscosity promoter and a magnesium compound and process using the composition. EP Patent 617 106, assigned to Phillips Petroleum Co., September 28, 1994.

Patel, B.B., 1994b. Tin/cerium compounds for lignosulfonate processing. EP Patent 600 343, assigned to Phillips Petroleum Co., June 08, 1994.

Patel, B.B., 1996. Liquid additive comprising a sulfonated asphalt and processes therefor and therewith. US Patent 5 502 030, assigned to Phillips Petroleum Co., March 26, 1996.

Patel, A.D., 2008. Methods for using reversible phase oil-based drilling fluid. US Patent 7 377 721, assigned to M-I L.L.C. (Houston, TX), May 27, 2008.

Patel, A.D., McLaurine, H.C., Stamatakis, E., Thaemlitz, C.J., 1995. Drilling fluid additive and method for inhibiting hydration. EP Patent 634 468, assigned to M I Drilling Fluids Co., January 18, 1995.

Patel, B.B., Muller, G.T., 1996. Compositions comprising an acrylamide-containing polymer and process therewith. EP Patent 728 826, assigned to Phillips Petroleum Co., August 28, 1996.

Patel, A.D., Stamatakis, E., Davis, E., 2001. Shale hydration inhibition agent and method of use. US Patent 6 247 543, assigned to M I Llc., June 19, 2001.

Patel, A.D., Stamatakis, E., Young, S., 2009. High performance water-based drilling mud and method of use. US Patent 7 514 389, assigned to M-I L.L.C. (Houston, TX), April 7, 2009.

Peiffer, D.G., Bock, J., Elward-Berry, J., 1991. Zwitterionic functionalized polymers as deflocculants in water based drilling fluids. US Patent 5 026 490, assigned to Exxon Research & Eng. Co., June 25, 1991.

Peiffer, D.G., Bock, J., Elward-Berry, J., 1992. Thermally stable hydrophobically associating rheological control additives for water-based drilling fluids. US Patent 5 096 603, assigned to Exxon Research & Eng. Co., March 17, 1992.

Peiffer, D.G., Bock, J., Elward-Berry, J., 1993. Thermally stable hydrophobically associating rheological control additives for water-based drilling fluids. CA Patent 2 055 011, assigned to Exxon Research & Eng. Co., May 07, 1993.

Ponsati, O., Trius, A., Herold, C.P., Mueller, H., Nitsch, C., von Tapavicza, S., 1992. Use of selected oleophilic compounds with quaternary nitrogen to improve the oil wettability of finely divided clay and their use as viscosity promoters. WO Patent 9 219 693, assigned to Henkel KG Auf Aktien, November 12, 1992.

Ponsati, O., Trius, A., Herold, C.P., Mueller, H., Nitsch, C., von Tapavicza, S., 1994. Use of selected oleophilic compounds with quaternary nitrogen to improve the oil wettability of finely divided clay and their use as viscosity promoters (verwendung ausgewaehlter oleophiler verbindungen mit quartaerem stickstoff zur verbesserung der oelbenetzbarkeit feinteiliger tone und deren anwendung als viskositaetsbildner). EP Patent 583 285, assigned to Henkel KG Auf Aktien, February 23, 1994.

Prokhorov, N.M., Smirnova, L.N., Luban, V.Z., 1993. Neutralisation of hydrogen sulphide in drilling solution - by introduction of additive consisting of iron sulphate and additionally sodium aluminate, to increase hydrogen sulphide absorption. SU Patent 1 798 358, assigned to Polt. Br. Ukr. Geoprosp. Inst., February 28, 1993.

Rae, R., Di Lullo, G., 2001. Chemically-enhanced drilling with coiled tubing in carbonate reservoirs. In: Proceedings Volume, SPE/Int. Coiled Tubing Ass. Coiled Tubing Roundtable (Houston, TX, 3/7–8/2001).

Rangus, S., Shaw, D.B., Jenness, P., 1993. Cellulose ether thickening compositions. WO Patent 9 308 230, assigned to Laporte Industries Ltd., April 29, 1993.

Rastegaev, B.A., Andreson, B.A., Raizberg, Y.L., 1999. Bactericidal protection of chemical agents from biodegradation while drilling deep wells. Stroit Neft Gaz Skvazhin Sushe More (7–8), 32–34.

Ravi, K.M., Whitfill, D.L., Reddy, B.R., 2009. Methods of drilling wellbores using variable density fluids comprising coated elastic particles. US Patent 7 482 309, assigned to Halliburton Energy Services, Inc. (Duncan, OK), January 27, 2009.

Recommended practice for chemical analysis of barite. 1996. API Standard API RP 13K. American Petroleum Institute, Washington, DC.

Reid, A.L., Grichuk, H.A., 1991. Polymer composition comprising phosphorous- containing gelling agent and process thereof. US Patent 5 034 139, assigned to Nalco Chemical Co., July 23, 1991.

Robinson, F., 1996. Polymers useful as ph responsive thickeners and monomers therefor. WOPatent 9 610 602, assigned to Rhone Poulenc Inc., April 11, 1996.

Robinson, F., 1999. Polymers useful as ph responsive thickeners and monomers therefor. US Patent 5 874 495, assigned to Rhodia, February 23, 1999.

Rose, R.A., 1996. Method of drilling with fluid including nut cork and drilling fluid additive. US Patent 5 484 028, assigned to Grinding & Sizing Co. Inc., January 16, 1996.

Saasen, A., Hoset, H., Rostad, E.J., Fjogstad, A., Aunan, O., Westgard, E., Norkyn, P.I., 2001. Application of ilmenite as weight material in water based and oil based drilling fluids. In: Proceedings Volume, Annu. SPE Tech. Conf. (New Orleans, LA, 9/30/2001-10/3/2001).

Santhanam, M., MacNally, K., 2001. Oil and oil invert emulsion drilling fluids with improved antisettling properties. EP Patent 1 111 024, assigned to Rheox Inc., June 27, 2001.

Sawdon, C., Tehrani, M., Craddock, P., 2000. Electrically conductive non-aqueous wellbore fluids. GB Patent 2 345 706, assigned to Sofitech NV, July 19, 2000.

Schlemmer, R.F., 2007. Membrane forming in-situ polymerization for water based drilling fluids. US Patent 7 279 445, assigned to M-I L.L.C. (Houston, TX), October 9, 2007.

Schroeder, R.E., 1987. Roller oven for testing fluids. US Patent 4 677 843, assigned to OFI Testing Equipment Inc. (Houston, TX), July 7, 1987.

Schroeder, R.E., 1992. Thermal test liner apparatus and method. US Patent 5 152 184, assigned to OFI Testing Equipment, Inc. (Houston, TX), October 6, 1992.

Shen, W., Pan, H., Du, T., Jia, D., 1998. Preparation and applications of oleophilic modified barite. Univ. J. Pet. China 22 (1), 66–69, 114.

Shen, W., Pan, H.F., Qin, Y.Q., 1999. Advances in chemical surface modification of barite. Oilfield Chem. 16 (1), 86–90.

Sheu, J.J., Bland, R.G., 1992. Drilling fluid with stabilized browning reaction anionic carbohydrate. US Patent 5 110 484, assigned to Baker Hughes Inc., May 05, 1992.

Shimomura, T., Irie, Y., Takahashi, H., Kajikawa, K., Saga, J., Fujiwara, T., Hatsuda, T., 1990. Process for production of acrylate and acrylate- containing polymer. EP Patent 372 706, assigned to Nippon Shokubai Kag Kog C, June 13, 1990.

Shuey, M.W., Custer, R.S., 1995. Quebracho-modified bitumen compositions, method of manufacture and use. US Patent 5 401 308, assigned to Saramco Inc., March 28, 1995.

Sikora, D., 1994. Hydrazine – a universal oxygen scavenger (hydrazyna – uniwersalny inhibitor korozji tlenowej w pluczkach wiertniczych). Nafta Gaz (Pol) 50 (4), 161–168.

Smith, C.K., Balson, T.G., 2000. Shale-stabilizing additives. GB Patent 2 340 521, assigned to Sofitech NV and Dow Chemical Co., February 23, 2000.

Smith, R.J., Jeanson, D.R., 2001. Dehydration of drilling mud. US Patent 6 216 361, assigned to Newpark Canada Inc., April 17, 2001.

Subramanian, S., Islam, M., Burgazli, C.R., 2001. Quaternary ammonium salts as thickening agents for aqueous systems. WO Patent 0 118 147, assigned to Crompton Corp., March 15, 2001.

Sunde, E., Olsen, H., 2000. Removal of H2S in drilling mud. WO Patent 0 023 538, assigned to Den Norske Stats Oljese A, April 27, 2000.

Sydansk, R.D., 1990. Lost circulation treatment for oil field drilling operations. US Patent 4 957 166, assigned to Marathon Oil Co., September 18, 1990.

Urquhart, J.C., 1997. Potassium silicate drilling fluid. WO Patent 9 705 212, February 13, 1997.

Vaussard, A., Ladret, A., Donche, A., 1991. Scleroglucan drilling mud (boue de forage au scleroglucane). FR Patent 2 661 186, assigned to Soc. Natl. Elf Aquitaine, October 25, 1991.

Vaussard, A., Ladret, A., Donche, A., 1997. Scleroglucan based drilling mud. US Patent 5 612 294, assigned to Elf Aquitaine, March 18, 1997.

Waehner, K., 1990. Experience with high temperature resistant water based drilling fluids (erfahrungen beim einsatz hochtemperatur-stabiler wasserbasischer bohrspülung). Erdöl Erdgas Kohle 106 (5), 200–201.

Walele, I.I., Syed, S.A., 1995. Process for making *N*-acyl taurides. US Patent 5 434 276, assigned to Finetex, Inc. (Elmwood Park, NJ), July 18, 1995.

Walker, C.O., 1986. Encapsulated lime as a lost circulation additive for aqueous drilling fluids. US Patent 4 614 599, September 30, 1986.

Walker, C.O., 1989. Method for controlling lost circulation of drilling fluids with water absorbent polymers. CA Patent 1 259 788, assigned to Texaco Development Corp., September 26, 1989.

Wall, K., Zard, P.W., Barclay-Miller, D.J., Martin, D.W., 1995. Surfactant composition. WO Patent 9 530 722, assigned to Burwood Corp. Ltd., November 16, 1995.

Wegner, C., Reichert, G., 1990. Hydrogen sulfide scavenger in drilling fluids (schwefelwasserstoffscavenger in bohrspülungen). In: Proceedings Volume, BASF et al Chem. Prod. in Petrol. Prod. Mtg. H2S – A Hazardous Gas in Crude Oil Recovery Discuss (Clausthal-Zellerfeld, Ger, 9/12–13/90).

West, G.C., Valenziano, R., Lutgring, K.A., 2001. Method and composition for sweep of cuttings beds in a deviated borehole. US Patent 6 290 001, assigned to Halliburton Energy Serv., September 18, 2001.

Westland, J.A., Penny, G.S., Lenk, D.A., 1992. Drilling mud compositions. WO Patent 9 222 621, assigned to Weyerhaeuser Co., December 23, 1992.

Whitfill, D.L., Kukena Jr., E., Cantu, T.S., Sooter, M.C., 1990. Method of controlling lost circulation in well drilling. US Patent 4 957 174, assigned to Conoco Inc., September 18, 1990.

Wilkerson, J.M.I., Verstrat, D.W., Barron, M.C., 1995. Associative monomers. US Patent 5 412 142, assigned to Natl. Starch Chem. Inv. Corp., May 02, 1995.

Wilkinson, A.O., Grigson, S.J., Turnbull, R.W., 1995. Drilling mud. WO Patent 9 526 386, assigned to Heriot Watt Univ., October 05, 1995.

Williamson, R.C., Lawrie, C.J., Miller, S.J., 1995. Skeletally isomerized linear olefins. WO Patent 9 521 225, assigned to Chevron Chemical Co., August 10, 1995.

Wood, R.R., 2001. Improved drilling fluids. WO Patent 0 153 429, July 26, 2001.

Yakovlev, S.S., Konovalov, E.A., 1987. Plugging mixtures on a base of hydrolyzed polyacrylonitrile. Neft Khoz (4), 25–27.

Yassin, A.A.M., Kamis, A., 1990. Palm oil derivative as a based fluid in formulating oil based drilling mud. In: Proceedings Volume, vol. 2, 4th SPE et al Latin Amer. Petrol. Eng. Conf. (Rio De Janeiro, Brazil, 10/14–19/90).

Yeh, M.H., 1995. Compositions based on cationic polymers and anionic xanthan gum (compositions a base de polymeres cationiques et de gomme xanthane anionique). EP Patent 654 482, assigned to Rhone Poulenc Spec. Chem. C, May 24, 1995.

Young, S., Young, A., 1994. Recent field experience using an acetal based invert emulsion fluid. In: Proceedings Volume, IBC Tech. Serv. Ltd Prev. of Oil Discharge from Drilling Oper. – The Options Conf. (Aberdeen, Scot, 6/15–16/94).

Zhao, L., Xie, Q., Luo, Y., Sun, Z., Xu, S., Su, H., Wang, Y., 1996. Utilization of slag mix mud conversion cement in the karamay oilfield, xinjiang. Jianghan, J., Pet. Inst. 18 (3), 63–66.

Zuzich, A.H., Blytas, G.C., 1994. Polyethercyclicpolyols from epihalohydrins, polyhydric alcohols and metal hydroxides or epoxy alcohol and optionally polyhydric alcohols with addition of epoxy resins. US Patent 5 286 882, assigned to Shell Oil Co., February 15, 1994.

Zuzich, A.H., Blytas, G.C., Frank, H., 1995. Polyethercyclicpolyols from epihalohydrins, polyhydric alcohols, and metal hydroxides or epoxy alcohols and optionally polyhydric alcohols with thermal condensation. US Patent 5 428 178, assigned to Shell Oil Co., June 27, 1995.

TRADENAMES

TABLE 1.13 Tradenames in References

Tradename Description	Supplier
Accolade® Drilling fluid (Bell and Shumway, 2009)	Halliburton Energy Services, Inc.
Adapta® Filtration control agent (Bell and Shumway, 2009; Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Aquagel® Sodium montmorillonite clay (Ravi et al., 2009)	Halliburton Energy Services, Inc.

TABLE 1.13 Tradenames in References–Cont'd

Tradename Description	Supplier
AquaPAC® Polyanionic cellulose (Melbouci and Sau, 2008)	Aqualon Corp.
BARABUF® Buffer (Ravi et al., 2009)	Halliburton Energy Services, Inc.
BARACARB® Ground marble (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
BARASIL® S Sodium silicate shale stabilizer (Ravi et al., 2009)	Halliburton Energy Services, Inc.
BARAZAN® Polysaccharide (Ravi et al., 2009)	Halliburton Energy Services, Inc.
BAROID® 41 Ground barium sulfate (Bell and Shumway, 2009; Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
CELLEX Carboxymethyl cellulose (Ravi et al., 2009)	Halliburton Energy Services, Inc.
Celpol® (Series) Polyanionic cellulose (Melbouci and Sau, 2008)	Noviant, Nijmegen
Clay Sync™ Shale stabilizer (Maresh, 2009)	Baroid
ClaySeal® Shale stabilizer (Maresh, 2009)	Baroid Fluid Services
COLDTROL™ Fatty alcohol thinner (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Disponil® Ether sulfonates (Emulsifyer) (Guichard et al., 2008)	Henkel
Driltreat™ Wetting agent (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
EDC95® *n*-Alkane cuts (Dalmazzone, 2007)	BHI

TABLE 1.13 Tradenames in References–Cont'd

Tradename Description	Supplier
EZMUD® Partially hydrolyzed polyacrylamide (Ravi et al., 2009)	Halliburton Energy Services, Inc.
FACTANT™ Concentrated emulsifier (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
FILTER-CHEK® Modified cellulose (Maresh, 2009; Ravi et al., 2009)	Halliburton Energy Services, Inc.
Geltone® (Series) Organophilic clay (Bell and Shumway, 2009; Miller, 2009; Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Grabber® Flocculant (Maresh, 2009)	Baroid
Hydro-Guard® Inhibitive water-based-fluid (Maresh, 2009)	Halliburton Energy Services, Inc.
IMPERMEX Pregelatinized cornstarch (Ravi et al., 2009)	Halliburton Energy Services, Inc.
Interdrill Emul HT® Emulgator (Dalmazzone, 2007)	Dowell Schlumberger
Interdrill® LORM Emulsification system (Dalmazzone, 2007)	Dowell Schlumberger
Invermul® Blends of oxidized tall oil and polyaminated fatty acids (Bell and Shumway, 2009; Ravi et al., 2009)	Halliburton Energy Services, Inc.
Kleemul® Emulsifier (Guichard et al., 2008)	BW Group
Kraton® Styrenic block copolymer (Guichard et al., 2008)	Shell
LE BASE™ Base drilling fluid (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
LE SUPERMUL™ Emulsifier (Bell and Shumway, 2009; Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.

TABLE 1.13 Tradenames in References–Cont'd

Tradename Description	Supplier
LIQUI-VIS Hydroxyethyl cellulose (Ravi et al., 2009)	Baroid
Lorm® Emulsifier (Dalmazzone, 2007)	Dowell Schlumberger
MICRO MATRIX® Cement (Dealy and Chatterji, 2010)	Halliburton Energy Services, Inc.
N-Dril™ HT Plus Filtration control agent (Maresh, 2009)	Baroid
PAC™ -L Filtration control agent (Maresh, 2009)	Baroid
PAC Polyanionic cellulose (Ravi et al., 2009)	Halliburton Energy Services, Inc.
PETROFREE® LV Ester-based invert emulsion (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
PETROFREE® SF Olefin-based invert emulsion (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Plex® Acrylate resin (Guichard et al., 2008)	Rohm & Haas
Plioflex® Styrene butadiene rubber (Guichard et al., 2008)	Goodyear Chemicals
Pliolite® DF01 Styrene-butadiene copolymer (Guichard et al., 2008)	Goodyear Tire & Rubber Co.
POLYAC® Polyacrylate (Ravi et al., 2009)	Halliburton Energy Services, Inc.
Resinoline® BD2 Tall oil fatty acid (Dalmazzone, 2007)	DRT-GRANEL
RHEMOD™ L Modified fatty acid (Bell and Shumway, 2009)	Halliburton Energy Services, Inc.
Scotchlite™ Reflective glass (Ravi et al., 2009)	3M Comp.

TABLE 1.13 Tradenames in References–Cont'd

Tradename Description	Supplier
SF BASE™ Base drilling fluid (Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Silwet® Ethyleneoxy surfactants (Patel, 2008)	O Si Specialities, Inc.
Staflo® PAC (Melbouci and Sau, 2008)	Akzo Nobel
Suspentone™ Attapulgite clay (Miller, 2009; Miller and Kirsner, 2009)	Diversity Technologies Corp.
Ultidrill® Hydrocarbon cuts (Dalmazzone, 2007)	Dowell Schlumberger
Versawet® NS Wetting agent (Patel, 2008)	M-I Drilling Fluids L.L.C.
XP07® *n*-Alkane cuts (Dalmazzone, 2007; Miller and Kirsner, 2009)	Baroid
X-VIS™ Suspension agent (Bell and Shumway, 2009; Miller and Kirsner, 2009)	Halliburton Energy Services, Inc.
Zeogel® Attapulgite clay (Ravi et al., 2009)	Halliburton Energy Services, Inc.

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Chapter 2

Fluid Loss Additives

Comparative tables of fluid loss additives, also called *filtrate-reducing agents*, can be found on the internet (Petrochem, 2009). Losses may occur when the fluid comes in contact with a porous formation. This is relevant for drilling and completion fluids, fracturing fluids, and cement slurries.

The extent of fluid loss is dependent on the porosity and thus the permeability of the formation, and it may reach approximately 10 t/h. Because the fluids used in petroleum technology are in some cases quite expensive, an extensive fluid loss may not be tolerable. Of course there are also environmental reasons to prevent fluid loss.

MECHANISM OF ACTION OF FLUID LOSS AGENTS

Reduced fluid loss is achieved by plugging a porous rock in some way. The basic mechanisms are shown in Table 2.1.

Action of Macroscopic Particles

A monograph concerning the mechanism of invasion of particles into the formation is given by Chin (1995).

One of the basic mechanisms used in fluid loss prevention is shown in Figure 2.1. The fluid contains suspended particles. These particles move with the lateral flow out of the drill hole into the porous formation, which acts like a sieve for the suspended particles. The particles will therefore be captured near the surface, and accumulate as a filter cake.

The hydrodynamic forces acting on the suspended colloids determine the rate of cake buildup and therefore the fluid loss rate. A simple model has been proposed in the literature, which predicts a power law relationship between the filtration rate and the shear stress at the cake surface (Jiao and Sharma, 1994).

The model shows that the cake formed will be inhomogeneous, with the particle size being deposited decreasing as the filtration proceeds. An equilibrium cake thickness is achieved when no particles small enough to be deposited are

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TABLE 2.1 Mechanisms of Fluid Loss Prevention

Particle Types	Description
Macroscopic particles	Suspended particles may clog the pores, forming a filter cake with reduced permeability.
Microscopic particles	Macromolecules form a gel in the boundary layer of a porous formation.
Chemical grouting	A resin is injected in the formation, which cures irreversibly; suitable for bigger caverns.

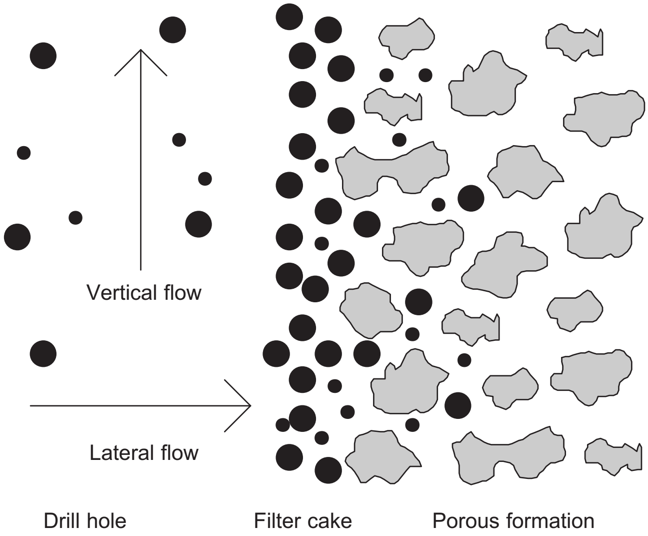


FIGURE 2.1 Formation of a filter cake in a porous formation from suspension (•) in a drilling fluid.

available in the suspension. The cake thickness can be computed as a function of time from the model.

For a given suspension rheology and flow rate there is a critical permeability of the filter, below which no cake will be formed. The model also suggests that the equilibrium cake thickness can be precisely controlled by an appropriate choice of suspension flow rate and filter permeability.

Action of Cement Fluid Loss Additives

Two stages are considered with respect to the fluid loss behavior of a cement slurry (Baret, 1988):

1. A dynamic stage corresponding to placement; and
2. A static stage, awaiting the setting of the cement.

During the first period, the slurry flow erodes the filter cake as it is growing; thus a steady state, in which the filtration occurs through a cake of constant thickness, is rapidly reached. At the same time, because the slurry is losing water but not solid particles, its density increases in line with the fluid loss rate.

During the second period, the cake grows because of the absence of flow. It may grow to a point at which it locally but completely fills the annulus: Bridging takes place and the hydrostatic pressure is no longer transmitted to the deeper zones. From the typical mud cake resistance values it can be estimated that under both dynamic and static conditions, the fluid loss could require reduction to an American Petroleum Institutue (API) value lower than what is generally considered a fair control of fluid loss.

Testing of Fluid Loss Additives

Fluid loss prevention is a key performance attribute of drilling fluids. For water-based drilling fluids, significant loss of water or fluid into the formation can cause irreversible changes in the drilling fluid properties, such as density and rheology, which can create instability in the borehole. Fluid loss control is measured in the laboratory according to a standard procedure for testing drilling fluids (Recommended practice for field testing water-based drilling fluids (API), 2009).

Predictions of the effectiveness of a formulation can be made on a laboratory scale, by characterizing the properties of the filter cake that is formed by appropriate experiments. Most of the fluids containing fluid loss additives are thixotropic, so the apparent viscosity will change when a shear stress in a vertical direction is applied, as is very normal in a circulating drilling fluid. For this reason, the results from static filtering experiments are expected to differ from dynamic experiments.

Static fluid loss measurements provide inadequate results for comparing fracturing fluid materials, or for understanding the complex mechanisms of viscous fluid invasion, filter cake formation, and filter cake erosion (Vitthal and McGowen, 1996). On the other hand, proper laboratory methods and dynamic fluid loss studies have not been developed for, which has led to erroneous and conflicting results.

Results from a large-scale, high-temperature, high-pressure simulator were compared with laboratory data, and significant differences in spurt loss values were found (Lord et al., 1995).

Static experiments with piston-like filtering can be reliable, however, for obtaining information on the fluid loss behavior at certain stages of a cementation process, in particular when the slurry is at rest.

Formation Damage

The damage to the formation that results from the use of a filtration loss agent can be a serious problem in certain fields of application. Providing effective fluid loss control without damaging formation permeability in completion operations has been a prime requirement for the ideal fluid loss control pill.

Filter cakes are hard to remove, and thus can cause considerable formation damage. Cakes with very low permeability can be broken up by reverse flow. No high-pressure spike occurs during the removal of the filter cake.

Typically, a high-pressure spike indicates damage to the formation and wellbore surface, because damage typically reduces the overall permeability of the formation. Often formation damage results from the incomplete back-production of viscous, fluid loss control pills, but there may be other reasons.

Reversible Gels

Another mechanism for fluid loss prevention is used by other additives, which are able to form gels via a molecular mechanism.

Bacteria

Instead of using polymers, the addition of bacterial cultures, which may form natural polymers that could then prevent fluid loss, has been suggested.

In one study, a bacterial culture selected for its abundant exopolymer production was added to drilling mud, to determine whether the polyanionic cellulose (PAC) component could be replaced without sacrificing viscosity or fluid retention (Anderson et al., 1991). The performance of the drilling mud was tested using a standard API test series. The bacterial inoculum was not as effective in maintaining viscosity or preventing fluid loss as was the PAC. However, the inoculum was capable of reducing the amount of PAC that was required in the drilling mud.

The combination of the bacterial inoculum with less expensive sources, for example carboxylated methyl cornstarch, crosslinked hydroxypropyl cornstarch, or amine-derivatized potato starch, gave viscosity and fluid loss control that was as good as or better than PAC alone. The bacterial strain tested was effective over a wide range of drilling mud conditions with growth occuring at varying pHs (3–11), varying salinities (0–15%), and a wide range of temperatures.

INORGANIC ADDITIVES

Bentonite

Bentonite is an impure clay that is formed by weathering of volcanic tuffs. It contains a high content of montmorillonite. Bentonites exhibit properties such as the ability to swell, a capacity for ion exchange, and thixotropy. Their properties can be modified by ion exchange, for example, exchange of earth alkali metals with alkali metals. The specific surface can be modified by acid treatment, and their organophilic properties can be increased by treatment with quaternary ammonia compounds.

Sodium Metasilicate

Sodium silicate has been successfully used as a chemical grouting material for many years. It is used in particular during the drilling of very permeable formations (Xiang, 2007). When an aqueous mixture of sodium silicate and an activating agent, such as an ester, is injected into the ground, the silicate solution reacts to form a colloid, which polymerizes further to form a gel. The gel provides increased strength, stiffness, and reduced permeability in predominantly granular soils.

These properties have been utilized in water-based drilling fluid systems, particularly during drill-in and completion operations (Xiang, 2009). The gel produced by the silicate reaction is soluble in both acids and bases.

The upper limit on amount of alkali metal silicate depends on the gel strength necessary and the pore size of the formation. The bigger the pore size, the higher the gel strength that is needed and, generally, the higher the desired concentration of alkaline silicate. As a practical matter, the concentration of alkaline silicate generally is about 40% because most commercial silicates are available at this concentration.

The drilling fluid system also contains activating agents, which becomes effective as it hydrolyzes, thereby decreasing the pH. Examples are formamide and water-soluble esters; accelerating agents may also be added to accelerate the gel formation such as sodium aluminate (Xiang, 2007, 2009). Examples of the formulation of drilling mud systems that use silicate for fluid loss control have been given in detail (Xiang, 2009).

Ultra-fine Filtrate-Reducing Agents

Methods are available for reducing the fluid loss and for reducing the concentration of polymer required to do this for a drilling fluid and to a well servicing fluid, respectively (Dobson et al., 1998). The fluids contain polymeric viscosifiers, a polymeric fluid loss additive and a water-soluble bridging agent suspended in a liquid in which the bridging agent is not soluble.

It is important to add a particulate, water-soluble, ultra-fine filtrate-reducing agent to the fluids. The particle size distribution should be such that approximately 90% of the particles are less than 10 μ, the average particle size being between 3 μ and 5 μ and the ultra-fine filtrate-reducing agent being insoluble in the liquid.

Bridging Agents for Fluid Loss Control

Common bridging agents include calcium carbonate, suspended salts, or oil soluble resins. For lost circulation treatments outside the production interval, any suitably sized product may be used, including mica, nutshells, and fibers (Munoz and Todd, 2008).

The selection of an appropriate bridging material is more critical in the production interval and during workover operations, since the barrier should be completely removed in preparation for placing the well back into production.

Chemically bonded ceramic particulates are useful as an alternative to conventional bridging agents, because they are customizable. These particulates are made via a process similar to that of mixing a cementitious material, so their composition and properties can be varied and they can be impregnated with desirable additives. Another advantageous feature of these particular bridging agents is that they are soluble in ammonium salts and chelating agents.

Starches derived from corn, wheat, oats, rice, potatoes, yucca, etc., are often used in conjunction with bridging agents. Most starches usually comprise about 27% amylose and about 73% amylopectin. These two polymers are intertwined within the starch granules. These granules are generally insoluble in cold water, but soaking in hot water or under steam pressure ruptures their covering and the polymers hydrate into a colloidal suspension. Amylose and amylopectin are non-ionic polymers that do not interact with electrolytes. Derivatized starches such as hydroxypropyl and carboxylmethyl starch are used in drill-in fluids, completion fluids, and various brine systems as well as in drilling fluid systems.

When conventional starches are added to fluids that consist of chemically bonded ceramic particulates, problems may arise. When combined, the fluid gels to a point where it ultimately has the consistency of paste, which makes it unusable in downhole applications. This is unfortunate because the starch provides an added means of ensuring fluid loss control in a process using the desirable chemically bonded ceramic particulates. However, modified starches can overcome these problems.

Ceramic particulate bridging agents are chemically bonded particulates. Chemically bonded particulates are preferred because they have an inherent flexibility in their composition, properties, and in their ability to act as carriers for desirable additives such as breakers.

The bridging agents are substantially insoluble in water, but soluble in aqueous ammonium salt clean-up solutions. An example of such a magnesium-based ceramic particulate bridging agent is:

$$\mathrm{MgO} + \mathrm{KH_2PO_4} + 5\,\mathrm{H_2O} \rightarrow \mathrm{MgKPO_4} \times 6\,\mathrm{H_2O} \tag{2.1}$$

Further examples are:

$$\begin{aligned} \mathrm{MgO} + \mathrm{H_3PO_4} + 2\,\mathrm{H_2O} &\rightarrow \mathrm{MgHPO_4} \times 3\,\mathrm{H_2O} \\ \mathrm{MgO} + \mathrm{NH_4H_2PO_4} + 5\,\mathrm{H_2O} &\rightarrow \mathrm{MgNH_4PO_4} \times 6\,\mathrm{H_2O} \end{aligned} \tag{2.2}$$

The examples of ceramic particulate bridging agents that are described in Eq. 2.2 are Newberyite and Struvite, respectively (Munoz and Todd, 2008). The ceramic particulate bridging agent utilized in treatment fluids is generally added in an amount of 10%.

Modified starch compositions provide enhanced fluid loss control when used in conjunction with ceramic bridging agents. These starches may be crosslinked

TABLE 2.2 Formulations of Muds (Munoz and Todd, 2008)

Component	Unit	Amount #1	Amount #2
Water	ml	–	317
NaCl	g	–	90.4
10% NaCl	g	336	–
NaOH	g	0.1	–
Xanthan	g	0.85	1.25
N-DRIL HT PLUS	g	7.4	–
BROMA FLA™	g	–	5.0
Newberyite	g	25.0	25.0

ether derivatives of a partially depolymerized starch. The molecular weight of the crosslinked starch derivative is decreased by the partial depolymerization of the starch polymer.

Formulations are shown in Table 2.2. The starch in formulation of #1 is N-DRIL HT PLUS, a commonly used starch available from Halliburton Energy Services. N-DRIL HT PLUS is a stabilized non-ionic starch derivative (waxy maize) that seeks to control high-pressure, high-temperature filtrate loss.

In combination with other polymers, such as xanthan, N-DRIL HT PLUS is synergistic and yields improved suspension. However, when used in combination with ceramic bridging agents, the combination will form a poor filter cake and will become a thick gel.

In contrast, a modified starch is used in formulation #2. This composition forms a tight filter cake, and does not form an unusable thick gel, even over a period of 24–48 h. The starch used in this recipe is BROMA FLA™, which is commercially available from TBC Brinadd of Houston, Texas.

ORGANIC ADDITIVES

Some polymers and copolymers used for fluid loss additives are shown in Table 2.3.

Tall Oil Pitch

Air-blown tall oil pitch, which has a softening point (ring and ball) of 100–165°C is a useful fluid loss additive for well drilling fluids. Tall oil pitch is available as the residue from the distillation of tall oil. It is largely insoluble in fatty acids, and soluble in fatty esters, higher alcohols, and sterols.

TABLE 2.3 Summary of Formulations of Fluid Loss Additives

Composition	References
Humic acid derivatives	Coates et al. (1990); Cowan et al. (1988); Crawford (2000); Huang (1996); House and Granquist (1986); Roark et al. (1986, 1987); Tan (1990)
Polyvinylacetate	Audebert et al. (1994, 1996); Audibert et al. (1999); Moran and Murray (1991)
Sulfonic acid polymers	Brake and Chatterji (1994); Stewart et al. (1988)
Acrylamide polymers	Boncan and Gandy (1986); Cheung (1993); Costello et al. (1990); Crema et al. (1991, 1993); Ganguli (1992); Hille et al. (1996); Kucera et al. (1989); Lange and Boehmer (1988); Peiffer et al. (1986); Sedillo et al. (1987)
2-Acrylamido-2-methyl-1-propane sulfonic acid polymers	Bardoliwalla (1986b); Brothers (1989); Ganguli (1992); Garvey et al. (1988); Giddings and Williamson (1987); Huddleston et al. (1992); Li et al. (1996); Oswald et al. (2000); Savoly et al. (1987); Stephens (1988); Stephens and Swanson (1992); Williamson (1989)
Acrylic acid polymers	Bardoliwalla (1986a); Huddleston and Williamson (1990)
Polyanionic cellulose	Hen (1991)
N-vinyl lactam polymers	Bharat (1990)
Polysaccharides	Audibert and Argillier (1996); Cawiezel et al. (1996); Dreveton et al. (1995); Francis et al. (1987); Johnson (1996); Lau (1994); Plank (1993); Raines (1986); Williamson et al. (1991b)
Peanut hulls	Forrest (1998)

Blowing air through tall oil pitch at an elevated temperature partially oxidizes and polymerizes the material and drives off volatiles. Blowing reduces the volume of the pitch by 30% and increases its viscosity and softening point. The softening point of the resultant blown pitch is therefore a measure of the degree of oxidation-polymerization that has occurred. It has been found that optimal properties as a fluid loss additive are given by blown tall oil pitches that have a softening point between 125°C and 130°C (Williamson, 1987).

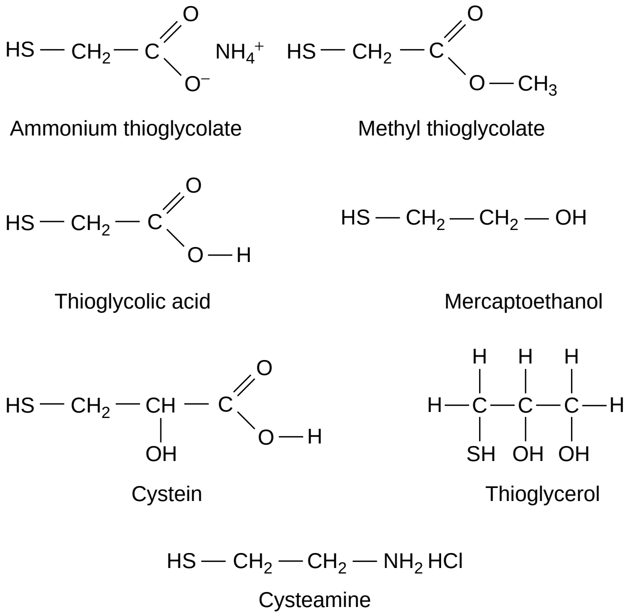
Mercaptans for Iron Control

Acid treatments are accompanied by very familiar problems, which are linked with the presence of iron in the acid, essentially because the acid dissolves the rust in the casings during pumping, and possibly also iron-containing minerals in the formation.

The presence of Fe^{3+} in the injected acid may cause, in contact with certain crude oils, the precipitation of the asphaltic products contained in the oil in the form of vitreous deposits, known as sludges. These cause practically irreversible damage to the zone treated. The scale of precipitation generally increases with the strength and concentration of the acid. The dispersibility of customary additives, such as surfactants, is also affected by the presence of Fe^{3+} through the formation of complexes.

When the injected acid is consumed by the dissolution of the minerals of the formation, the presence of Fe^{3+} leads to the precipitation of a colloidal precipitate of ferric hydroxide, which damages the formation. For this reason, the use of iron control additives is necessary in most acid treatments (Feraud et al., 2001). Suitable reducing agents are compounds with a mercaptan functionality, as shown in Figure 2.2.

The efficiency of a copper catalyst reducing agent was tested with regard to the reduction of Fe^{3+} to Fe^{2+} in media of varying acidities. The concentration


Ammonium thioglycolate

Methyl thioglycolate

Thioglycolic acid

Mercaptoethanol

Cystein

Thioglycerol

Cysteamine

FIGURE 2.2 Mercaptans for iron control.

TABLE 2.4 Amount of Iron Reduced (Feraud et al., 2001)

		Fe^{3+} Reduced/[10^{-3} mol]	
Reducing Agent	**T/[°C]**	**5% HCl**	**15% HCl**
Ammonium thioglycolate	20	2.9	2.7
	90	2.9	2.6
Thioglycolic acid	20	2.6	2.3
	90	2.4	2.3
Methyl thioglycolate	20	2.8	–
	90	2.7	–
Mercaptoethanol	20	2.7	2.8
	90	2.9	2.9
Cysteamine	20	3.1	2.6
	90	3.4	2.2
Thioglycerol	20	3	2.6
	90	2.9	2.5

of the reducing agent was 3×10^{-3} mol l^{-1}. Copper chloride is used as catalyst. The results are shown in Table 2.4.

POLYSACCHARIDES

Cellulose-based Fluid Loss Additives

Polyanionic Cellulose

A composition containing PAC and a synthetic sulfonate polymer has been tested for fluid loss reduction and thermal stabilization of a water-based drilling fluid for extended periods at deep well drilling temperatures (Hen, 1991).

Improved fluid loss is obtained when PAC and the sulfonate-containing polymer, which has a molecular weight of 300–10,000 kDalton, are combined in a water-based drilling mud (WBM), after prolonged aging at 300°F (150°C).

Carboxymethyl Cellulose

Certain admixtures of carboxymethyl hydroxyethyl cellulose or copolymers and copolymer salts of *N*,*N*-dimethylacrylamide and 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS), together with a copolymer of acrylic acid (AA), may provide fluid loss control to cement compositions under elevated temperature conditions.

Hydroxyethyl Cellulose

Hydroxyethyl cellulose (HEC) with a degree of substitution of 1.1–1.6 has been tested for fluid loss control in water-based drilling fluids (Raines, 1986). An apparent viscosity in water of at least 15 cP is needed to achieve an API fluid loss of less than 50 ml/30 min. Crosslinked HEC is suitable for high-permeability formations (Chang et al., 1998; Chang and Parlar, 1999).

A derivatized HEC polymer gel exhibited excellent fluid loss control over a wide range of conditions in most common completion fluids. This particular grated gel was compatible with the formation material, and caused little or no damage to its original permeability (Nguyen et al., 1996).

Detailed measurements of fluid loss, injection, and regained permeability were taken to determine the polymer particulate's effectiveness in controlling fluid loss and to assess its ease of removal. HEC can be etherified or esterified with long chain alcohols or esters. An ether bond is more stable in aqueous solution than is an ester bond (Audibert et al., 1997).

Starch

Starch, (c.f., Figure 2.3) has been traditionally used to control the fluid loss properties of a drilling mud. The characteristics of the fluid loss of several newly developed starch types with different amylose contents have been assessed. Details are shown in Table 2.5.

The products are manufactured by a gelatinization process during reactive extrusion. The extrusion was carried out at 80 bar and 140°C with a residence time of 3 min. For the crosslinked, high amylose type a chemical was introduced in the course of the extrusion process.

The starches have negligible impurities. No solvent is needed during gelatinization, and further, no waste water is produced as a by-product. Thus, these types are suitable for environmentally sensitive areas.

The presence of most of the starches in a bentonite mud reduce its API filtration at room temperature. However, the presence of the chemically modified,

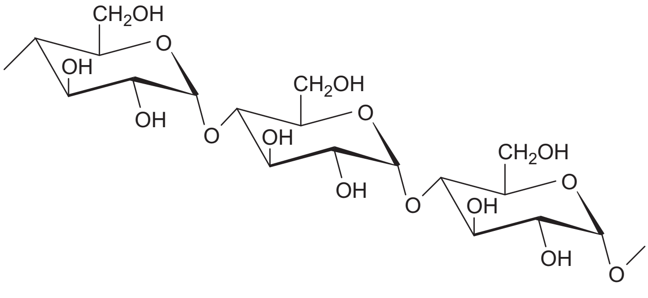


FIGURE 2.3 Starch.

TABLE 2.5 Starch Products (Amanullah and Yu, 2005)

Starch Type	Moisture/ [%]	Amylose/ [%]	Molecular Weight/ [k Dalton]
Waxy	12.9	0	20,787
Low amylose	12.7	26	13,000
Intermediate amylose	12.3	50	5115
High amylose	12.2	80	673
Crosslinked high amylose	–	80	–

crosslinked high amylose did not confer any improvement to the filtration behavior of a bentonite mud.

The static fluid loss properties have been measured after thermal treatment at different temperatures. These indicate that the new starch products can be used as fluid loss additives for drilling boreholes having a bottom hole temperature of up to 150°C (Amanullah and Yu, 2005).

The results indicate that some of the starches have static and dynamic fluid loss characteristics that are similar to, or better than, those of a widely used modified starch.

Crosslinked Starch

A crosslinked starch was described as a fluid loss additive for drilling fluids (Francis et al., 1987; Sifferman et al., 1999). The additive resists degradation and functions satisfactorily after exposure to temperatures of 250°F (120°C) for periods of up to 32 hours. To obtain crosslinked starch, a crosslinking agent is reacted with granular starch in an aqueous slurry. The crosslinking reaction is controlled by a Brabender viscometer test. Typical crosslinked starches are obtained when the initial rise of the viscosity of the product is between 104°C and 144°C, and the viscosity of the product does not rise above 200 Brabender units at temperatures less than 130°C.

The crosslinked starch slurry is then drum-dried and milled to obtain a dry product. The effectiveness of the product is checked by the API Fluid Loss Test or other standards after static aging of sample drilling fluids containing the starch at elevated temperatures. The milled dry product can then be incorporated into the oil well drilling fluid of the drill site (Recommended practice for laboratory testing of drilling fluids (API), 2009; Standard test method for fluid loss of clay component of geosynthetic clay liners, 2009).

Pregelatinized Starch

The properties of the filter cake formed by macroscopic particles can be significantly influenced by certain organic additives. The overall mechanism of water-soluble fluid loss additives has been studied by determining the electrophoretic mobility of filter cake fines. Water-soluble fluid loss additives are divided into four types according to their different effects on the negative electrical charge density of filter cake fines (Zhang et al., 1995):

1. Electrical charge density is reduced by polyethylene, glycol, and pregelatinized starch,
2. Electrical charge density is not changed by carboxymethyl starch, and
3. Electrical charge density is increased by a sulfonated phenolic resin, carboxymethyl cellulose (CMC), and hydrolyzed polyacrylonitrile.

The properties of filtrate reducers are governed by their different molecular structures. Non-ionic filtrate reducers work by completely blocking the filter cake pore, and anionic ones work by increasing the negative charge density of filter cakes and decreasing pore size. Anionic species cause further clay dispersion, but non-ionic species do not, and both of them are beneficial to colloid stability (Zhang et al., 1996).

The change of properties of the filter cake that occured as a result of salinity and polymeric additives has been studied by scanning electron microscope (SEM) photography (Plank and Gossen, 1989). Fresh water muds with and without polymers such as starch, PAC, and a synthetic, high-temperature-stable polymer, were prepared, contaminated with electrolytes (NaCl, $CaCl_2$, $MgCl_2$), and aged at 200–350°F (90–189°C).

Static API filtrates before and after contamination and aging were measured. The freeze-dried API filter cakes were used for SEM studies. The filter cake structure was influenced by electrolytes, temperature, and polymers.

In an unaged, uncontaminated mud, bentonite forms a card-house structure with low porosity. Electrolyte addition increases the average filter cake pore size. Temperature causes coagulation and dehydration of clay platelets. Polymers protect bentonite from such negative effects.

Granular Starch and Mica

A fluid loss additive consisting of granular starch composition and fine particulate mica has been described (Cawiezel et al., 1996). It has been applied in a method for fracturing a subterranean formation penetrated by a borehole. The method comprises injecting the additive into the borehole and into contact with the formation, at a rate and pressure sufficient to fracture the formation, in an amount sufficient to provide fluid loss control.

Depolymerized Starch

Partially depolymerized starch provides decreased fluid losses at much lower viscosities than the corresponding starch derivatives that have not been partially depolymerized (Dobson and Mondshine, 1997).

Controlled Degradable Fluid Loss Additives

A fluid loss additive for a fracturing fluid comprises a mixture of natural and modified starches plus an enzyme (Williamson et al., 1991b). The enzyme degrades the α-linkage of starch but does not degrade the β-linkage of guar and modified guar gums when used as a thickener.

Natural or modified starches are utilized in a preferred ratio of 3:7 to 7:3, with optimum at 1:1, and the mix is used in the dry form for application from the surface down the well. The preferred modified starches are carboxymethyl and hydroxypropyl derivatives. Natural starches may be those of corn, potatoes, wheat, or soy, with cornstarch the most preferred.

Blends include two or more modified starches, as well as blends of natural and modified starches. The starches can be coated with a surfactant, such as sorbitan monooleate, ethoxylated butanol, or ethoxylated nonyl phenol, which act to aid dispersion into the fracturing fluid.

A fluid loss additive is described (Williamson et al., 1991a) that helps achieve a desired fracture geometry by lowering the spurt loss and leak-off rate of the fracturing fluid into the surrounding formation by rapidly forming a filter cake with low permeability. The fluid loss additive is readily degraded after the completion of the fracturing process. The additive has a broad particulate size distribution that is ideal for use in effectively treating a wide range of formation porosities and is easily dispersed in the fracturing fluid.

This fluid loss additive comprises a blend of modified starches or blends of one or more modified starches and one or more natural starches. They have been found to maintain injected fluid within the created fracture more effectively than natural starches. The additive is subject to controlled degradation into soluble products by a naturally proceeding oxidation reaction, or by bacterial attack by bacteria that are naturally present in the formation. The oxidation may be accelerated by adding oxidizing agents, such as persulfates and peroxides.

Multimodal Distributed Polymers

A polymeric material with a multimodal distribution refers to a material that contains at least two pluralities of polymer molecules, which have different average molecular weights.

Polymeric materials that are found in nature are generally monomodal with a rather narrow polydispersity (P) (Weaver et al., 2010). The polydispersity is in general defined as the ratio of two different averages of molecular weight, i.e., the ratio of weight average M_w to the number average, M_n. These averages are defined as:

$$\begin{aligned} M_n &= \sum\nolimits_{M=1}^{M=\infty} x_M M \\ M_w &= \sum\nolimits_{M=1}^{M=\infty} w_M M \end{aligned} \qquad (2.3)$$

where x_M is the mole fraction of polymer with a molecular weight of M and w_M is the weight fraction of polymer with a molecular weight of M.

Thus the polydispersity is:

$$P = \frac{M_w}{M_n} \geq 1. \qquad (2.4)$$

Polydisperse materials can be obtained by mixing chemically equivalent materials that have different molecular weights. The latter can be obtained by synthesis of artificial materials under different conditions, or by controlled degradation of naturally occurring polymers.

Polymeric materials with small polydispersities may not be able to fill the pore spaces sufficiently to prevent fluid loss into the formation. For example, if the polymer molecules are all relatively large, all of them may be unable to fit within certain pore throats in the formation to plug the pore spaces therein.

On the other hand, polymers with a multimodal distribution contain a number of molecules that will fill and plug small pores, a number of molecules that will plug medium-sized pores, etc. The principle developed above is suitable for polymers as fluid loss additives in general, i.e., it is independent of the particular chemical nature of the polymer.

A wide variety of examples of polymers have been listed that operate according to this principle. Natural polymers include polysaccharides, while synthetic polymers include 2,2′-azobis(2,4-dimethyl valeronitril) (Weaver et al. 2010, pp. 5–15).

Borate Crosslinkers

Organic polyhydroxy compounds with hydroxyl moieties positioned in the cis-position on adjacent carbon atoms, or on carbon atoms that have a 1,3-relationship can react with borates to form five or six membered ring complexes. The reaction is fully reversible with changes in pH.

Depending on concentration of the polymer and the borate anion, the crosslinking reaction may produce useful gels. Aqueous borate concentrates that provide a controllable crosslink time are very useful. Sparingly soluble borate suspensions are suitable for hydraulic fracturing operations, since they adjust the time of crosslinking more consistently (Dobson et al., 2005).

Examples of borate minerals are shown in Table 2.6.

TABLE 2.6 Sparingly Soluble Borate Minerals (Dobson et al., 2005; Mondshine, 1986)

Mineral	Formula
Probertite	$NaCaB_5O_9 \times 5 H_2O$
Ulexite	$NaCaB_5O_9 \times 8 H_2O$
Nobleite	$CaB_6O_{10} \times 4 H_2O$
Gowerite	$CaB_6O_{10} \times 5 H_2O$
Frolovite	$Ca_2B_4O_8 \times 7 H_2O$
Colemanite	$Ca_2B_6O_{11} \times 5 H_2O$
Meyerhofferite	$Ca_2B_6O_{11} \times 7 H_2O$
Inyoite	$Ca_2B_6O_{11} \times 13 H_2O$
Priceite	$Ca_4B_{10}O_{19} \times 7 H_2O$
Tertschite	$Ca_4B_{10}O_{19} \times 20 H_2O$
Ginorite	$Ca_2B_{14}O_{23} \times 8 H_2O$
Pinnoite	$MgB_2O_4 \times 3 H_2O$
Paternoite	$MgB_2O_{13} \times 4 H_2O$
Kurnakovite	$Mg_1B_6O_{11} \times 15 H_2O$
Inderite	$Mg_2B_6O_{11} \times 15 H_2O$
Preobrazhenskite	$Mg_3B_{10}O_{18} \times 4½ H_2O$
Hydroboracite	$CaMgB_6O_{11} \times 6 H_2O$
Inderborite	$CaMgB_6O_{11} \times 11 H_2O$
Kaliborite (Heintzite)	$KMg_2B11O_{19} \times 9 H_2O$
Veatchite	$SrB_6O_{10} \times 2 H_2O$

Guar

A hydrophobically modified guar gum can be used as an additive for drilling, completion, or servicing fluids (Audibert and Argillier, 1996, 1998). The modified gum is used together with polymers or reactive clay.

Hydroxypropyl Guar Gum

Hydroxypropyl guar gum gel can be crosslinked with borates (Miller et al., 1996), titanates, or zirconates. Borate crosslinked fluids and linear HEC gels are the most commonly used fluids for high-permeability fracture treatments. They are used for hydraulic fracturing fluid under high temperature and high shear stress.

Succinoglycan

Succinoglycan is a biopolymer, which has been shown to possess a combination of desirable properties for fluid loss control (Lau, 1994). These include ease of mixing, cleanliness, shear thinning rheology, temperature-insensitive viscosity below its transition temperature (T_m), and an adjustable transition temperature (T_m) over a wide range of temperatures. Succinoglycan fluids rely solely on viscosity to reduce fluid loss. It does not form a hard-to-remove filter cake, so avoiding considerable formation damage.

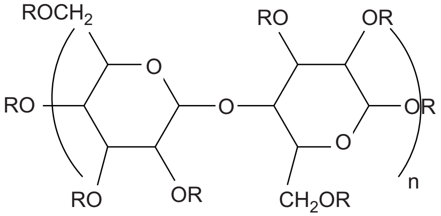
Based on these findings, succinoglycan has been used successfully as a fluid loss pill before and after gravel packing in more than 100 offshore wells. Calculations based on laboratory-measured rheology and field experience have shown it to be effective in situations in which HEC is not. Fluid loss, even over 40 barrels/h, was reduced to several barrels per hour after application of a properly designed succinoglycan pill. Most wells experienced no problem in production after completion.

Succinoglycan can be degraded with an internal acid breaker (Bouts et al., 1997). The formation damage that results from the incomplete back-production of viscous fluid loss control pills can be minimized if a slow-acting internal breaker is employed. In particular, core-flow tests have indicated that combining a succinoglycan-based pill with a hydrochloric acid internal breaker enables a fluid loss system with sustained control, followed by delayed break back that creates only low levels of impairment. To describe the delayed breaking of the succinoglycan/hydrochloric acid system, a model, based on bond breaking rate, has been used.

With this model, it is possible to predict the change in the rheological properties of the polymer as a function of time, for various formation temperatures, transition temperatures of the succinoglycan, and acid concentrations. The model can be used to identify optimal formulations of succinoglycan and acid breaker on the basis of field requirements, such as the time interval over which fluid loss control is needed, the overbalance pressure a pill should be able to withstand, and the brine density required.

Polyether-modified Polysaccharides

Some cellulose compounds are shown in Figure 2.4. Compositions that contain mixtures of metal hydroxides and a polysaccharide, partially etherified with hydroxyethyl and hydroxypropyl groups, are used as fluid loss additives for aqueous, clay-mineral-based drilling muds (Plank, 1993).



Hydroxyethylcellulose $R=(CH_2CH_2O)_mOH$

Carboxymethylcellulose $R=(CH_2CO)OH$

FIGURE 2.4 Starch derivates.

Scleroglucan

A combination of graded calcium carbonate particle sizes, a non-ionic polysaccharide of the scleroglucan type, and a modified starch, has been claimed for use in fluid loss formulations (Johnson, 1996). It is important that the calcium carbonate particles have a wide size range distribution to prevent filtration or fluid loss into the formation. Because the filter cake particles do not invade the wellbore due to the action of the biopolymer and the starch, no high-pressure spike occurs during the removal of the filter cake.

The rheological properties of the fluid allow it to be used in a number of applications where protection of the original permeable formation is desirable. These include drilling, fracturing, and controlling fluid losses during completion operations, such as gravel packing or well workovers.

Gellan

It has been found that gellan has good characteristics as a filtrate reducer in water-based drilling fluids (Dreveton et al., 1995, 1998). Preferential use is made of native gellan, which has a considerable gelling capacity and good solubility. It should be noted that native gellan contains cellular debris or other insoluble residue. Xanthan gum has been used extensively in the oil industry as a viscosifier for various applications (Navarrete et al., 2000). Deacetylated xanthan gum is used in guar-free compositions instead of guar (Langlois, 1999).

HUMIC ACID DERIVATES

Polysulfonated humic acid is a drilling fluid filtrate loss additive that is composed of three mud additives: sulfonated chromium humate, sulfonated phenolic resin, and hydrolytic ammonium polyacrylate (Tan, 1990).

The field application and the effectiveness of this material, especially in extra-deep wells, in sylvite and undersaturated salt muds, have been described. It resists high temperature, salt concentration, and calcium contamination. This type of drilling fluid has stable properties and good rheological characteristics, and it can improve cementing quality.

Oil-based Well Working Fluids

Adducts of aminoethylethanol amine and polyethylene amines with humic acid and fatty acids (Patel and McLaurine, 1992) are useful as fluid loss additives in oil-based drilling muds (OBMs) (House and Granquist, 1986).

In addition, a fluid loss additive for OBMs consisting of fatty acid compounds and lignite or humic acid, an oil-soluble or oil-dispersible amine with phosphoric acid, or an aliphatic amide or hydroxyamide (Coates et al., 1990), has been described.

Lignosulfonates

Grafted Lignin or Lignite

In hydraulic cement slurries, fluid loss additives that are based on sulfonated or sulfomethylated lignins have been described.

Sulfonated or sulfomethylated lignins are reacted with phenol-blocking reagents, such as ethylene oxide, propylene oxide, or 1,2-butylene oxide (Schilling, 1990). The fluid loss and thickening time characteristics of the cement slurry so produced is altered, either by increasing the molecular weight of the lignin through crosslinking with formaldehyde or epichlorohydrin, or by adding agents such as sodium sulfite, sodium metasilicate, sodium phosphate, and sodium naphthalene sulfonate.

Another method of altering lignins is amination with a polyamine and an aldehyde (Schilling, 1991). The formulation also contains sodium carbonate, sodium phosphate, sodium sulfite, sodium metasilicate, or naphthalene sulfonate. The sulfonated or sulfomethylated aminated lignin shows less retardation (shorter thickening time) than a sulfonated or sulfomethylated lignin without the attached amine.

Lignite can be grafted with synthetic comonomers to obtain lignite fluid loss additives (Huddleston and Williamson, 1990). The comonomers can be AMPS, *N*,*N*-dimethylacrylamide, acrylamide (AAm), vinylpyrrolidone, vinylacetate, acrylonitrile, dimethyl amino ethyl methacrylate, styrene sulfonate, vinylsulfonate, dimethyl amino ethyl methacrylate methyl chloride quaternary, or AA and its salts.

Various polymers, for example, lignin, lignite, derivatized cellulose polyvinyl alcohol (PVA), polyethylene oxide, polypropylene oxide, and polyethyleneimine, can be used as the backbone polymer onto which the other groups are grafted (Fry et al., 1987). The grafted pendant groups can be AMPS, acrylonitrile, *N*,*N*-dimethylacrylamide, AA, *N*,*N*-dialkylaminoethylmethacrylate, and their salts. One commercial example of such compounds is HALAD™ 413 (Lewis et al., 2008; Morgan et al., 2008).

A polymeric composition for reducing fluid loss in drilling muds and well cement compositions is obtained by the free radical polymerization of a water-soluble vinyl monomer in an aqueous suspension of lignin, modified lignins, lignite, and brown coal (Giddings and Williamson, 1987; Williamson, 1989). The vinyl monomers can be methacrylic acid, methacrylamide, hydroxyethyl acrylate, hydroxypropyl acrylate, vinylacetate, methylvinylether, ethylvinylether, *N*-methylmethacrylamide, *N*,*N*-dimethylmethacrylamide, vinylsulfonate, and additional AMPS. In this process, a grafting process to the coals by chain transfer may occur. Vinyl ethers are shown in Figure 2.5, and some acrylics are shown in Figure 2.6.

The polymers are prepared by common polymerization techniques (Zhang et al., 1990). For example, they are made by providing a foamed, aqueous solution of water-soluble monomeric material, in which polymerization is started by

$H_2C{=}CH{-}O{-}CH_3$ $\quad$ $H_2C{=}CH{-}O{-}CH_2{-}CH_3$

Methylvinylether $\quad$ Ethylvinylether

FIGURE 2.5 Vinyl ethers.

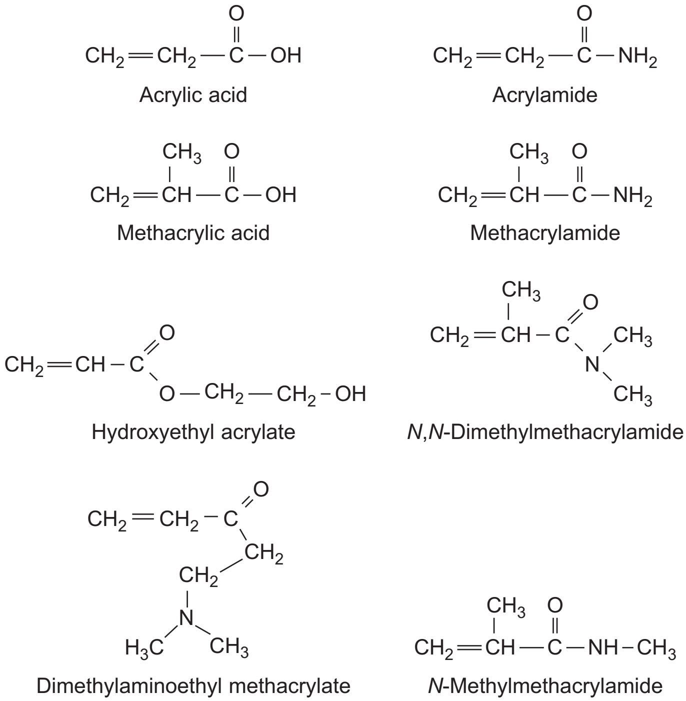


FIGURE 2.6 Acrylic compounds.

adding an initiator. The monomeric material is exothermically polymerizing to form a foamed gel, which is then comminuted.

Preferably, the polymerization temperature is held below 60°C for at least the first 10 min of the reaction and it then rises due to its exothermic nature. Graft copolymers that can be made by this technique and that are of particular value as fluid loss additives are formed from a polyhydroxy polymer, a sulfonate monomer, further AAm and AA.

Vinyl-grafted wattle tannin comprises a wattle tannin grafted with AMPS and small amounts of AAm (Huddleston et al., 1992). The wattle tannin is present at levels of 2–14%, and the AMPS is present at 98–84% accordingly.

Greek Lignites

Lignites that originated from Greece have been tested for their ability to control the filtration characteristics of water-bentonite suspensions (Kelessidis et al., 2009, 2007). The properties of a series of lignite samples from various peat/lignite deposits in Greece were compared with a commercial lignite product.

The samples were characterized with respect to their contents of humic and fulvic acids, humins, oxygen, ash, and their cation exchange capacity.

Most samples show a good filtration control when used in water-bentonite suspensions, even after exposure to temperatures of 177°C, and some were found to be superior to the commercial product. The fluid loss was dependent on the humic and fulvic acid content and thus also on the total organic content of the samples. The correlation is shown in Figure 2.7.

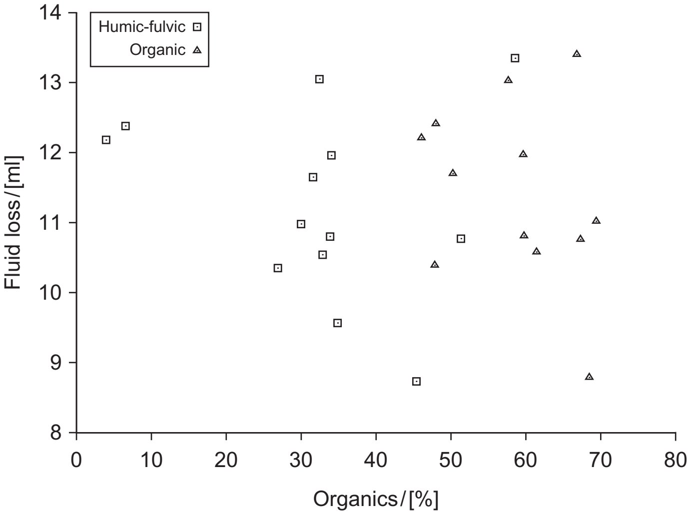


FIGURE 2.7 Fluid loss and content of organics (Kelessidis et al., 2007).

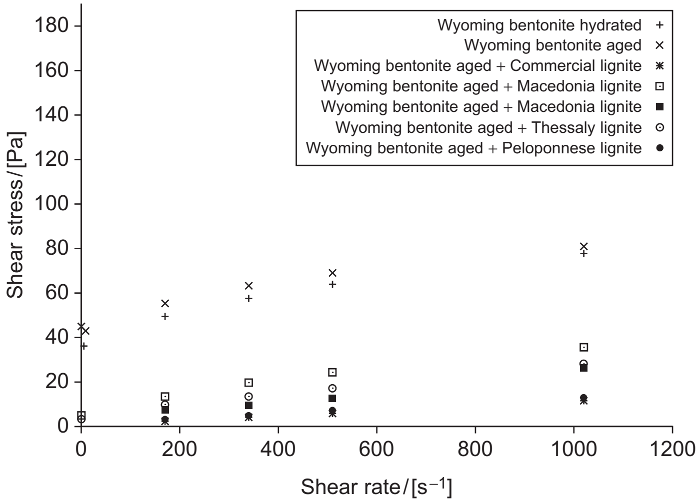


FIGURE 2.8 Rheograms of bentonite-lignite formulations (Kelessidis et al., 2009).

An improvement index η, has been used, which is defined as follows:

$$\eta = 100\frac{V_a - V_b}{V_b}. \tag{2.5}$$

Here, V_a is the volume of fluid loss after aging and V_b is the fluid loss of the base fluid under standardized conditions.

Better performance was observed after addition of 3% w/v lignite. Total humic and fulvic acids as percentage of dry lignite matter and the organic matter as lignite percentage showed a weak inverse correlation with the fluid loss volumes.

The rheograms of bentonite suspensions in its hydrated and thermally aged states has been measured. Three percent lignite of varying origin has been added to the aged suspensions. The resulting rheograms are given in Figure 2.8.

The addition of lignite reduces the shear stress. In the high shear rate range, the rheograms exhibit a linear behavior (Kelessidis et al., 2009). The reduction in the shear stress is very similar for all the lignite types tested.

SYNTHETIC POLYMERS

Polyorthoesters

Aliphatic polyesters degrade chemically by hydrolytic cleavage. The process of hydrolysis can be catalyzed by both acids and bases. During the hydrolysis, carboxylic end groups are formed during chain scission, and this may enhance the rate of further hydrolysis. This mechanism is known as autocatalysis, and it is thought to make polyester matrices more bulk-eroding.

TABLE 2.7 Fracturing Fluid Composition (Todd et al., 2006)

Compound	Tradename[a]	%
Water		
Potassium chloride		1
De-emulsifier	LO-SURF 300	0.05
Polyester		0.15
Guar		0.2
Buffer (CH_3COOH)	BA-20	0.005
Caustic	MO-67	0.1
Borate crosslinking agent	CL-28M	0.05
Gel breaker ($NaClO_3$)	VICON NF	0.1
Bactericide (2,2-dibromo-3-nitrilopropionamide)	BE-3S	0.001
Bactericide (2-Bromo-2-nitro-1,3-propanediol)	BE-6	0.001
Fracturing sand		50

a) Halliburton Energy Services, Inc.

Among the esters, polyorthoesters and aliphatic polyesters, i.e., polylactides are preferred. They can be synthesized either from lactic acid by a condensation reaction, or more commonly by ring opening polymerization of a cyclic lactide monomer.

The degradation by hydrolysis should proceed rather slowly over time. In fracturing operations, the material should not begin to degrade until after the proppant has been placed in the fracture, because slow degradation helps to provide fluid loss control during its placement (Todd et al., 2006). An example of a fracturing fluid composition is given in Table 2.7.

Polyhydroxyacetic Acid

A low molecular weight condensation product of hydroxyacetic acid with itself, or with compounds containing other hydroxy acid, carboxylic acid, or hydroxy carboxylic acid moieties has been suggested as a fluid loss additive (Bellis and McBride, 1987). Production methods of the polymer have been described.

The reaction products are ground to a particle size of 0.1–1500 μ. The condensation product can be used as a fluid loss material in a hydraulic fracturing process in which the fracturing fluid comprises a hydrolyzable, aqueous gel.

The hydroxyacetic acid condensation product hydrolyzes under formation conditions to produce hydroxyacetic acid, which breaks the aqueous gel autocatalytically and eventually provides the restored formation permeability without the need for the separate addition of a gel breaker (Cantu et al., 1989, 1990, 1993; Casad et al., 1991).

Polydrill

Polydrill is a sulfonated polymer, used for filtration control in water-based drilling fluids (Ujma and Plank, 1987). Tests have demonstrated the product's thermal stability up to 200°C and its outstanding electrolyte tolerance. It can be used in NaCl-saturated drilling fluids, as well as in muds containing up to 75,000 ppm of calcium or 100,000 ppm of magnesium. A combination of starch with Polydrill was used successfully while drilling several wells. The deepest hole was drilled with 11–22 $\mathrm{kg\,m^{-3}}$ of pregelatinized starch and 2.5–5.5 $\mathrm{kg\,m^{-3}}$ of Polydrill to a depth of 4800 m. Field experience with the calcium tolerant starch/Polydrill system useful up to 145°C has been discussed in detail (Ujma et al., 1987).

In dispersed muds (e.g., lignite or lignosulfonate), minor Polydrill addition results in a significantly improved high-temperature, high-pressure filtrate. Major benefits come from a synergism of the polymer with starch and polysaccharides, since it exerts a thermally stabilizing effect on those polymers.

In conventional or clay-free drilling and completion fluids, Polydrill can be used by itself or in combination with other filtrate reducers for various purposes (Plank, 1990). Handling and discharge of the product, as well as the waste mud was found to create no problem in the field.

Polymer of Monoallylamine

A water-soluble polymer of monoallylamine, c.f., Figure 2.9, can be used in conjunction with a sulfonated polymer such as a water-soluble lignosulfonate, condensed naphthalene sulfonate, or sulfonated vinyl aromatic polymer to minimize fluid loss from the slurry during well cementing operations (Roark et al., 1986, 1987). The polymer may be a homopolymer or a copolymer, and may be crosslinked or not.

These components react with each other in the presence of water to produce a gelatinous material that tends to plug porous zones and to minimize premature water loss from the cement slurry into the formation.

Polyphenolics

Organophilic polyphenolic materials for OBMs have been described (Cowan et al., 1988). The additives are prepared from a polyphenolic material and one

$$\mathrm{H_2C{=}CH{-}CH_2{-}NH_2}$$

Allylamine

FIGURE 2.9 Monoallylamine.

or more phosphatides, these being phosphoglycerides obtained from vegetable oils, preferably commercial lecithin.

The oxidized, sulfonated, or sulfomethylated derivatives of humic acids, lignosulfonic acid, lignins, phenolic condensates, or tannins may serve as polyphenolic materials.

A fluid loss additive is described that uses graded calcium carbonate particle sizes and a modified lignosulfonate (Johnson and Smejkal, 1993). Optionally, a thixotropic polymer, such as a wellan or xanthan gum polymer is used to keep the $CaCO_3$ and lignosulfonate in suspension.

In this application, it is important that the calcium carbonate particles are distributed across a wide size range to prevent filtration or fluid loss into the formation. Furthermore, the lignosulfonate must be polymerized enough to reduce its water solubility. The modified lignosulfonate is necessary for the formation of a filter cake essentially on the surface of the wellbore.

Because the modified lignosulfonate, prevents the filter cake particles from invading the wellbore no high-pressure spike occurs during the removal of the filter cake, which would indicate damage of the formation and wellbore surface. The additive is useful in fracturing fluids, completion fluids, and workover fluids.

Tests have shown that a fluid loss additive based on a sulfonated tannic-phenolic resin is effective for fluid loss control at high temperatures and pressures, and it exhibits good resistance to salt and acid (Huang, 1996).

Latex

Polymeric latex, when added to a water-based drilling fluid, can reduce the rate at which the drilling fluid invades through the borehole wall during drilling, by providing a deformable latex film or seal on the borehole wall.

The permeability of the seal is sufficient to at least partially block the transmission of the fluid, which gives a great improvement in osmotic efficiency (Halliday et al., 2007, 2008). Latexes may include the following components (Reddy and Palmer, 2009):

- Vulcanizable groups, e.g., butadiene,
- Vulcanizing agents such as sulfur, 2,2′-dithiobisbenzothiazole, organic peroxides, azo compounds, alkylthiuram disulfides, and selenium phenolic derivatives,
- Vulcanization accelerators, including fatty acids such as stearic acid, metallic oxides such as zinc oxide, aldehyde amine compounds, guanidine derivates, and disulfide thiuram compounds,
- Vulcanization retarders such as salicylic acid, sodium acetate, phthalic anhydride, and *N*-cyclohexyl thiophthalimide,
- Defoamers, and
- Fillers to increase or decrease the treatment density as required.

Latex emulsions are also used in cement compositions to reduce fluid loss (Reddy and Palmer, 2009), and they can be also used to reduce the brittleness of the sealant compositions and thus improve their flexibility.

Further, latex emulsions prevent gas migration. This property is useful when the sealant starts curing, i.e., the sealant composition changes from a non-viscous fluid to a highly viscous mass. During this transition phase, the sealant mass can no longer transmit hydrostatic pressure.

When the pressure exerted on the formation by the sealant composition falls below the pressure of the gas in the formation, the gas initially migrates into and through the composition. This migration causes flow channels to form in the sealant composition, which permit further migration of the gas after the sealant composition sets (Reddy and Palmer, 2009).

Polymeric latexes can also be incorporated into OBMs. In these fluids, the polymer latex seals can be formed without the need for a precipitating agent, a surfactant or any salt in the water phase (Halliday et al., 2007).

Where water is present at the continuous phase, the latex is in turn suspended in a hydrocarbon base fluid, which contains some emulsifier. Under optimal conditions, the polymer latex can be simply mixed with the hydrocarbon base fluid without the need for adding any emulsifier.

Some latex products exhibit a synergistic effect with aluminum complexes, with regard to their sealing properties.

Latex is a carboxylated styrene/butadiene copolymer or a sulfonated styrene/butadiene copolymer. Examples are commercially available, e.g., Gencal® 7463 (Halliday et al., 2008).

Sulfonated latexes can be often used in the absence of a surfactant, which may simplify the formulation and transportation of the drilling fluid additives to the production sites. A precipitating agent, such as sodium aluminate is preferably used (Halliday et al., 2008).

In the course of testing these materials, photomicrographs showed an accumulation of latex along microfractures in the shale. Since the volume and the velocity of filtration flow into these cracks is very small, filtration alone cannot account for this accumulation. It seems that precipitation effects are responsible for these findings.

When sufficient latex is deposited to bridge the crack opening, the fracture is sealed and differential pressure is established across the latex. The differential pressure consolidates the latex deposit into a solid seal.

Optionally, a surfactant that behaves as an emulsifier and a wetting agent and a weighting agent, e.g., calcium carbonate, barite, or hematite, is included. Suitable emulsifiers and wetting agents include surfactants; ionic surfactants such as fatty acids, amines, amides, and organic sulfonates; and mixtures of any of these with non-ionic surfactants such as ethoxylated surfactants. The water-in-oil emulsion may consist of an oil phase, a water phase (salt or fresh), a surfactant, a weighting agent, and salts or electrolytes (Bailey, 2001; Hernandez et al., 1999a,b).

Stable drilling fluid systems have been formulated with latex that remains dispersed and flexible in highly saline fluids. The stabilization is caused by two factors (Halliday et al., 2007):

1. The ultra-fine, deformable latex particles with a diameter of 0.2 μ mechanically seal shale microfractures and physically prevent further intrusion of drilling fluids into sensitive shale zones.
2. The co-precipitation of the latex with precipitating agents such as aluminum complexes produces a semi-permeable membrane on shale surfaces that chemically improves the osmotic efficiency between the fluid and the borehole.

Colloidally Stabilized Latex

Latex emulsions that are prepared by conventional emulsion polymerization become unstable in the presence of salt. In order to improve the salt tolerance of latex emulsions in sealant compositions, it is usual to add surfactants, such as ethoxylated nonyl phenol sulfates. Alternatively, a cheaper solution is to use a colloidally stabilized latex, which contains a protective colloid. Suitable examples include partially and fully hydrolyzed PVA, cellulose ethers, starch derivatives, natural and synthetic gums, and synthetic copolymers (Reddy and Palmer, 2009).

As another alternative, the backbone of the latex may be modified by incorporating moieties with surfactants properties. Since the surfactant is then chemically bound to the polymer, it cannot be easily removed. An example of such a material is a carboxylated butadiene acrylonitrile latex. The carboxyl groups confer electrical charge to the polymeric backbone.

Alternatively, functionalized silane can be introduced into the polymer. This moiety is capable of adsorbing the protective colloid. A suitable functionalized silane is γ-mercaptopropyl trimethoxy silane.

It has been demonstrated that a carboxyl modified latex can produce slurries with satisfactory properties without needing latex-stabilizing surfactants (Reddy and Palmer, 2009).

Polyvinyl Alcohol

Partially hydrolyzed polyvinyl acetate (PVAc), a crosslinker for the polymer, and other additives such as calcium sulfate can be used in cementing casing strings (Moran and Murray, 1991). PVAc is not totally water-soluble below 50°C, but is instead water swellable.

It is believed that the individual PVAc particles swell and soften to form small gel-balls in the slurry. These gel-balls deform by flattening and become a part of the filter cake, hence greatly reducing its permeability, thus giving good fluid loss control. Because PVAc is not totally water soluble, it does not significantly increase the viscosity of the slurry, and it does not delay the setting of the cement. It also has high-temperature properties that are relatively insensitive to external conditions.

PVAc can be crosslinked with a crosslinker that is present in a molar concentration, relative to monomer residues, of 0.01–1.0%. This may be formaldehyde, acetaldehyde, glyoxal, glutaraldehyde, maleic acid, oxalic acid, dimethylurea, polyacrolein, diisocyanate, divinylsulfonate, or a chloride of a diacid (Audebert et al., 1994, 1996, 1998).

Polyethyleneimine

A reported liquid fluid loss-reducing additive for well cementing compositions consists of water, polyethyleneimine, an alkali metal salt of alkyl benzene sulfonic acid, and an alkali metal salt of naphthalene sulfonic acid, condensed with formaldehyde (Brake and Chatterji, 1994). The polyethyleneimine has a molecular weight of 40–60 kDalton and is present at 50–55% by weight of the additive. The alkali metal salt of the alkyl benzene sulfonic acid is sodium dodecyl benzene sulfonate, and this is present at 3–4% of the additive. The alkali metal salt of the naphthalene sulfonic acid that is condensed with formaldehyde is sodium naphthalene sulfonate.

The sodium naphthalene sulfonate-formaldehyde condensation product has a molecular weight of 1.4–2.4 kDalton, and the condensation product is present in an amount of 3–4% of the additive. The alkyl group of the alkyl benzene sulfonic acid salt contains 8–16 carbon atoms.

Acrylics

Permeability Control

The water permeability of a formation can be controlled by the addition of a water-soluble copolymer, formed from a hydrophobic or hydrophobically modified hydrophilic monomer and a hydrophilic monomer (Zamora et al., 2007). Suitable monomers are shown in Table 2.8.

The polymerization proceeds in an aqueous solution or emulsion. 2,2′-Azo bis(2-amidinopropane)dihydrochloride is added as radical initiator (Zamora et al., 2007). This azo-type initiator is water soluble. In order to quaternize the polymers, if desired, benzylcetyldimethyl ammonium bromide can be added.

Copolymers

Homopolymers and copolymers from amido sulfonic acid- or salt-containing monomers can be prepared by reactive extrusion, preferably in a twin screw extruder (Sopko and Lorentz, 1991). The process produces a solid polymer. Copolymers of AAm, *N*-vinyl-2-pyrrolidone, and sodium-2-acrylamido-2-methylpropanesulfonate (NaAMPS) are proposed to be active as fluid loss agents. Another component of the formulations is the sodium salt of naphthalene

TABLE 2.8 Hydrophobic and Hydrophilic Monomers (Zamora et al., 2007)

Hydrophobic Monomers
Alkyl acrylates
Alkyl methacrylates
Alkyl acrylamides
Alkyl methacrylamides
Alkyl dimethyl ammonium ethyl methacrylate halides
Alkyl dimethyl ammonium propyl methacrylamide halides
C-16 alkyl(*n*-hexadecyl)dimethyl ammonium ethyl methacrylate bromide
Octadecyl methacrylate
Hydrophilic Monomers
Acrylamide
2-Acrylamido-2-methyl-1-propane sulfonic acid
N,N-Dimethylacrylamide
Vinylpyrrolidone
Acrylic acid
Dimethyl aminopropyl methacrylamide
Trimethylammonium ethyl methacrylate chloride
Methacrylamide
Hydroxyethyl acrylate dimethyl amino ethyl methacrylate

formaldehyde sulfonate (Boncan and Gandy, 1986). The fluid loss additive is mixed with hydraulic cements in suitable amounts.

A fluid loss additive for hard brine environments has been developed (Stewart et al., 1988), consisting of a hydrocarbon, an anionic surfactant, an alcohol, a sulfonated asphalt, a biopolymer, and optionally an organophilic clay, a copolymer of *N*-vinyl-2-pyrrolidone and NaAMPS. Methylenebisacrylamide can be used as a crosslinker (Patel, 1998). Crosslinking imparts thermal stability and resistance to alkaline hydrolysis.

Terpolymers and tetrapolymers have been proposed as fluid loss additives for drilling fluids (Stephens, 1988; Stephens and Swanson, 1992). The constituent monomers are a combination of non-ionic monomers and ionic monomers. The non-ionic monomer can be AAm, *N*,*N*-dimethylacrylamide, *N*-vinyl-2-pyrrolidone, *N*-vinylacetamide, or dimethyl amino ethyl methacrylate. Ionic monomers are AMPS, sodium vinylsulfonate, and vinylbenzene sulfonate. The terpolymer should have a molecular weight between 0.2 M Dalton and 1 M Dalton.

A formulation consisting of AMPS, AAm, and itaconic acid has been proposed (Garvey et al., 1988). Such polymers are used as fluid loss control additives for aqueous drilling fluids, and are advantageous when used with lime or gypsum-based drilling muds containing soluble calcium ions.

For sea water muds, another example (Bardoliwalla, 1986b) is a copolymer of 10% AMPS and 90% AA in its sodium salt form. The polymers have an average molecular weight of 50–1000 k Dalton.

A terpolymer from a family of intramolecular polymeric complexes (i.e., polyampholytes), which are terpolymers of AAm–methyl styrene sulfonate-methacrylamido propyltrimethyl ammonium chloride has been reported (Audibert-Hayet et al., 1998; Peiffer et al., 1986).

A terpolymer formed from ionic monomers AMPS, sodium vinylsulfonate, or vinylbenzene sulfonate itaconic acid, and a non-ionic monomer, for example, AAm, *N,N*-dimethylacrylamide, *N*-vinylpyrrolidone, *N*-vinylacetamide, and dimethyl amino ethyl methacrylate, is used as a fluid loss agent in oil well cements (Savoly et al., 1987).

The terpolymer should have a molecular weight of 0.2–1 M Dalton, and comprises AMPS, AAm, and itaconic acid. Such copolymers also serve in drilling fluids (Zhang and Ye, 1998).

A tetrapolymer consisting of 40–80 mol-% of AMPS, 10–30 mol-% of vinylpyrrolidone, 0–30 mol-% of AAm, and 0–15 mol-% of acrylonitrile was also suggested as a fluid loss additive (Lange and Boehmer, 1988). Even at high salt concentrations, these polymers yield high-temperature-stable, protective colloids that provide minimal fluid loss under pressure.

For water-based drilling fluids, water-soluble polymers are adequate, typically polyacrylamide, but they have a limited temperature stability.

Polymers based on AAm have been developed that exhibit effective rheological properties and high-temperature/high-pressure (HTHP) filtration control at temperatures of 260°C or more (Jarrett and Clapper, 2010). They are terpolymers composed of AAm, AMPS, or alkali metal salts, and a third monommer that can be an acrylate, *N*-vinyl lactam, or *N*-vinylpyridine (Jarrett and Clapper, 2010). Examples of copolymers are listed in Table 2.9.

In order to assist effective seal forming for filtration control, a plugging agent is added (Jarrett and Clapper, 2010). Examples of suitable plugging agents include the following: sized sulfonated asphalt, limestone, marble, mica, graphite, cellulosics and lignins, and cellophanes.

Other additives may be used in the drilling fluid system, including shale stabilizers, further filtration control additives, suspending agents, dispersants, antiballing additives, lubricants, weighting agents, seepage control additives, lost circulation additives, drilling enhancers, penetration rate enhancers, corrosion inhibitors, buffers, gelling agents, crosslinking agents, salts, biocides, and bridging agents (Jarrett and Clapper, 2010).

TABLE 2.9 Examples of Copolymers (Jarrett and Clapper, 2010)

Monomer 1	mol-%	Monomer 2	mol-%	Monomer 3	mol-%
AMPS	10	AAm	90	–	–
AMPS	20	AAm	80	–	–
AMPS	40	AAm	60	–	–
AMPS	37.5	AAm	50	Acrylate	12.5
AMPS	55	AAm	15	NVP	30
Monomer 1	**% w/w**	**Monomer 2**	**% w/w**	**Monomer 3**	**% w/w**
NaAMPS	90	DMAAm	10	–	–

AMPS	*2-Acrylamido-2-methyl-1-propane sulfonic acid*
AAm	*Acrylamide*
NVP	*N-Vinyl-2-pyrrolidone*
NaAMPS	*Sodium AMPS*
DMAAm	*N,N-Dimethylacrylamide*

TABLE 2.10 Copolymer Blends for Fluid Loss (Crema et al., 1991, 1993; Kucera et al., 1989)

Copolymer	Molecular Weight/[k Dalton]
Acrylamide/vinyl imidazole	100 to 3000
Vinylpyrrolidone/sodium vinylsulfonate	100 to 3000

After static aging up to 260°C for 16 h, the HTHP filtrate was measured extensively, with results of less than 25 $\mathrm{cm^3 min^{-1}}$ (Jarrett and Clapper, 2010).

Similar copolymers with *N*-vinyl-*N*-methylacetamide as a comonomer have been proposed for hydraulic cement compositions (Ganguli, 1992).

The polymers are effective at well bottom hole temperatures ranging from 93–260°C (200–500°F) and are not adversely affected by brine. Terpolymers of 30–90 mol-% AMPS, 5–60 mol-% of styrene, and residual AA are also suitable for well cementing operations.

A fluid loss additive useful for cementing oil and gas wells is a blend of a copolymer of AAm/vinyl imidazole (Crema et al., 1991, 1993; Kucera et al., 1989). The second component in the blend is a copolymer of vinylpyrrolidone and the sodium salt of vinylsulfonate. Details are given in Table 2.10. The copolymers are mixed together in proportions between 20:80 and 80:20. Sodium or potassium salts or a sulfonated naphthalene formaldehyde condensate can be used as a dispersant.

An *N*-vinylpyrrolidone/AAm random copolymer (0.05–5.0%) is used for cementing compositions (Cheung, 1993; Le et al., 1998). Furthermore, a sulfonate-containing cement dispersant is necessary. The additive can be used in wells with a bottom hole temperature of 80–300°F (30–150°C).

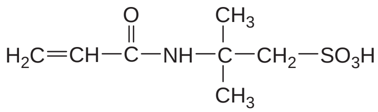
The fluid loss additive mixture is especially effective at low temperatures, for example, below 100°F (40°C) and in sodium silicate–extended slurries. For aqueous cement slurries a copolymer of *N*-vinylpyrrolidone and a salt of styrene sulfonic acid has been proposed (Sedillo et al., 1987). A naphthalene sulfonic acid salt condensed with formaldehyde serves as a dispersant.

The fluid loss control of aqueous, clay-based drilling mud compositions is enhanced by the addition of a hydrolyzed copolymer of AAm and an *N*-vinylamide (Costello et al., 1990). The copolymer, which is effective over a broad range of molecular weights, contains at least 5 mol-% of the *N*-vinylamide units, which are hydrolyzed to *N*-vinylamine units. The copolymers can be made from various ratios of *N*-vinylamide and AAm by using common radical polymerization techniques.

N-Vinylamide can be polymerized by the inverse emulsion polymerization technique (Lai and Vijayendran, 1989). The polymers so produced are used for cementing compositions for oil and gas wells. The method for preparing the inverse, or water-in-oil, emulsion involves colloidally dispersing an aqueous solution containing 10–90% water-soluble *N*-vinylamide in a hydrocarbon liquid, using a surfactant with a hydrophilic-lipophilic balance value between 4 and 9. The weight ratio of monomer-containing aqueous solution to hydrocarbon liquid is preferably from 1:2 to 2:1. To initiate the polymerization, an azo-type free radical initiator is used. The resultant high molecular weight polymer emulsion has a low viscosity, ranging from 2 to less than 10 cP at 15% solids (60 rpm Brookfield and 20°C), thus eliminating problems of solution viscosity that arise when it is prepared by a solution polymerization process.

Copolymers of styrene with AMPS that have fluid loss capabilities suitable for use in well cementing operations have been described (Brothers, 1989). The styrene is present at 15–60 mol-%, and the AMPS at 40–85 mol-%. The polystyrene units are not hydrophilic, so AMPS will affect the solubility in water. AMPS is shown in Figure 2.10.

Copolymers of mainly AA with 2–20% of itaconic acid are described as fluid loss additives for aqueous drilling fluids (Bardoliwalla, 1986a). The polymers have an average molecular weight of 100–500 kDalton and are water-dispersible. They are advantageous when used with muds containing soluble calcium and muds containing chloride ions, such as sea water muds.



$$H_2C{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}CH_2{-}SO_3H$$

FIGURE 2.10 2-Acrylamido-2-methyl-1-propane sulfonic acid.

Copolymers from the monomers AMPS, diallyldimethylammonium chloride (DADMAC), *N*-vinyl-*N*-methylacetamide, AAms, and acrylates are particularly useful as fluid loss additives (Hille et al., 1996). The molecular weights of the copolymers range from 200–1000 k Dalton, and are used in suspensions of solids in aqueous systems, including saline, as water binders. In these systems, the water release to a formation is substantially reduced by the addition of one or more of these copolymers.

A copolymer of AMPS and other vinyl monomers produces a suitable formulation for filtration reducers, which has good temperature resistance (over 200°C), and good tolerance to salts and calcium compounds (Li et al., 1996).

Polymers or copolymers of *N*-vinyl lactam monomers or vinyl-containing sulfonate monomers produce an additive for reducing the water loss and enhancing other properties of well-treating fluids in high-temperature subterranean environments. Organic compounds like lignites, tannins, and asphaltic materials are added as dispersants (Bharat, 1990).

Oil-soluble Styrene Acrylate Copolymers

Oil-soluble polymers in the form of a gel can be used as a fluid loss additive for drilling WBM compositions to improve the high-temperature stability. Also, improved shear resistance can be obtained (Guichard et al., 2007, 2008). Such oil-soluble polymers are copolymers based on acrylates, styrene, vinyl toluene, butadiene, and others (Braden, 2006).

Crosslinking monomers include allyl maleate, divinylbenzene, and multifunctional acrylates, as well as methacrylates. The monomers are detailed in the literature (Guichard et al., 2006). These acrylic copolymers are also used as binders for masonry applications, concrete and metal protection, intumescent coatings (Magnet et al., 2008), and as modifiers for toner compositions.

Oil-soluble polymers are highly efficient in small proportions as a fluid loss reducers, and may be incorporated in the mud at levels of only 0.5–2.5%. The polymer is added to a WBM prepared by conventional methods, either to replace the conventional fluid loss reducers, or in addition (Guichard et al., 2008). Mud formulations have been given in detail elsewhere (Guichard et al., 2006).

In addition, the filtration value is significantly reduced after high-temperature aging when a crosslinked copolymer is used in a standard water-based drilling fluid formulation (Guichard et al., 2008).

AMPS Terpolymer

Fluid loss can be reduced by adding a terpolymer. The monomers and the composition are given in Table 2.11.

Silicones

Compositions based on silicone MQ resins have been proposed for fluid loss control for WBMs. These compositions are non-damaging (Berry et al., 2008).

TABLE 2.11 Monomers for a Terpolymer for Fluid Loss Control (Munoz and Todd, 2008)

Monomer	%
Na-2-acrylamido-2-methyl-1-propane sulfonic acid	80
N-Vinyl-2-pyrrolidone	10
Acrylamide	10

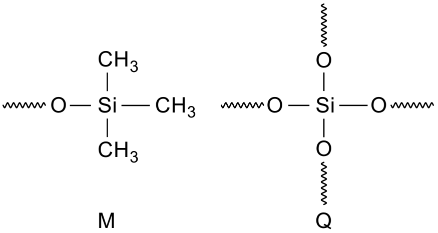


FIGURE 2.11 Moieties of an MQ silicone resin.

An MQ resin contains only monovalent trimethylsiloxane units $(CH_3)_3SiO_{1/2}$, abbreviated as M, and tetravalent siloxane units Q, $SiO_{4/2}$, c.f., Figure 2.11.

The terms 1/2 and 4/2 after the oxygen indicates that the oxygen atom is shared between groups M and Q. The resin does not contain more than 15 mol-% hydroxyl units.

Such silicone resins remain soluble in hydrocarbons across a wide range of molecular weights. Silicone resins with a large proportion of Q units also show a high glass transition temperature(T_g) thus allowing wellbore fluids to be used at temperatures far higher than comparable fluids without silicone moieties.

The silicone resin is used as an emulsion, e.g., Dow Corning® 1430 Antifoam (Andrea, 2000). The formulations also contain conventional ingredients, such as surfactants, viscosity modifying agents, and biocides.

Phthalimide as a Diverting Material

Phthalimide, c.f., Figure 2.12, has been described as a diverting material, or fluid loss additive, for diverting aqueous treating fluids, including acids, into progressively less permeable portions of a subterranean formation (Dill, 1987).

This additive also reduces the fluid loss to the formation of an aqueous or hydrocarbon treating fluid utilized, for example, in fracturing treatments. Its use depends on the particle size of the material that is present.

Phthalimide will withstand high formation temperatures and can be readily removed from the formation by dissolution in the produced fluids, or by

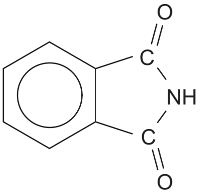


FIGURE 2.12 Phthalimide.

sublimation at elevated temperatures. The material is compatible either with other formation permeability-reducing materials, or formation permeability-increasing materials. The phthalimide particles act by sealing off portions of a subterranean formation by blocking off the fissures, pores, channels, and vugs that give access to the formation from the wellbore.

Special Applications

Coal-bed Methane Drilling

A series of mud systems and additives that have been in common use in coal-bed methane drilling have been evaluated with respect to their impact on the permeability of the coal matrix. Laboratory tests using both artificially cleated gypstone rock, as well as large-diameter coal cores, were performed as an assessment. In particular, various mud systems have been tested, including polyanionic and non-ionic cellulose and starch.

Muds based on xanthan gum, HEC, and Na-CMC did not have a negative impact on coal permeability. FLC™ 2000 and Q-Stop are very effective in building a thin filter cake on the coal surface almost instantaneously.

FLC™ 2000 is a micelle surfactant that very quickly forms a deformable barrier across coal cleats. Q-Stop consists of cellulose fibers. During production simulation experiments, a small pressure drop was sufficient to remove the filter cake.

It was shown that the permeability of the coal returned to its original value. This indicates that no permanent permeability damage is caused by the use of these additives. On the other hand, using the same coal type, the near-wellbore coal permeability was reduced by 87.5% by the addition of coal fines. Based on these laboratory studies, successful field applications in horizontal drilling could be achieved (Gentzis et al., 2009). The damage is illustrated in Table 2.12.

Sand Control

The rate of hydrocarbon flow declines when the bottom hole pressure falls below the dew point. When this occurs, a liquid aqueous phase accumulates near the well, sometimes termed condensate blocking. This effect reduces the

TABLE 2.12 Fluid Damage on Coal-beds in Overbalanced Drilling

Fluid	Initial Permeability [mD]	Final Permeability [mD]	Reduction [%]
Pure PAC	3.3	0.7	77.7
Xanthan gum + PAC	1.4	0.3	76.0
Xanthan gum, pH = 12	0.1	0.1	87.0
Xanthan gum, pH = 7	1.4	0.3	79.2
Base foaming solution	1.2	0.3	77.0
Xanthan gum field mud	5.1	1.4	72.9
Xanthan gum + fiber bridging agent	8.9	1.2	86.3
Cationic shale inhibitor/HEC	2.2	0.6	74.9

relative permeability of the hydrocarbons and thus the productivity of the well (Nguyen et al., 2010b).

Also, if water swellable clays are present in this region, swelling is likely to occur, which reduces the permeability of the formation further. Well treatment fluids sometimes decrease the relative permeability of hydrocarbons. Capillary forces can tightly hold these treatment fluids. The rate of hydrocarbon flow can be also reduced by other factors, namely (Nguyen et al., 2010b):

1. The production of fines,
2. Sand migration in the formation, or
3. Precipitation.

The high velocity in the porous medium near the wellbore is sometimes sufficient to mobilize fines that subsequently can plug channels in the formation. Formation sand and fines often become unstable and migrate due to water movement through the formation. This is most likely to occur when the water phase is mobile because most of the fines are water-wet.

The presence of a mobile water phase can cause the migration of fines and subsequent formation damage. This needs to be minimized, since fines block flow paths, choking the potential production of the well, and also cause damage to downhole and surface equipment (Nguyen et al., 2010b).

Unconsolidated subterranean zones include those that contain loose particulates and those where the bonded particulates have insufficient bond strength to withstand the forces produced by the production of fluids through the zones. Support devices, such as screens and slotted liners, are often used to provide support for these unconsolidated formations in order to prevent a collapse of the formation.

In some instances, the annulus around the support device is gravel packed to reduce the voids between the device and the wellbore wall. Gravel packing forms a filtration bed near the wellbore, which acts as a physical barrier to the transport of unconsolidated formation fines with the production of hydrocarbons.

One common type of gravel packing operation involves placing a gravel pack screen in the wellbore, and packing the surrounding annulus with gravel of a specific mesh size, designed to prevent the passage of formation sand. Basically, the gravel pack screen is a filter, designed to retain the gravel placed during a gravel pack operation. Gravel packs may be time-consuming and expensive to install. Due to the time and expense needed it is sometimes advantageous to place a screen without the gravel.

An expandable screen is often installed to maintain the diameter of the wellbore for ease of access at a later time by eliminating installation of conventional screens, gravel placement, and other equipment.

Consolidation of a subterranean formation zone is often performed by pumping in a sequence of a resin, a spacer fluid and a catalyst. Such a resin application may be problematic when an insufficient amount of the spacer fluid is used, since the resin may contact the external catalyst too early.

An extensive review of literature concerning the methods for controlling unconsolidated particulates has been presented (Nguyen et al., 2010b). In addition, treatment fluids for controlling the migration of unconsolidated particulates in subterranean formations have been developed, which use a diluted epoxy resin. As diluent, a fluid that is miscible with water is used, i.e., methanol (Nguyen et al., 2010a). The addition of this solvent adjusts the viscosity of the resin composite so that a high degree of penetration into the subterranean formation can occur.

Fracturing

Hydrocarbon-producing wells are often stimulated by hydraulic fracturing operations, wherein a viscous fracturing fluid is introduced into the hydrocarbon-producing zone at a hydraulic pressure that is enough to create or enhance a fracture.

Generally, the fracturing fluid contains suspended proppant particles that are to be placed in the fractures to prevent them from fully closing (once the hydraulic pressure is released). This process forms conductive channels within the formation through which hydrocarbons can flow. Once at least one fracture is created, and at least a portion of the proppant is substantially in place, the viscosity of the fracturing fluid may be reduced, to remove it from the formation.

In certain circumstances, a portion of the fracturing fluid may be lost, e.g., through undesirable leak-off into natural fractures present in the formation. This is problematic because such natural fractures often have higher stresses than those created by a fracturing operation. These higher stresses may damage the proppant and cause it to form an impermeable plug in the natural fractures, which may prevent hydrocarbons from flowing through the natural fractures.

Conventionally, operators have attempted to solve this problem by including a fluid loss control additive in the fracturing fluid. These are generally rigid particles having a spheroid shape, but their use can be problematic in itself, since they may require particles that have a distinct particle size distribution in order to achieve efficient fluid loss control. For example, when used to block the pore throats in the formation, enough large particles will be required to obstruct most of the pore throat, and a sufficient proportion of relatively small particles will also be required to obstruct the interstices between the large particles. Such a particle size distribution may be difficult to obtain without incurring the added expense of reprocessing the materials, for example, by cryogenic grinding (Todd et al., 2006).

Cement Compositions

Polymers have been used as fluid loss control additives in cementing operations, including HEC and carboxymethylhydroxyethyl cellulose; copolymers of AMPS and AAm or *N*,*N*-dimethylacrylamide; and lignin or lignite grafted with AMPS, acrylonitrile, and *N*,*N*-dimethylacrylamide.

They may not provide the desired level of fluid loss control at high temperatures, however, i.e., at least about 260°C (Lewis et al., 2009). Alternatively, a backbone of a humic acid salt has been proposed that has the moieties mentioned above grafted onto it. These graft copolymers are particularly suitable for use as fluid loss control additives in high-temperature applications.

Humic acids are produced by the decomposition of organic matter, such as dead plants, and may contain allomelanins found in soils, coals, and peat. The backbone may also contain PVA, PEO, polypropylene oxide, polyethyleneimine, and combinations of these moieties. Humic acid may be treated with KOH, NaOH, or NH_4OH to make it soluble in water.

The solution so produced is further concentrated to increase its humic acid content, or it may be used directly in the grafting process. The graft copolymers may be prepared by free radical polymerization techniques. The initiator employed is usually a redox reagent, capable of generating a free radical in the humic acid.

Preparation 2–1: Usually the grafting is done in aqueous solution. To a reactor vessel, sodium humate, water, a defoamer, and ethylene diamine tetraacetic acid are added. Then AMPS, AAm, DADMAC, and AA are added. Then this mixture is heated and kept at 70°C for one hour while purging with nitrogen.

Afterwards, ammonium persulfate is added to initiate the polymerization. After two hours, sodium metabisulfite is added, and the mixture is allowed to cool. When the mixture reaches room temperature, a 50% solution of sodium hydroxide is added to

TABLE 2.13 Formulations for Grafting (Lewis et al., 2009)

Component → Formulation	#1/[%]	#2/[%]
Sodium humate	4.7	4.7
Water	42.84	41.01
NaOH, 50% solution	1.69	1.28
Defoamer	0.01	0.01
NaAMPS, 58% solution	31.48	31.48
Acrylamide, 48% solution	5.92	5.92
AA	1.44	–
Vinylphosphonic acid	–	1.08
DADMAC, 62% solution	5.22	7.82
NaEDTA	0.1	0.1
Ammonium persulfate, 27% solution	3.3	3.3
Sodium metabisulfite, 27% solution	3.3	3.3

adjust the pH to 7–8 (Lewis et al., 2009). The amounts of the individual compounds are summarized in Table 2.13. ■

The performance of these additives has been tested with regard to cementing. Compressive strength and thickening time tests were performed to compare the performance of a range of cement compositions. The fluid loss of these compositions was tested at high temperatures (Lewis et al., 2009). The formulations provide desirable thickening times and compressive strengths.

Viscoelasticity

Viscoelastic materials exhibit both viscous and elastic properties under mechanical deformation. Such materials exhibit a hysteresis in their stress strain curves. Further, a relaxation of stress occurs under constant strain, i.e., the stress is diminished. Moreover, viscoelastic materials exhibit creep.

A simple model for such materials was developed by James Clerk Maxwell in 1867 (Maxwell, 1867). A Maxwell fluid or Maxwell body can be modeled by an idealized viscous damper and an idealized elastic spring connected in series. The basic device is shown in Figure 2.13.

The Maxwell model can hence explain both the elastic and viscous properties of a body. Some basic issues of the Maxwell model have been revisited (Rao and Rajagopal, 2007). The basic Maxwell model can be represented by:

$$\frac{d\varepsilon_t}{dt} = \frac{d\varepsilon_d}{dt} + \frac{d\varepsilon_s}{dt} = \frac{\sigma}{\eta} + \frac{1}{E}\frac{d\sigma}{dt}. \tag{2.6}$$

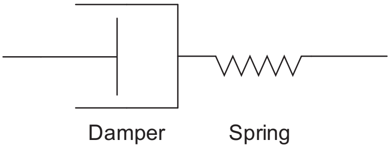


FIGURE 2.13 Maxwell model.

The change in total elongation ε_t in time t is the sum of the change of elongation of the damper ε_D and the change of elongation of the spring ε_t. The right hand side of Eq. 2.6 is simply Newton's law of flow together with Hooke's law of the elongation of an ideal spring, i.e.,

$$\frac{d\varepsilon_d}{dt} = \frac{\sigma}{\eta}, \quad \varepsilon_s = \frac{1}{E}\sigma.$$

The latter is given in the more uncommon differential form. Thus, η is the Newtonian viscosity, σ is the stress, and E is the elastic modulus. (By the way, if the spring and the damper are coupled in parallel instead of consecutively, the Kelvin-Voigt model emerges, which may be experienced in self-closing doors.)

The property of viscoelasticity has been well investigated (Rehage and Hoffmann, 1988). Aqueous solutions of cationic surfactants with strong binding forces of the ions show properties similar to gels.

Microstructural transitions and rheological properties of viscoelastic solutions formed in a catanionic surfactant system were studied using a combination of rheology and dynamic light scattering (Yin et al., 2009). The rheological behavior of such systems can be very complicated. In a study of a surfactant system based on dodecyltriethylammonium bromide and sodium dodecyl sulfate, worm-like micelles began to form above a certain surfactant concentration. In an intermediate concentration range, the system exhibits a linear viscoelasticity with the characteristics of a Maxwell fluid. Eventually, at higher surfactant concentrations, a transition from linear micelles to branched structures may take place.

The changes of the viscosity at zero shear rate with the total concentration of surfactant with a ratio of dodecyltriethylammonium bromide to sodium dodecyl sulfate of 27/73 are shown in Figure 2.14.

Viscoelastic Surfactants

Viscoelasticity is caused by a different type of micelle formation to the usual spherical micelles, which are formed by most surfactants. Viscoelastic surfactants (VESs) are believed to impart viscosity to an aqueous fluid by the molecules organizing themselves into micelles, and when the micelles have an elongated configuration, for instance, rod-shaped or worm-shaped, they become entangled with one another, thereby increasing the viscosity of the fluid (Crews and Huang, 2010a).

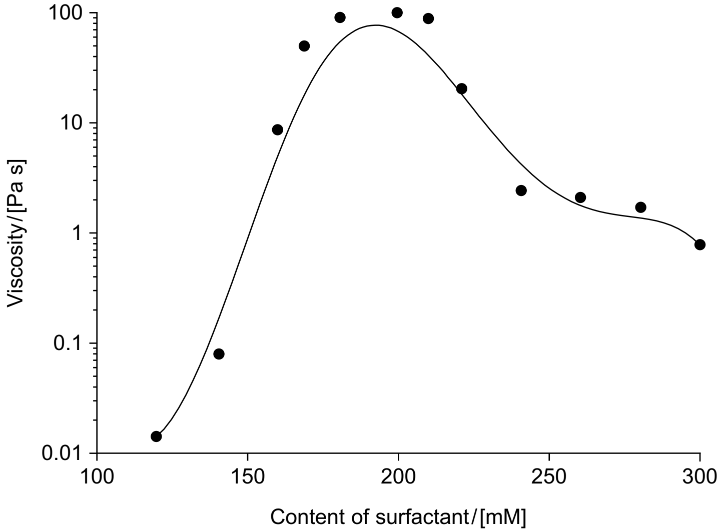


FIGURE 2.14 Viscosity viz. concentration of surfactant (Yin et al., 2009).

Elongated VES structures are referred to as living, because there is a continuous exchange between surfactants leaving the micelle structures to enter the aqueous solution and those leaving the aqueous solution to entering or reentering the micelles.

VES solutions exhibit shear thinning behavior, but they remain stable despite repeated high shear applications. By comparison, a typical polymeric thickener will irreversibly degrade under high shear (Colaco et al., 2007).

Internal breakers work by the rearranging the VES micelle from rod-shaped or worm-shaped elongated structures to spherical structures. In other words, they perform the collapse or rearrangement of the viscous elongated micelle structures to nonviscous, more spherical, micelle structures (Crews and Huang, 2010a).

Enhanced Shear Recovery Agents Some VESs exhibit low shear recovery when subjected to high shear. However, unacceptably long shear recovery times hinder deep well operations.

Enhanced shear recovery agents reduce the shear recovery time of a VES fluid. They are based on alkylated polyglucosides, polyglucamides, or on copolymers based on ethylene glycol ethyl ether acrylate. Glucamides consist of cyclic forms of glucose in which the hydrogen of the hemiacetal group has been replaced with an alkyl or aryl moiety, as shown in Figure 2.15.

Enzyme-based Gel Breaking The viscosities of fluids viscosified with VES may be reduced by the direct or indirect action of a biochemical agent, such as

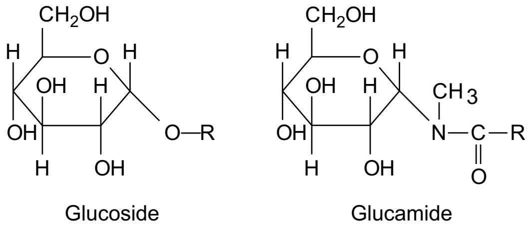


FIGURE 2.15 Glucoside and glucamide structures (Colaco et al., 2007).

bacteria, fungi, or enzymes. This agent may directly attack the VES itself, or some other component in the fluid that produces a by-product that then causes viscosity reduction. The biochemical agent may disaggregate or otherwise attack the micellar structure of the VES-gelled fluid. The biochemical agent may produce an enzyme that reduces viscosity by one of these mechanisms.

A single biochemical agent may operate simultaneously by two different mechanisms, such as by degrading the VES directly, as well as another component, such as a glycol, the latter mechanism in turn producing a by-product, e.g. an alcohol that causes viscosity reduction.

Alternatively, two or more different biochemical agents may be used simultaneously. In a specific, non-limiting instance, a brine fluid gelled with an amine oxide surfactant can have its viscosity broken with bacteria such as *Enterobacter cloacae*, *Pseudomonas fluorescens*, *Pseudomonas aeruginosa*, etc (Crews, 2006).

Breaker Enhancers for VES Oil-soluble surfactants may be used as breaker enhancers for internal breakers for VES gelled aqueous fluids (Crews and Huang, 2010a). The oil-soluble surfactant breaker enhancers can overcome the rate-slowing effect that salinity has on the internal breakers, particularly at lower temperatures. Oil-soluble surfactant breaker enhancers may also allow lower internal breaker concentrations to be used to achieve quick and complete VES gelled fluid breaks.

Oil-soluble surfactant breaker enhancers include various sorbitan (unsaturated) fatty acid esters (Crews and Huang, 2010a,b). These esters are mixed with mineral oils. Unsaturated fatty acids have been found to break down by autooxidation into VES breaking products or compositions.

Each oil with various monoenoic and polyenoic acids uniquely shows the breakdown of the VES surfactant micelle structure by the presence of these autooxidation generated by-products.

Various hydroperoxides may be formed in the course of these autooxidation reactions, The end-products of these reactions typically include carbonyl compounds, alcohols, acids, and hydrocarbons. The rate of autooxidation of various fatty acids is shown in Table 2.14.

TABLE 2.14 Relative Rate of Autooxidation of C_{18} Acids (Crews and Huang, 2010a)

Fatty Acid	Double Bonds	Relative Oxidation Rate
Stearic	0	1
Oleic	1	100
Linoleic	2	1200
Linolenic	3	2500

Surfactant Polymer Compositions

The stability of VES-based fluids can be enhanced by using monomeric VESs, together with an oligomeric or polymeric compound with a thermally stable backbone. On this structure, VES functional groups are pending (Horton et al., 2009).

A VES solution can be synthesized from *N*-dodecene-1-yl-*N*,*N*-bis (2-hydroxyethyl)-*N*-methylammonium chloride in aqueous ammonium chloride. The aqueous solution is purged with nitrogen to remove residual oxygen and then oligomerized with 2,2′-azo(bis-amidinopropane)dihydrochloride as radical initiator. The oligomerization is shown schematically in Figure 2.16. In the same way, potassium octadeceneoate,

$$\mathrm{CH_2{=}CH{-}(CH_2)_{15}{-}COO^{-}K^{+}}$$

can be oligomerized. The resulting oligomer can be imagined as being related to an oligo ethylene backbone, to which relatively long, pendant, surfactant moieties are linked. If the double bonds are conjugated, as in the case of potassium octadecadieneoate,

$$\mathrm{CH_2{=}CH{-}CH{=}CH{-}(CH_2)_{13}COOK^{+}}$$

the resulting oligomeric structure is related to polybutadiene.

The oligomerization of surfactant monomers in micelles causes the viscosity of the gel to be comparatively insensitive to contact with hydrocarbons. Further, the viscosity of the surfactant gel is little altered by oligomerization of the surfactant monomers.

The preparation of several other oligomeric surfactants has been described in detail, including the use of comonomers (Horton et al., 2007, 2009). An example for a cooligomer is shown in Figure 2.17.

The vicinal diol functionality renders the oligomers readily crosslinkable with polyvalent metal ions or complexes. Such formulations have been characterized with respect to fluid loss control by an API standard (Recommended practice for field testing water-based drilling fluids (API), 2009).

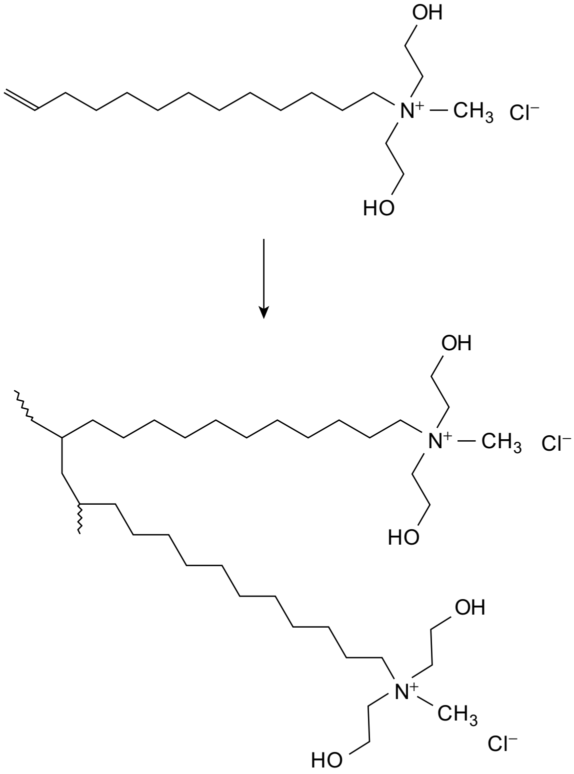


FIGURE 2.16 Oligomerization of unsaturated quaternary compounds (Horton et al., 2009).

Additives to Reduce Fluid Loss

Viscoelastic surfactant fluids are made by mixing suitable surfactants. When the surfactant concentration significantly exceeds a critical level, and subject to the presence of an electrolyte, the surfactant molecules aggregate and form structures such as micelles that can interact to form a network, which exhibits viscoelastic behavior (Sullivan et al., 2006).

These solutions can be formed by the addition of certain reagents to concentrated surfactant solution. The surfactants are long chain quaternary ammonium salts such as cetyltrimethyl ammonium bromide.

Salts, e.g., ammonium chloride, potassium chloride, sodium salicylate, and sodium isocyanate generate viscoelasticity in surfactant solutions. In addition, non-ionic organic molecules, such as chloroform are active in generating viscoelasticity. The electrolyte content of surfactant solutions is also an important parameter for its viscoelasticity (Sullivan et al., 2006). Aqueous fluids gelled with VESs have been used for hydraulic fracturing operations.

However, the property that makes VES fluids less damaging tends to cause significantly higher fluid leakage into the reservoir matrix, which reduces the

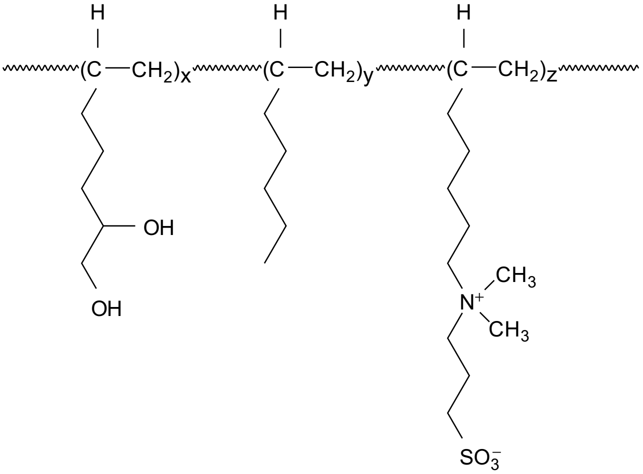


FIGURE 2.17 Cooligomeric surfactant (Horton et al., 2007).

efficiency of the fluid, especially during VES fracturing treatments. Thus, it is important to use fluid loss agents for VES fracturing treatments in high-permeability formations (Huang and Crews, 2009).

The fluid loss properties of such fluids can be improved by the addition of mineral oil with a viscosity greater than 20 mPa s at ambient temperature. The mineral oil may initially be dispersed as oil droplets in an internal, discontinuous phase of the fluid, and is added to the fluid after it has been substantially gelled.

In the experiments shown below, tallow amido propylamine oxide available from Akzo Nobel has been used as VES surfactant (Podwysocki, 2004). It has been demonstrated that the viscosity of aqueous fluids containing 3% KCl and gelled with 6% VES at 66°C with and without 2% mineral oil is adversely affected. This behavior contrasts with other observations, since larger amounts of hydrocarbons and mineral oils tend to inhibit or break the gel of VES-gelled fluids (Huang and Crews, 2009).

On the other hand, fluid loss is improved, as shown in model experiments. The fluid loss as a function of testing time is shown in Figure 2.18. The test is conducted at 0.7 MPa with 400 mD ceramic disks at 66°C.

It has been discovered that the addition of magnesium oxide, or calcium hydroxide, to an aqueous fluid gelled with a VES improves the fluid loss of these brines (Huang et al., 2009).

It is useful that these fluid loss control agents dissolve slowly, since this permits their easy removal from the formation, so sustaining little or no damage to the formation.

The introduction of these additives to a VES-gelled aqueous system will limit and reduce the amount of VES fluid that leaks into the pores of a reservoir during a fracturing or frac-packing treatment, thus minimizing the formation damage that may occur by the VES fluid within the reservoir pores.

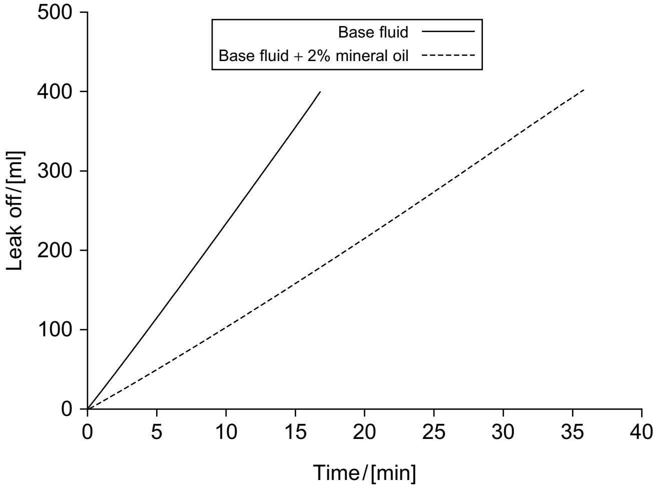


FIGURE 2.18 Fluid loss viz. time (Huang and Crews, 2009).

Moreover, differences in reservoir permeability do not significantly change the rate of fluid loss. Thus, the rate of leak-off in 2000 mD reservoirs will be comparable that of 100 mD reservoirs. This behavior expands the range in reservoir permeability to which the VES fluid may be applied.

It is believed that fluid loss agents associate with the VES micelles. As the VES fluid is leaked-off into the reservoir, a viscous layer of micelles and fluid loss control particles accumulate on the formation face, thus reducing the rate of VES fluid leak-off.

Particulate plugging of the reservoir pores is not the mechanism of leak-off control. Tests with nanometer-sized fluid loss agents that definitely cannot bridge or plug reservoir pores of 1 mD or higher reservoir permeability, still develop a viscous micelle layer. Thus, the size of the fluid loss agent is not a controlling or primary factor for controlling the leak-off rate (Huang et al., 2009).

REFERENCES

Amanullah, M., Yu, L., 2005. Environment friendly fluid loss additives to protect the marine environment from the detrimental effect of mud additives. J. Pet. Sci. Eng. 48 (3–4), 199–208.

Anderson, C.P., Blenkinsopp, S.A., Cusack, F.M., Costerton, J.W., 1991. Drilling mud fluid loss – an alternative to expensive bulk polymers. In: Proceedings Volume, 4th Inst. Gas Technol. Gas, Oil, & Environ. Biotechnol. Int. Symp. (Colorado Springs, CO, 12/9–11/91), pp. 481–489.

Andrea, 2000. Dow Corning® 1430 Antifoam, Product Information 22-030G-01, FPH22781, Dow Corning Corporation, Midland, OH [electronic:] http://www1.dowcorning.com/DataFiles/090007c880002832.pdf.

Audebert, R., Janca, J., Maroy, P., Hendriks, H., 1994. Chemically crosslinked polyvinyl alcohol (PVA), process for synthesizing same and its applications as a fluid loss control agent in oil fluids. GB Patent 2 278 359, assigned to Sofitech NV, November 30, 1994.

Audebert, R., Janca, J., Maroy, P., Hendriks, H., 1996. Chemically crosslinked polyvinyl alcohol (PVA), process for synthesizing same and its applications as a fluid loss control agent in oil fluids. CA Patent 2 118 070, assigned to Schlumberger Canada Ltd., April 14, 1996.

Audebert, R., Maroy, P., Janca, J., Hendriks, H., 1998. Chemically crosslinked polyvinyl alcohol (PVA), and its applications as a fluid loss control agent in oil fluids. EP Patent 705 850, assigned to Sofitech NV, September 02, 1998.

Audibert, A., Argillier, J.F., 1996. Process and water-based fluid utilizing hydrophobically modified guar gums as filtrate (loss) reducer (procede et fluide a base d'eau utilisant des guars modifiees hydrophobiquement comme reducteur de filtrat). EP Patent 722 036, assigned to Inst. Francais Du Petrole, July 17, 1996.

Audibert, A., Argillier, J.F., 1998. Process and water-base fluid utilizing hydrophobically modified guars as filtrate reducers. US Patent 5 720 347, assigned to Inst. Francais Du Petrole, February 24, 1998.

Audibert, A., Argillier, J.F., Bailey, L., Reid, P.I., 1997. Process and water-base fluid utilizing hydrophobically modified cellulose derivatives as filtrate reducers. US Patent 5 669 456, assigned to Inst. Francais Du Petrole and Dowell Schlumberger Inc., September 23, 1997.

Audibert-Hayet, A., Argillier, J.F., Rousseau, L., 1998. Filtrate reducing additive and well fluid (additif reducteur de filtrat et fluide de puits). WO Patent 9 859 014, assigned to Inst. Francais Du Petrole, December 30, 1998.

Audibert, A., Rousseau, L., Kieffer, J., 1999. Novel high-pressure/high temperature fluid loss reducer for water-based formulation. In: Proceedings Volume, SPE Oilfield Chem. Int. Symp. (Houston, 2/16–19/1999), pp. 235–242.

Bailey, L., 2001. Latex additive for water-based drilling fluids. GB Patent 2 351 986, assigned to Sofitech NV, January 17, 2001.

Bardoliwalla, D.F., 1986a. Aqueous drilling fluids containing fluid loss additives. US Patent 4 622 370, November 11, 1986.

Bardoliwalla, D.F., 1986b. Fluid loss control additives from AMPS (2-acrylamido-2-methylpropane sulfonic acid) polymers. US Patent 4 622 373, November 11, 1986.

Baret, J.F., 1988. Why cement fluid loss additives are necessary. In: Proceedings Volume, SPE Petrol. Eng. Int. Mtg. (Tianjin, China, 11/1–4/88), pp. 853–860.

Bellis, H.E., McBride, E.F., 1987. Composition and method for temporarily reducing the permeability of subterranean formations. EP Patent 228 196, assigned to Du Pont De Nemours & Co., July 08, 1987.

Berry, V.L., Cook, J.L., Gelderbloom, S.J., Kosal, D.M., Liles, D.T., Olsen Jr., C.W., Rome, C.F.C., 2008. Silicone resin for drilling fluid loss control. US Patent 7 452 849, assigned to Dow Corning Corporation (Midland, MI), November 18, 2008.

Bharat, P., 1990. Well treating fluids and additives therefor. EP Patent 372 469, June 13, 1990.

Boncan, V.G., Gandy, R., 1986. Well cementing method using an AM/AMPS fluid loss additive blend. US Patent 4 632 186, December 30, 1986.

Bouts, M.N., Trompert, R.A., Samuel, A.J., 1997. Time delayed and low-impairment fluid-loss control using a succinoglycan biopolymer with an internal acid breaker. SPE J. 2 (4), 417–426.

Braden, J., 2006. PLIOLITE®VT/VTL Resin, Product Data Sheet PDS-PLEVT-2006-04/1, Eliokem, Inc., Akron, OH, [electronic:] http://www.eliokem.com/pdf/PLEVTL.pdf.

Brake, B.G., Chatterji, J., 1994. Fluid loss reducing additive for cement compositions. EP Patent 595 660, assigned to Halliburton Co., May 04, 1994.

Brothers, L.E., 1989. Method of reducing fluid loss in cement compositions. US Patent 4 806 164, February 21, 1989.

Cantu, L.A., McBride, E.F., Osborne, M.W., 1989. Formation fracturing process. US Patent 4 848 467, assigned to Conoco Inc. and Du Pont De Nemours & Co., July 18, 1989.

Cantu, L.A., McBride, E.F., Osborne, M., 1990. Well treatment process. EP Patent 404 489, assigned to Conoco Inc. and Du Pont De Nemours & Co., December 27, 1990.

Cantu, L.A., McBride, E.F., Osborne, M.W., 1993. Formation fracturing process. CA Patent 1 319 819, assigned to Conoco Inc., July 06, 1993.

Casad, B.M., Clark, C.R., Cantu, L.A., Cords, D.P., McBride, E.F., 1991. Process for the preparation of fluid loss additive and gel breaker. US Patent 4 986 355, assigned to Conoco Inc., January 22, 1991.

Cawiezel, K.E., Navarrete, R., Constien, V., 1996. Fluid loss control. GB Patent 2 291 906, assigned to Sofitech NV, February 07, 1996.

Chang, F.F., Bowman, M., Parlar, M., Ali, S.A., Cromb, J., 1998. Development of a new crosslinked-hec (hydroxyethylcellulose) fluid loss control pill for highly-overbalanced, high-permeability and/or high temperature formations. In: Proceedings Volume, SPE Formation Damage Contr. Int. Symp. (Lafayette, LA, 2/18–19/98), pp. 215–227.

Chang, F.F., Parlar, M., 1999. Method and composition for controlling fluid loss in high permeability hydrocarbon bearing formations. US Patent 5 981 447, assigned to Schlumberger Technol. Corp., November 09, 1999.

Cheung, P.S.R., 1993. Fluid loss additives for cementing compositions. US Patent 5 217 531, assigned to Western Co. North America, June 08, 1993.

Chin, W.C., 1995. Formation Invasion: With Applications To Measurement-While-Drilling, Time Lapse Analysis, and Formation Damage. Gulf Publishing Co., Houston, TX.

Coates, J.A., Farrar, J.M., Graham, M.H., 1990. Fluid loss-reducing additives for oil-based well working fluid. US Patent 4 941 983, July 17, 1990.

Colaco, A., Marchand, J.-P., Li, F., Dahanayake, M.S., 2007. Viscoelastic surfactant fluids having enhanced shear recovery, rheology and stability performance. US Patent 7 279 446, assigned to Rhodia Inc. (Cranbury, NJ) Schlumberger Technology Corporation (Sugarland, TX), October 9, 2007.

Costello, C.A., Lai, T.W., Pinschmidt Jr., R.K., 1990. Aqueous, clay-based drilling mud. GB Patent 2 225 364, May 30, 1990.

Cowan, J.C., Granquist, V.M., House, R.F., 1988. Organophilic polyphenolic acid adducts. US Patent 4 737 295, assigned to Venture Chemicals Inc., April 12, 1988.

Crawford, D., 2000. High pressure high temperature (hpht) fluid loss control aid for drilling fluids. WO Patent 0 026 322, assigned to Sun Drilling Products Inc., May 11, 2000.

Crema, S.C., Kucera, C.H., Konrad, G., Hartmann, H., 1991. Fluid loss control additives for oil well cementing compositions. US Patent 5 025 040, assigned to BASF Corp., June 18, 1991.

Crema, S.C., Kucera, C.H., Konrad, G., Hartmann, H., 1993. Fluid loss control additives for oil well cementing compositions. US Patent 5 228 915, assigned to BASF Corp., July 20, 1993.

Crews, J.B., 2006. Bacteria-based and enzyme-based mechanisms and products for viscosity reduction breaking of viscoelastic fluids. US Patent 7 052 901, assigned to Baker Hughes Incorporated (Houston, TX), May 30, 2006.

Crews, J.B., Huang, T., 2010a. Use of oil-soluble surfactants as breaker enhancers for ves-gelled fluids. US Patent 7 696 135, assigned to Baker Hughes Incorporated (Houston, TX), April 13, 2010.

Crews, J.B., Huang, T., 2010b. Unsaturated fatty acids and mineral oils as internal breakers for ves-gelled fluids. US Patent 7 696 134, assigned to Baker Hughes Incorporated (Houston, TX), April 13, 2010.

Dill, W.R., 1987. Diverting material and method of use for well treatment. CA Patent 1 217 320, February 03, 1987.

Dobson Jr., J.W., Harrison, J.C.I., Kayga, P.D., 1998. Methods of reducing fluid loss and polymer concentration of well drilling and servicing fluids. AU Patent 697 559, assigned to Texas United Chem. Co. LLC., October 08, 1998.

Dobson Jr., J.W., Hayden, S.L., Hinojosa, B.E., 2005. Borate crosslinker suspensions with more consistent crosslink times. US Patent 6 936 575, assigned to Texas United Chemical Company, LLC. (Houston, TX), August 30, 2005.

Dobson, J.W., Mondshine, K.B., 1997. Method of reducing fluid loss of well drilling and servicing fluids. EP Patent 758 011, assigned to Texas United Chem. Co. LLC., February 12, 1997.

Dreveton, E., Lecourtier, J., Ballerini, D., Choplin, L., 1995. Process utilizing gellan as filtrate reducer for water-based drilling fluids (procede utilisant le gellane comme reducteur de filtrat pour les fluides de forage a base d'eau). EP Patent 662 563, assigned to Inst. Francais Du Petrole, July 12, 1995.

Dreveton, E., Lecourtier, J., Ballerini, D., Choplin, L., 1998. Process using gellan as a filtrate reducer for water-based drilling fluids. US Patent 5 744 428, assigned to Inst. Francais Du Petrole, April 28, 1998.

Feraud, J.P., Perthuis, H., Dejeux, P., 2001. Compositions for iron control in acid treatments for oil wells. US Patent 6 306 799, assigned to Schlumberger Technology Corporation (Sugar Land, TX), October 23, 2001.

Forrest, G.T., 1998. Drilling, completion, and workover fluid comprising ground peanut hulls. WO Patent 9 821 290, May 22, 1998.

Francis, H.P., Deboer, E.D., Wermers, V.L., 1987. High temperature drilling fluid component. US Patent 4 652 384, March 24, 1987.

Fry, S.E., Childs, J.D., Brothers, L.E., Lindsey, D.W., 1987. Method of reducing fluid loss in cement compositions which may contain substantial salt concentrations. US Patent 4 676 317, assigned to Halliburton Company (Duncan, OK), June 30, 1987.

Ganguli, K.K., 1992. High temperature fluid loss additive for cement slurry and method of cementing. US Patent 5 116 421, assigned to Western Co. North America, May 26, 1992.

Garvey, C.M., Savoly, A., Resnick, A.L., 1988. Fluid loss control additives and drilling fluids containing same. US Patent 4 741 843, May 03, 1988.

Gentzis, T., Deisman, N., Chalaturnyk, R.J., 2009. Effect of drilling fluids on coal permeability: Impact on horizontal wellbore stability. Int. J. Coal Geol. 78 (3), 177–191.

Giddings, D.M., Williamson, C.D., 1987. Terpolymer composition for aqueous drilling fluids. US Patent 4 678 591, July 07, 1987.

Growcock, F.B., Simon, G.A., 2006. Stabilized colloidal and colloidal-like systems. US Patent 7 037 881, May 2, 2006.

Guichard, B., Wood, B., Vongphouthone, P., 2006. Fluid loss reducer for high temperature and high pressure water-based mud application. US Patent 7 101 829, assigned to Eliokem S.A.S. (Villejust, FR), September 5, 2006.

Guichard, B., Wood, B., Vongphouthone, P., 2007. Fluid loss reducer for high temperature high pressure water based-mud application. US Patent 7 256 159, assigned to Eliokem S.A.S. (Villejust, FR), August 14, 2007.

Guichard, B., Wood, B., Vongphouthone, P., 2008. Fluid loss reducer for high temperature high pressure water based-mud application. US Patent 7 449 430, assigned to Eliokem S.A.S. (Villejust, FR), November 11, 2008.

Halliday, W.S., Schwertner, D., Xiang, T., Clapper, D.K., 2007. Fluid loss control and sealing agent for drilling depleted sand formations. US Patent 7 271 131, assigned to Baker Hughes Incorporated (Houston, TX), September 18, 2007.

Halliday, W.S., Schwertner, D., Xiang, T., Clapper, D.K., 2008. Water-based drilling fluids using latex additives. US Patent 7 393 813, assigned to Baker Hughes Incorporated (Houston, TX), July 1, 2008.

Hen, J., 1991. Sulfonate-containing polymer/polyanionic cellulose combination for high temperature/high pressure filtration control in water base drilling fluids. US Patent 5 008 025, assigned to Mobil Oil Corp., April 16, 1991.

Hernandez, M.I., Mas, M., Gabay, R.J., Quintero, L., 1999a. Thermally stable drilling fluid. US Patent 5 883 054, assigned to Intevep, March 16, 1999.

Hernandez, M.I., Mas, M., Gabay, R.J., Quintero, L., 1999b. Thermally stable drilling fluid which includes styrene-butadiene copolymers. GB Patent 2 329 657, assigned to Intevep, March 31, 1999.

Hille, M., Wittkus, H., Tonhauser, J., Engelhardt, F., Riegel, U., 1996. Water-soluble copolymers useful in drilling fluids. US Patent 5 510 436, assigned to Hoechst AG, April 23, 1996.

Horton, R.L., Prasek, B., Growcock, F.B., Kippie, D., Vian, J.W., Abdur-Rahman, K.B., Arvie Jr., M., 2007. Surfactant-polymer compositions for enhancing the stability of viscoelastic-surfactant based fluid. US Patent 7 157 409, assigned to M-I LLC (Houston, TX), January 2, 2007.

Horton, R.L., Prasek, B.B., Growcock, F.B., Kippie, D.P., Vian, J.W., Abdur-Rahman, K.B., Arvie, M., 2009. Surfactant-polymer compositions for enhancing the stability of viscoelastic-fluid surfactant based. US Patent 7 517 835, assigned to M-I LLC (Houston, TX), April 14, 2009.

Huang, N., 1996. Synthesis of fluid loss additive of sulfonate tannic-phenolic resin. Oil Drill. Prod. Technol. 18 (2), 39–42, 106–107.

Huang, T., Crews, J.B., 2009. Use of mineral oils to reduce fluid loss for viscoelastic surfactant gelled fluids. US Patent 7 615 517, assigned to Baker Hughes Incorporated (Houston, TX), November 10, 2009.

Huang, T., Crews, J.B., Treadway Jr., J.H., 2009. Fluid loss control agents for viscoelastic surfactant fluids. US Patent 7 550 413, assigned to Baker Hughes Incorporated (Houston, TX), June 23, 2009.

Huddleston, D.A., Gabel, R.K., Williamson, C.D., 1992. Method for reducing fluid loss from oilfield cement slurries using vinyl grafted wattle tannin. US Patent 5 134 215, assigned to Nalco Chemical Co., July 28, 1992.

Huddleston, D.A., Williamson, C.D., 1990. Vinyl grafted lignite fluid loss additives. US Patent 4 938 803, assigned to Nalco Chemical Co., July 03, 1990.

House, R.F., Granquist, V.M., 1986. Polyphenolic acid adducts. US Patent 4 597 878, assigned to Venture Innovations Inc., July 01, 1986.

Jarrett, M., Clapper, D., 2010. High temperature filtration control using water based drilling fluid systems comprising water soluble polymers. US Patent 7 651 980, assigned to Baker Hughes Incorporated (Houston, TX), January 26, 2010.

Jiao, D., Sharma, M.M., 1994. Mechanism of cake buildup in crossflow filtration of colloidal suspensions. J. Colloid Interface Sci. 162 (2), 454–462.

Johnson, M., 1996. Fluid systems for controlling fluid losses during hydrocarbon recovery operations. EP Patent 691 454, assigned to Baker Hughes Inc., January 10, 1996.

Johnson, M.H., Smejkal, K.D., 1993. Fluid system for controlling fluid losses during hydrocarbon recovery operations. US Patent 5 228 524, assigned to Baker Hughes Inc., July 20, 1993.

Kelessidis, V.C., Papanicolaou, C., Foscolos, A., 2009. Application of greek lignite as an additive for controlling rheological and filtration properties of water-bentonite suspensions at high temperatures: A review. Int. J. Coal Geol. 77 (3–4), 394–400.

Kelessidis, V.C., Tsamantaki, C., Michalakis, A., Christidis, G.E., Makri, P., Papanicolaou, K., Foscolos, A., 2007. Greek lignites as additives for controlling filtration properties of water-bentonite suspensions at high temperatures. Fuel 86 (7–8), 1112–1121.

Kucera, C.H., Crema, S.C., Roznowski, M.D., Konrad, G., Hartmann, H., 1989. Fluid loss control additives for oil well cementing compositions. EP Patent 342 500, November 23, 1989.

Lai, T.W., Vijayendran, B.R., 1989. Cement composition for oil well drilling holes containing high molecular weight polyvinylamines. EP Patent 331 045, September 06, 1989.

Lau, H.C., 1994. Laboratory development and field testing of succinoglycan as a fluid-loss-control fluid. SPE, Shell Development Co. J. SPE Drill. Completion 9 (4), 221–226.

Lange, W., Boehmer, B., 1988. Water-soluble polymers and their use as flushing liquid additives for drilling. US Patent 4 749 498, June 07, 1988.

Langlois, B., 1999. Fluids useful for oil mining comprising de- acetylated xanthane gum and at least one compound increasing the medium ionic strength (fluides a utilisables dans l'exploitation du petrole comprenant de la gomme xanthane desacetylee et au moins un compose augmentant la force ionique du milieu). WO Patent 9 903 948, assigned to Rhodia Chimie, January 28, 1999.

Le, H.V., Kesavan, S., Dawson, J.C., Mack, D.J., Nelson, S.G., 1998. Compositions and methods for hydraulic fracturing. CA Patent 2 239 599, assigned to BJ Services Co., December 05, 1998.

Lewis, S., Chatterji, J., King, B., Brennels, C., 2008. Cement compositions comprising lignite grafted fluid loss control additives. US Patent 7 388 045, assigned to Halliburton Energy Services, Inc. (Duncan, OK), June 17, 2008.

Lewis, S., Chatterji, J., King, B., Brenneis, D.C., 2009. Cement compositions comprising humic acid grafted fluid loss control additives. US Patent 7 576 040, assigned to Halliburton Energy Services, Inc. (Duncan, OK), August 18, 2009.

Li, Y.G., Li, S.L., Wang, Z.L., 1996. New high temperature filtration reducer fla for drilling fluid. Drill. Fluid Completion Fluid 13 (3), 33–35.

Lord, D.L., Vinod, P.S., Shah, S., Bishop, M.L., 1995. An investigation of fluid leakoff phenomena employing a high-pressure simulator. In: Proceedings Volume, Annu. SPE Tech. Conf. (Dallas, 10/22–25/95), pp. 465–474.

Magnet, S., Duquesne, S., Delobel, R., Jama, C., 2008. Polymer binder for intumescent coatings. US Patent 7 417 091, assigned to Eliokem SAS (Villejust, FR), August 26, 2008.

Maxwell, J.C., 1867. On the dynamical theory of gases. Phil. Trans. R. Soc. Lond. 157 (1), 49–88.

Miller, W.K., Roberts, G.A., Carnell, S.J., 1996. Fracturing fluid loss and treatment design under high shear conditions in a partially depleted, moderate permeability gas reservoir. In: Proceedings Volume, SPE Asia Pacific Oil & Gas Conf. (Adelaide, Australia, 10/28–31/96), pp. 451–460.

Mondshine, T.C., 1986. Crosslinked fracturing fluids. US Patent 4 619 776, assigned to Texas United Chemical Corp. (Houston, TX), October 28, 1986.

Moran, L.K., Murray, T.R., 1991. Well cement fluid loss additive and method. US Patent 5 009 269, assigned to Conoco Inc., April 23, 1991.

Morgan, R.L., Caveny, W.J., Koch, R.R., 2008. Cement compositions with improved fluid loss characteristics and methods of cementing in surface and subterranean applications. US Patent 7 384 893, assigned to Halliburton Energy Services, Inc. (Duncan, OK), June 10, 2008.

Munoz Jr., T., Todd, B.L., 2008. Treatment fluids comprising starch and ceramic particulate bridging agents and methods of using these fluids to provide fluid loss control. US Patent 7 462 581, assigned to Halliburton Energy Services, Inc. (Duncan, OK), December 9, 2008.

Navarrete, R.C., Seheult, J.M., Himes, R.E., 2000. Applications of xanthan gum in fluid-loss control and related formation damage. In: Proceedings Volume, SPE Permian Basin Oil & Gas Recovery Conf. (Midland, TX, 3/21–23/2000).

Nguyen, P.D., Dusterhoft, R.G., Barton, J.A., 2010a. Methods for controlling particulate migration. US Patent 7 712 531, assigned to Halliburton Energy Services, Inc. (Duncan, OK), May 11, 2010.

Nguyen, P.D., Rickman, R.D., Dusterhoft, R.G., 2010b. Method of stabilizing unconsolidated formation for sand control. US Patent 7 673 686, assigned to Halliburton Energy Services, Inc. (Duncan, OK), March 9, 2010.

Nguyen, P.D., Weaver, J.D., Cole, R.C., Schulze, C.R., 1996. Development and field application of a new fluid-loss control material. In: Proceedings Volume, Annu. SPE Tech. Conf. (Denver, 10/6–9/96), pp. 933–941.

Oswald, R.J., Morschhaeuser, R., Heier, K.H., Tardi, A., Tonhauser, J., Kayser, C., Patterson, D., 2000. Water-soluble copolymers and their use for the exploration and recuperation of oil and gas. EP Patent 1 059 316, assigned to Clariant GmbH, December 13, 2000.

Patel, A.D., 1998. Water-based drilling fluids with high temperature fluid loss control additive. US Patent 5 789 349, assigned to M I Drilling Fluids Llc., August 04, 1998.

Patel, A.D., McLaurine, H.C., 1992. Drilling fluid additive and method for inhibiting hydration. US Patent 5 149 690, assigned to M I Drilling Fluids Co., September 22, 1992.

Peiffer, D.G., Lundberg, R.D., Sedillo, L., Newlove, J.C., 1986. Fluid loss control in oil field cements. US Patent 4 626 285, December 02, 1986.

Petrochem, 2009. Fluid-loss control additives, [electronic:] http://www.petrochem-usa.com/.

Plank, J., 1990. Field results with a novel fluid loss polymer for drilling muds. Oil Gas Europe Mag. 16 (3), 20–23.

Plank, J., 1993. Drilling mud composition and process for reducing the filtrate of metal hydroxide mixtures containing drilling mud compositions. WO Patent 9 312 194, assigned to Skw Trostberg AG, June 24, 1993.

Plank, J.P., Gossen, F.A., 1989. Visualization of fluid-loss polymers in drilling mud filter cakes. In: Proceedings Volume, 64th Annu. SPE Tech. Conf. (San Antonio, 10/8–11/89), pp. 165–176.

Podwysocki, M., 2004. Akzo nobel surfactants, Technical Bulletin SC05-0707, Akzo Nobel Surface Chemistry LLC, 525 W. Van Buren Street Chicago, IL 60607-3823, http://www.surface.akzonobel.com/bulletins/Aromox%20APA%20T.pdf.

Raines, R.H., 1986. Use of low m.s. (molar substitution) hydroxyethyl cellulose for fluid loss control in oil well applications. US Patent 4 629 573, assigned to Union Carbide Corp., December 16, 1986.

Rao, I.J., Rajagopal, K.R., 2007. On a new interpretation of the classical Maxwell model. Mech. Res. Commun. 34 (7–8), 509–514.

Recommended practice for field testing water-based drilling fluids (API), 2009. Standard API RP 13B-1, American Petroleum Institute, Washington, DC.

Recommended practice for laboratory testing of drilling fluids (API), 2009. Standard API RP 13I, American Petroleum Institute, Washington, DC.

Reddy, B.R., Palmer, A.V., 2009. Sealant compositions comprising colloidally stabilized latex and methods of using the same. US Patent 7 607 483, assigned to Halliburton Energy Services, Inc. (Duncan, OK), October 27, 2009.

Rehage, H., Hoffmann, H., 1988. Rheological properties of viscoelastic surfactant systems. J. Phys. Chem. 92 (16), 4712–4719.

Roark, D.N., Nugent Jr., A., Bandlish, B.K., 1986. Fluid loss control and compositions for use therein. EP Patent 201 355, November 12, 1986.

Roark, D.N., Nugent Jr., A., Bandlish, B.K., 1987. Fluid loss control in well cement slurries. US Patent 4 698 380, assigned to Ethyl Corp., October 06, 1987.

Savoly, A., Villa, J.L., Garvey, C.M., Resnick, A.L., 1987. Fluid loss agents for oil well cementing composition. US Patent 4 674 574, June 23, 1987.

Schilling, S., 1990. Lignin-based cement fluid loss control additive. US Patent 4 926 944, May 22, 1990.

Schilling, P., 1991. Aminated sulfonated or sulfomethylated lignins as cement fluid loss control additives. US Patent 4 990 191, assigned to Westvaco Corp., February 05, 1991.

Sebba, F., 1984. Preparation of biliquid foam compositions. US Patent 4 486 333, December 4, 1984.

Sedillo, L.P., Newlove, J.C., Portnoy, R.C., 1987. Fluid loss control in oil field cements. US Patent 4 659 750, April 21, 1987.

Sifferman, T.R., Swazey, J.M., Skaggs, C.B., Nguyen, N., Solarek, D.B., 1999. Fluid loss control additives and subterranean treatment fluids containing the same. WO Patent 9 905 235, assigned to Monsanto Co. and Natl. Starch Chem. Inv. Corp., February 04, 1999.

Sopko, T.M., Lorentz, R.E., 1991. Method of using polymers of amido-sulfonic acid containing monomers and salts as drilling additive. US Patent 5 039 433, assigned to Lubrizol Corp., August 13, 1991.

Standard test method for fluid loss of clay component of geosynthetic clay liners, 2009. ASTM Standard, Book of Standards, Vol. 04.13 ASTM D5891-02. ASTM International, West Conshohocken, PA.

Stephens, M., 1988. Fluid loss additives for well cementing compositions. GB Patent 2 202 526, September 28, 1988.

Stephens, M., Swanson, B.L., 1992. Drilling mud comprising tetrapolymer consisting of N-vinyl-2-pyrrolidone, acrylamidopropanesulfonic acid, acrylamide, and acrylic acid. US Patent 5 135 909, assigned to Phillips Petroleum Co., August 04, 1992.

Stewart, W.S., Dixon, G.G., Elsen, J.M., Swanson, B.L., 1988. Drilling fluid additives for use in hard brine environments. US Patent 4 743 383, May 10, 1988.

Sullivan, P., Christanti, Y., Couillet, I., Davies, S., Hughes, T., Wilson, A., 2006. Methods for controlling the fluid loss properties of viscoelastic surfactant based fluids. US Patent 7 081 439, assigned to Schlumberger Technology Corporation (Sugar Land, TX), July 25, 2006.

Tan, D., 1990. Test and application of drilling fluid filtrate reducer polysulfonated humic acid resin. Oil Drilling Prod. Technol. 12 (1), 27–32, 97–98.

Todd, B.L., Slabaugh, B.F., Munoz Jr., T., Parker, M.A., 2006. Fluid loss control additives for use in fracturing subterranean formations. US Patent 7 096 947, assigned to Halliburton Energy Services, Inc. (Duncan, OK), August 29, 2006.

Ujma, K. H.W., Plank, J.P., 1987. A new calcium-tolerant polymer helps to improve drilling mud performance and reduce costs. In: Proceedings Volume, 62nd Annu. SPE Tech. Conf. (Dallas, 9/27–30/87), pp. 327–334.

Ujma, K.H., Sahr, M., Plank, J., Schoenlinner, J., 1987. Cost reduction and improvement of drilling mud properties by using polydrill (Kostenreduzierung und Verbesserung der Spülungseigenschaften mit Polydrill). Erdöl Erdgas Kohle 103 (5), 219–222.

Vitthal, S., McGowen, J.M., 1996. Fracturing fluid leakoff under dynamic conditions: Pt.2: Effect of shear rate, permeability, and pressure. In: Proceedings Volume, Annu. SPE Tech. Conf. (Denver, 10/6–9/96), pp. 821–835.

Weaver, J.D., Slabaugh, B.F., Walters, H.G., 2010. Subterranean treatment fluids with improved fluid loss control. US Patent 7 645 725, assigned to Halliburton Energy Services, Inc. (Duncan, OK), January 12, 2010.

Williamson, C.D., 1989. Chemically modified lignin materials and their use in controlling fluid loss. GB Patent 2 210 888, June 21, 1989.

Williamson, C.D., Allenson, S.J., Gabel, R.K., 1991a. Additive and method for temporarily reducing permeability of subterranean formations. US Patent 4 997 581, assigned to Nalco Chemical Co., March 05, 1991.

Williamson, C.D., Allenson, S.J., Gabel, R.K., Huddleston, D.A., 1991b. Enzymatically degradable fluid loss additive. US Patent 5 032 297, assigned to Nalco Chemical Co., July 16, 1991.

Williamson, R., 1987. Well drilling fluids, fluid loss additives therefor and preparation of such additives. GB Patent 2 178 785, February 18, 1987.

Xiang, T., 2007. Drilling fluid systems for reducing circulation losses. US Patent 7 226 895, assigned to Baker Hughes Incorporated (Houston, TX), June 5, 2007.

Xiang, T., 2009. Methods for reducing circulation loss during drilling operations. US Patent 7 507 692, assigned to Baker Hughes Incorporated (Houston, TX), March 24, 2009.

Yin, H., Lin, Y., Huang, J., 2009. Microstructures and rheological dynamics of viscoelastic solutions in a catanionic surfactant system. J. Colloid Interface Sci. 338 (1), 177–183.

Zamora, F., Eoff, L.S., Dalrymple, E.D., Reddy, B.R., 2007. Drilling fluid component. US Patent 7 220 708, assigned to Halliburton Energy Services, Inc. (Duncan, OK), May 22, 2007.

Zhang, C.G., Sun, M.B., Hou, W.G., Sun, D., 1995. Study on function mechanism of filtration reducer: The influence of fluid loss additive on electrical charge density of filter cake fines. Drill. Fluid Completion Fluid 12 (4), 1–5.

Zhang, C.G., Sun, M.B., Hou, W.G., Liu, Y.Y., Sun, D.J., 1996. Study on function mechanism of filtration reducer: Comparison. Drill. Fluid Completion Fluid 13 (3), 11–17.

Zhang, L.S., Wang, Y.Q., Farrar, D., 1990. Polymerisation processes and products. EP Patent 356 242, February 28, 1990.

Zhang, G.P., Ye, H.C., 1998. AM/MA/AMPS terpolymer as non-viscosifying filtrate loss reducer for drilling fulids. Oilfield Chem. 15 (3), 269–271.

TRADENAMES

TABLE 2.15 Tradenames in References

Tradename Description	Supplier
Activator™ I 90% oligosaccharide, 10% magnesium oxide (Growcock and Simon, 2006)	MASI Technologies L.L.C.

TABLE 2.15 Tradenames in References–Cont'd

Tradename Description	Supplier
Airflex® (Series) Vinyl acetate/ethylene copolymer emulsions (Halliday et al., 2007)	Air Products and Chemicals, Inc.
ALL-TEMP® Acrylate tetrapolymer (Jarrett and Clapper, 2010)	Baker Hughes Drilling Fluids
Aquacol-S® Poly(ether glycol) (Halliday et al., 2007)	Baker Hughes
BARACARB® Ground marble (Reddy and Palmer, 2009)	Halliburton Energy Services, Inc.
Barodense® Ground hematite (Reddy and Palmer, 2009)	Halliburton Energy Services, Inc.
Benol® White mineral oil (Crews and Huang, 2010a,b)	Sonneborn Refined Products
BIO-LOSE™ Complexed polysaccharide, filtration control agent (Halliday et al., 2007, 2008; Xiang, 2007)	Baker Hughes
BIO-PAQ™ Water-soluble polymer (Xiang, 2007)	Baker Hughes INTEQ
Blue Streak™ Compostion containing alcohol ether sulfate, cocobetaine, and hydroxypropylguar (surfactant) (Growcock and Simon, 2006)	MASI Technologies L.L.C.
BORE-DRILL™ Anionic polymer (Jarrett and Clapper, 2010)	Borden Chemicals
Britolo® 35 USP High viscosity mineral oil (Huang and Crews, 2009)	Sonneborn Refined Products
BROMA™ FLA Starch (Munoz and Todd, 2008)	TBC Brinadd
Captivates® liquid Fish gelatin and gum acacia encapsulation coating (Crews and Huang, 2010a,b)	ISP Hallcrest

TABLE 2.15 Tradenames in References–Cont'd

Tradename Description	Supplier
Carbo-Gel® Amine modified, gel-forming organophilic clay (Halliday et al., 2007, 2008)	Baker Hughes
Carbo-Mul™ Emulsifier (Halliday et al., 2007, 2008)	Baker Hughes
Carbotec® -S Poly(fatty acids), emulsifier (Halliday et al., 2007)	Baker Hughes
Carbotron™ Cellulose derivative (Morgan et al., 2008)	Dow
Carnation® White mineral oil (Crews and Huang, 2010a,b)	Sonneborn Refined Products
Ceramicrete Magnesium-based ceramic particulate bridging agent (Munoz and Todd, 2008)	Argon National Labs.
CFR™ 3 Cement friction reducer dispersant (Morgan et al., 2008; Reddy and Palmer, 2009)	Halliburton Energy Services, Inc.
CFR™ (Series) Formaldehyde acetone condensate, dispersant (Morgan et al., 2008)	Halliburton Energy Services, Inc.
Chek-Loss® PLUS Ultra-fine lignin (Jarrett and Clapper, 2010; Xiang, 2007)	Baker Hughes
CHEMTROL® X Blend of ground lignitic earth and synthetic maleic anhydride copolymers (Jarrett and Clapper, 2010)	Baker Hughes
Claytone® II Organophilic bentonite (Reddy and Palmer, 2009)	Claytone
ClearFRAC™ Stimulating fluid (Crews, 2006; Crews and Huang, 2010a,b; Huang and Crews, 2009; Huang et al., 2009)	Schlumberger Technology Corp.

TABLE 2.15 Tradenames in References–Cont'd

Tradename Description	Supplier
Corning® 1430 Water dilutable silicone emulsion (Berry et al., 2008)	Dow Corning Corp.
DFE-129™ Acrylamide/AMPS copolymer (Jarrett and Clapper, 2010)	Baker Hughes Drilling Fluids
DFE-243 Partially hydrolyzed polyacrylamide/ trimethylaminoethyl acrylate (Xiang, 2007)	Baker Hughes INTEQ
Diamond FRAQ™ VES breaker (Crews and Huang, 2010a; Huang and Crews, 2009)	Baker Oil Tools
Diamond FRAQ™ VES System (Crews and Huang, 2010a,b; Huang and Crews, 2009)	Baker Oil Tools
Disponil® Ether sulfonates (Emulsifyer) (Guichard et al., 2006, 2007, 2008)	Henkel
DrillAhead® Software (Reddy and Palmer, 2009)	Halliburton Energy Services, Inc.
Driltreat™ Wetting agent (Reddy and Palmer, 2009)	Halliburton Energy Services, Inc.
Driscal® D Water-soluble polymer (Jarrett and Clapper, 2010)	Drilling Specialties Comp.
Elvace (Series) Vinylacetate/ethylene copolymer latex (Halliday et al., 2007)	Reichhold
Escaid® (Series) Mineral oils (Crews and Huang, 2010a,b)	Crompton Corp.
EZ MUL® NT Emulsifier (Reddy and Palmer, 2009)	Halliburton Energy Services, Inc.
FlexPlug® OBM Reactive, nonparticulate lost-circulation materia (Reddy and Palmer, 2009)	Halliburton Energy Services, Inc.
FlexPlug® W Reactive, nonparticulate lost-circulation materia (Reddy and Palmer, 2009)	Halliburton Energy Services, Inc.

TABLE 2.15 Tradenames in References–Cont'd

Tradename Description	Supplier
Flo-Chek® Lost circulation additive (Reddy and Palmer, 2009)	Halliburton Energy Services, Inc.
Germall® II Biocid compostion (Berry et al., 2008)	Sutton Laboratories, Chatham, N.J.
Gloria® High viscosity mineral oil (Huang and Crews, 2009)	Sonneborn Refined Products
Glycacil® L Iodopropynl butyl carbamate (biocide) (Berry et al., 2008)	Lonza Inc.
Go Devil™ II Xanthan gum-based blend, 70% xanthan gum, 20% starch, 9% oligosaccharide, 1% magnesium oxide (Growcock and Simon, 2006)	MASI Technologies L.L.C.
Halad® (Series) Fluid loss control additive (Lewis et al., 2008, 2009; Morgan et al., 2008)	Halliburton Energy Services, Inc.
HR® (Series) Organic acids (cement set retarder) (Morgan et al., 2008)	Halliburton Energy Services, Inc.
Hydrobrite® 200 White mineral oil (Crews and Huang, 2010a,b; Huang and Crews, 2009)	Sonneborn Inc.
HYPERDRILL™ CP-904L Acrylamide copolymer (Xiang, 2007, 2009)	Hychem, Inc.
Invermul® Blends of oxidized tall oil and polyaminated fatty acids (Reddy and Palmer, 2009)	Halliburton Energy Services, Inc.
Isopar® (Series) Isoparaffinic solvent (Crews and Huang, 2010a,b)	Exxon
Isoteq™ Drilling fluid (Halliday et al., 2007)	Baker Hughes
Kathon® CG 5-Chloro-2-methyl4-isothiazolin-3-one (biocide) (Berry et al., 2008)	Rohm & Haas

TABLE 2.15 Tradenames in References–Cont'd

Tradename Description	Supplier
Kaydol® oil Mineral oil (Huang and Crews, 2009)	Witco Corp.
KEM-SEAL® PLUS NaAMPS/*N*,*N*-dimethylacrylamide copolymer (Jarrett and Clapper, 2010)	Baker Hughes Drilling Fluids
Kemseal® Fluid loss additive (Jarrett and Clapper, 2010)	Baker Hughes Norge
Kleemul® Emulsifier (Guichard et al., 2006, 2007, 2008)	BW Group
Kraton® Styrenic block copolymer (Guichard et al., 2006, 2007, 2008)	Shell
Ligco® Lignite (Jarrett and Clapper, 2010)	Baker Hughes
Ligcon® Causticized lignite (Jarrett and Clapper, 2010)	Milchem Inc.
MAX-PLEX® Resin and aluminate (Halliday et al., 2008)	Baker Hughes
MAX-SEAL™ Poly(olefin) hydrocarbon base fluid (Halliday et al., 2007)	Baker Hughes
MAX-TROL® Sulfonated resin (Jarrett and Clapper, 2010)	Baker Hughes Drilling Fluids
Microbond™ Cement expanding additive (Lewis et al., 2008, 2009)	Halliburton Energy Services, Inc.
MicroPolymer™ Multimodal polymer compostion (Weaver et al., 2010)	Halliburton Energy Services, Inc.
Microsponge™ Porous solid substrate (Crews, 2006; Crews and Huang, 2010a,b)	Advanced Polymer Systems
Mil-Bar® Barite weighting agent (Halliday et al., 2007, 2008; Jarrett and Clapper, 2010)	Baker Hughes

TABLE 2.15 Tradenames in References–Cont'd

Tradename Description	Supplier
Mil-Carb® Ground marble (Halliday et al., 2007, 2008; Jarrett and Clapper, 2010; Xiang, 2007, 2009)	Baker Hughes Drilling Fluids
Mil-Gel™ Ground montmorillonite (Jarrett and Clapper, 2010)	Baker Hughes
Mil-Gel-NT® Bentonite quartz mixture (Jarrett and Clapper, 2010)	Baker Hughes
Mil-Pac LV Low viscosity polyamine cellulose (Halliday et al., 2008)	Baker Hughes
Mil-Temp® Maleic anhydride copolymer (Jarrett and Clapper, 2010)	Baker Hughes
Mranol® Imidazoline and imidazoline derivatives (cationic surfactants) (Berry et al., 2008)	Rhone-Poulenc, Inc.
Newdrill Plus Partially hydrolyzed poly(acrylamide) (Halliday et al., 2007)	Baker Hughes
NEW-DRILL® PLUS Partially hydrolyzed poly(acrylamide) (Halliday et al., 2008; Xiang, 2007)	Baker Hughes INTEQ
OMNI-MUL™ Non-ionic emulsifier (Halliday et al., 2007)	Baker Hughes
Performance® 225N Base oil (Huang and Crews, 2009)	ConocoPhillips
Plex® Acrylate resin (Guichard et al., 2006, 2007, 2008)	Rohm & Haas
Plioflex® Styrene butadiene rubber (Guichard et al., 2006, 2007, 2008)	Goodyear Chemicals
Pliolite® DF01 Styrene-butadiene copolymer (Guichard et al., 2006, 2007, 2008)	Goodyear Tire & Rubber Co.

TABLE 2.15 Tradenames in References–Cont'd

Tradename **Description**	**Supplier**
Plioway® EC1 *p*-Methylstyrene copolymer (Magnet et al., 2008)	Goodyear Tire & Rubber Co.
Plioway® Ultra 200 *p*-*tert*-Butylstyrene/*p*-methylstyrene/2-ethylhexylacrylate/isobutyl methacrylate copolymer (Magnet et al., 2008)	Goodyear Tire & Rubber Co.
Polydrill® Anionic polymer (Jarrett and Clapper, 2010)	Degussa AG
Poly-S.RTM Polymer encapsulation coating (Crews, 2006; Crews and Huang, 2010a,b)	Scotts Comp.
Protecto-Magic™ Ground asphalt (Jarrett and Clapper, 2010)	Baker Hughes
PYRO-TROL® Acrylamide/AMPS copolymer (Jarrett and Clapper, 2010)	Baker Hughes
Rev Dust Artificial drill solids (Jarrett and Clapper, 2010)	Milwhite, Inc.
Silicalite® High surface area amorphous silica (Lewis et al., 2008, 2009; Morgan et al., 2008)	Halliburton Energy Services, Inc.
Soltex® Sulfonated asphalt (Jarrett and Clapper, 2010)	Chevron Phillips Chemical Comp.
Span® 20 Sorbitan monolaurate (Crews and Huang, 2010a)	Uniqema
Span® 40 Sorbitan monopalmitate (Crews and Huang, 2010a)	Uniqema
Span® 61 Sorbitan monostearate (Crews and Huang, 2010a)	Uniqema
Span® 65 Sorbitan tristearate (Crews and Huang, 2010a)	Uniqema
Span® 80 Sorbitan monooleate (Crews and Huang, 2010a)	Uniqema

TABLE 2.15 Tradenames in References–Cont'd

Tradename Description	Supplier
Span® 85 Sorbitan trioleate (Crews and Huang, 2010a)	Uniqema
SULFA-TROL® Sulfonated asphalt (Jarrett and Clapper, 2010)	Baker Hughes Drilling Fluids
Superfloc™ Acrylamide copolymer (Xiang, 2007, 2009)	Cytec Industries, Inc.
SurFRAQ™ VES Tallow amido propylamine oxide (Huang and Crews, 2009; Huang et al., 2009)	Baker Oil Tools
Synthemul® (Series) Carboxylated acrylic copolymer (Halliday et al., 2007)	Reichold
Teflon® Tetrafluoro polymer (Weaver et al., 2010)	DuPont
Tergitol® 15-S (Series) Ethoxylated C11-15-secondary alcohols, surfactant (Sebba, 1984)	Union Carbide Corp.
Tween® 20 Sorbitan monolaurate (Crews and Huang, 2010a)	Uniqema
Tween® 21 Sorbitan monolaurate (Crews and Huang, 2010a)	Uniqema
Tween® 40 Sorbitan monopalmitate (Crews and Huang, 2010a)	Uniqema
Tween® 60 Sorbitan monostearate (Crews and Huang, 2010a)	Uniqema
Tween® 61 Sorbitan monostearate (Crews and Huang, 2010a)	Uniqema
Tween® 65 Sorbitan tristearate (Crews and Huang, 2010a)	Uniqema
Tween® 81 Sorbitan monooleate (Crews and Huang, 2010a)	Uniqema

TABLE 2.15 Tradenames in References–Cont'd

Tradename Description	Supplier
Tween® 85 Sorbitan monooleate (Crews and Huang, 2010a)	Uniqema
Tychem® 68710 Carboxylated styrene/butadiene copolymer (Reddy and Palmer, 2009)	Reichhold
Tylac® CPS 812 Carboxylated styrene/butadiene copolymer (Reddy and Palmer, 2009)	Reichhold
VES-STA 1 Gel stabilizer (Crews and Huang, 2010a,b)	Baker Oil Tools
WG-3L VES-AROMOX® APA-T Viscoelastic surfactant (Crews and Huang, 2010b)	Akzo Nobel
XAN-PLEX™ D Polysaccharide viscosifying polymer (Halliday et al., 2007, 2008; Xiang, 2007)	Baker Hughes INTEQ
XANVIS™ Polysaccharide viscosifying polymer (Xiang, 2007, 2009)	Baker Hughes INTEQ

Chapter 3

Clay Stabilization

Problems caused by shales in petroleum activities are not new. At the beginning of the 1950s, many soil mechanics experts were interested in the swelling of clays, which are important for maintaining wellbore stability during drilling, especially in water-sensitive shale and clay formations.

The rocks within these types of formations absorb the fluid used in drilling, which causes them and may lead to a wellbore collapse. The swelling of clays and the problems that may so arise have been reviewed in the literature (Durand et al., 1995a,b; Van Oort, 1997; Zhou et al., 1995). Various additives for clay stabilization are shown in Table 3.1.

PROPERTIES OF CLAYS

Clay minerals are generally crystalline in nature, and the structure of these crystals determines their properties. Typically, clays have a flaky, mica-type structure, with the flakes being made up of a number of crystal platelets stacked face to face. Each platelet is called a unit layer, and the surfaces of the unit layer are called basal surfaces. A unit layer is composed of multiple sheets. One sheet type is called the octahedral sheet. It is composed of either aluminum or magnesium atoms, octahedrally coordinated with the oxygen atoms of hydroxyl groups. Another sheet type is called the tetrahedral sheet, which consists of silicon atoms tetrahedrally coordinated with oxygen atoms. Sheets within a unit layer link together by sharing oxygen atoms.

When this linking occurs between one octahedral and one tetrahedral sheet, one basal surface contains exposed oxygen atoms, while the other has exposed hydroxyl groups. It is also quite common for two tetrahedral sheets to bond with one octahedral sheet by sharing oxygen atoms. The resulting structure, known as the Hoffmann structure, has an octahedral sheet that is sandwiched between the two tetrahedral sheets (Hoffmann and Lipscomb, 1962). As a result, both basal surfaces in a Hoffmann structure contain exposed oxygen atoms.

The unit layers stack together face-to-face and are held in place by weak attractive forces. The distance between corresponding planes in adjacent unit

Petroleum Engineer's Guide to Oil Field Chemicals and Fluids. DOI: 10.1016/B978-0-12-383844-5.00003-9

TABLE 3.1 Clay Stabilizers

Additive	References
Polymer latices	Stowe et al. (2002)
Partially hydrolyzed polyvinylacetate[a]	Kubena Jr., et al. (1993)
Polyacrylamide[b]	Zaitoun and Berton (1990), Zaltoun and Berton (1992)
Copolymer of anionic and cationic monomers: Acrylic acid (AA), methacrylic acid, 2-acrylamido-2-methyl-1-propane sulfonic acid, dimethyl diallyl ammonium chloride	Aviles-Alcantara et al. (2000), Smith and Thomas (1995a,b, 1997)
Nitrogen[c]	Sloat (1989, 1991)
Partially hydrolyzed acrylamide-acrylate copolymer, potassium chloride, and polyanionic cellulose (PAC)	Halliday and Thielen (1987)
Aluminum/guanidine complexes with cationic starches and polyalkylene glycols[MA]	Branch (1988)
Hydroxyaldehydes or hydroxyketones	Westerkamp et al. (1991)
Polyols and alkaline salt	Hale and van Oort (1997)
Tetramethylammonium chloride and methyl chloride quaternary salt of polyethyleneimine[SF]	Aften and Gabel (1992a,b, 1994)
Pyruvic aldehyde and a triamine	Crawshaw et al. (2002)
Quaternary ammonium compounds	
In situ crosslinking of epoxide resins	Coveney et al. (1999a,b)
Oligomer (methyl quaternary amine containing 3–6 moles of epihalohydrin)	Himes and Vinson (1989)
Quaternary ammonium carboxylates[BD, LT]	Himes (1992)
Quaternized trihydroxyalkyl amine[LT]	Patel and McLaurine (1993)
Polyvinyl alcohol, potassium silicate, and potassium carbonate	Alford (1991)
Copolymer of styrene and substituted maleic anhydride (MA)	Smith and Balson (2000)
Potassium salt of carboxymethyl cellulose	Palumbo et al. (1989)

TABLE 3.1 Clay Stabilizers–Cont'd

Additive	References
Water-soluble polymers with sulfosuccinate derivative-based surfactants, zwitterionic surfactants[BD, LT]	Alonso-Debolt and Jarrett (1994, 1995)

BD) Biodegradable
LT) Low toxicity
SF) Well stimulation fluid
a) 75% Hydrolyzed, 50 k Dalton
b) Shear-degraded, for montmorillonite clay dispersed in sand packs
c) Injection of unreactive gas

layers is called the c-spacing. A clay crystal structure with a unit layer consisting of three sheets typically has a c-spacing of about 9.5×10^{-7} mm.

In clay mineral crystals, atoms having different valences will be commonly positioned within the sheets of the structure to create a negative potential at the crystal surface. In that case, a cation will be adsorbed onto the surface. These adsorbed cations are called exchangeable cations, because they may chemically trade places with other cations when the clay crystal is suspended in water. In addition, ions may also be adsorbed on the clay crystal edges and exchange with other ions in the water (Patel et al., 2007).

The type of substitutions occurring within the clay crystal structure and the exchangeable cations adsorbed on the crystal surface greatly affect clay swelling, a property of primary importance in the drilling fluid industry. In this phenomenon, water molecules surround a clay crystal structure and position themselves in such a way as to increase the structure's c-spacing, thus resulting in an increase in its volume.

Swelling of Clays

Two types of swelling may occur in clays (Patel et al., 2007). Surface hydration is one type, where water molecules are adsorbed on crystal surfaces. Hydrogen bonding holds a layer of water molecules to the oxygen atoms, which are exposed on the crystal surfaces. Subsequent layers of water molecules align to form a quasi-crystalline structure between unit layers, which results in an increased c-spacing. All types of clays swell in this manner.

Osmotic swelling is a second type of swelling. Where the concentration of cations between unit layers in a clay mineral is higher than that in the surrounding water, water is osmotically drawn between the unit layers and the c-spacing is increased. Osmotic swelling results in larger overall volume increases than surface hydration, but only a few clays, like sodium montmorillonite, swell in this manner (Patel et al., 2007).

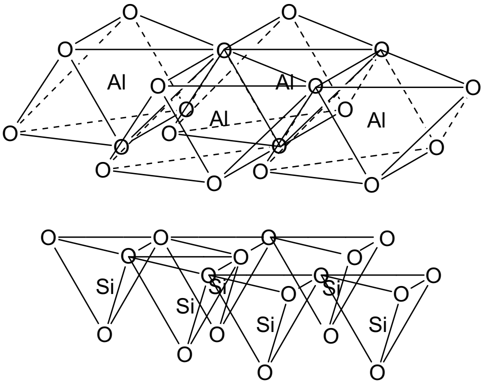


FIGURE 3.1 Octahedral and tetrahedral layers in clays (Murray, 2007, p. 9).

Clays are naturally occurring layered minerals formed by weathering and decomposition of igneous rocks. Details of clay mineralogy can be found in the literature (Grim, 1968; Murray, 2007). Each layer is comprised of fused sheets of octahedra of Al^{3+}, Mg^{2+}, or Fe^{3+} oxides and sheets of tetrahedra of Si^{4+} oxides (Auerbach, 2007). If a clay mineral contains one tetrahedral and one octahedral sheet, it is known as a 1:1 clay, and if it contains two tetrahedral sheets sandwiching one central octahedral sheet, it is called a 2:1 clay. Octahedral and tetrahedral layers are illustrated in Figure 3.1.

The metal atoms in the clay lattice can be substituted with others, which results in an overall negative charge on individual clay layers. This charge is compensated for by cations located in the interlayer region, which can be freely exchanged. The cation exchange capacity of the mineral depends on crystal size, pH, and the type of the cation its involved. These may not only be small ions, but poly-cations (Blachier et al., 2009) also.

Studies on the adsorption of a polycationic quaternary amine polymer onto clays have been presented. In charge scale, it can be observed that both the adsorption curve of the quaternary amine polymer and that corresponding to the released sodium are superimposed, as shown in Figure 3.2. The replacement of the counter ions by the amine polymer almost follows a 1:1 relationship at low polymer concentrations. Further, the silicate surfaces of the tetrahedral sheets of clay minerals are comparatively hydrophobic. This property may allow the intercalation of neutral organic compounds including polymers.

Smectite clays are of the type 2:1 and frequently occur in drilling situations (Anderson et al., 2010). Sodium-saturated smectite swells macroscopically, which causes in instability of shales during drilling operations. In the worst case, the wellbore may collapse as a result of clay swelling.

The type of exchangeable cations found in clay minerals is reported to have a significant impact on the amount of swelling that takes place. They compete

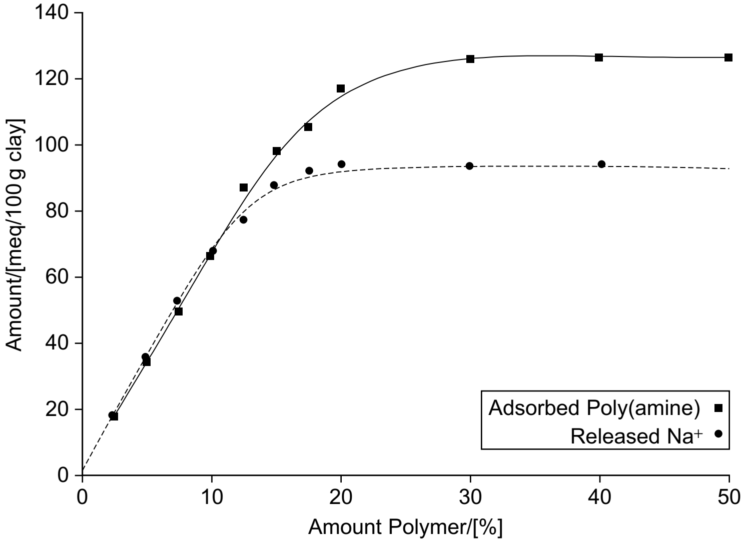


FIGURE 3.2 Exchange of sodium cations against polyamine cations (Blachier et al., 2009).

with water molecules for the available reactive sites in the clay structure. Generally, cations with high valences are more strongly adsorbed than ones with low valences. Thus, clays with low valence exchangeable cations will swell more than those with high valences.

Water-based drilling fluids are generally considered to be more environmentally acceptable than oil-based or synthetic-based fluids. However, the former type of drilling fluid facilitates clay hydration and swelling, which can lead to significantly increased oil well construction costs (Anderson et al., 2010). For this reason, minimizing clay swelling is an important field of research. In order to reduce the extent of clay swelling effectively, its mechanism needs to be understood, so that efficient swelling inhibitors may be developed. Suitable clay swelling inhibitors must significantly reduce the hydration of the clay, and must also meet increasingly stringent environmental guidelines.

It is known that swelling takes place in a discrete fashion, in a stepwise formation of integer-layer hydrates. The transitions of the distances of the layers are thermodynamically analogous to phase transitions. Electro-osmotic swelling can occur only in clay minerals that contain exchangeable cations in the interlayer region. This type of swelling may yield significantly greater expansion than crystalline swelling.

Sodium-saturated smectites have a strong tendency to electro-osmotic swelling, but potassium-saturated smectites do not swell in this way. Thus, an appropriate ion exchange reaction may be helpful in clay stabilization (Anderson et al., 2010).

The water desorption isotherms of montmorillonite intercalated with exchangeable cations of the alkali metal group have show that for larger cations, less water is adsorbed (Mooney et al., 1952), and there is a relationship between the tendency to swell and the energy of hydration of the cation (Norrish, 1954).

Clay swelling during the drilling of a subterranean well can have a tremendous adverse impact on drilling operations. The overall increase in bulk volume impedes the removal of cuttings from beneath the drill bit, increases friction between the drill string and the sides of the borehole, and inhibits formation of the thin filter cake that seals formations. Clay swelling can also create other drilling problems, such as loss of circulation or cause pipes to stick (Patel et al., 2001).

In the North Sea and the United States Gulf Coast, drillers commonly encounter argillaceous sediments in which the predominant clay mineral is sodium montmorillonite, commonly called gumbo clay, in which sodium cations are predominately the exchangeable cations. Because the sodium cation has a low positive valence, (i.e., a $+1$ valence), it easily disperses into water. Consequently, gumbo clay is notorious for its swelling. Given the frequency in which this material is encountered in subterranean wells, the development of a substance and method for reducing clay swelling is of primary importance (Klein and Godinich, 2006).

Montmorillonite

Montmorillonite clays, for example, bentonite and kaolinite clays, are suitable for preparing a solids-stabilized oil-in-water emulsion. Bentonite clay can be easily exfoliated (Bragg and Varadaraj, 2006). As mined, bentonite clays naturally consist of aggregates of particles that can be dispersed in water, or broken up by shearing into units with an average particle size of 2 μ or less. However, each of these particles is a laminated unit containing approximately 100 layers of fundamental silicate layers of 1 nm thickness bonded together by inclusions of atoms such as calcium in the layers.

By exchanging calcium with sodium or lithium, which are larger and have a strong attraction for water molecules in fresh water, and then exposing the bentonite to fresh water, it can be broken into individual 1 nm thick layers, called fundamental particles. The result of this delamination process is a gel consisting of a finely divided bentonite clay (Bragg and Varadaraj, 2006).

Guidelines

The literature offers several papers that may serve as guidelines for issues such as selecting a proper clay stabilizing system or completing wellbore stability analysis of practical well designs (Chen et al., 1996; Crowe, 1990, 1991; Evans and Ali, 1997; Scheuerman and Bergersen, 1989).

MECHANISMS CAUSING INSTABILITY

Shale stability is an important problem faced during drilling and is most often attributed to the swelling of shales. It has been shown that several mechanisms can be involved (Gazaniol et al., 1994, 1995): pore pressure diffusion, plasticity, anisotropy, capillary effects, osmosis, and physicochemical alterations. Most importantly, three processes that contribute to the instability of shales must be considered (Bailey et al., 1994):

1. Movement of fluid between the wellbore and shale (limited to flow from the wellbore into the shale),
2. Changes in stress (and strain) that occur during shale-filtrate interaction, and
3. Softening and erosion caused by invasion of mud filtrate and consequent chemical changes in the shale.

The major reason for these effects is due to the hydration of clays. Borehole instabilities have been observed even with the most inhibitive fluids, that is oil-based drilling mud, which demonstrates that mechanical aspects are also important. In fact, the coupling of both chemical and mechanical mechanisms has to be considered. For this reason, it is still difficult to predict the behavior of rock at medium-to-large depth under certain loading conditions.

The stability of shales is governed by a complex relationship between transport processes (e.g., hydraulic flow, osmosis, diffusion of ions, pressure) and chemical changes (e.g., ion exchange, alteration of water content, swelling pressure).

They have the ability to absorb water, thus causing the instability of wells either because of the swelling of some mineral species or because the supporting pressure is suppressed by modification of the pore pressure. The response of a shale to a water-based fluid depends on its initial water activity and on the composition of the fluid.

The behavior of shales can be classified into either deformation mechanisms or transport mechanisms (Tshibangu et al., 1996). Optimization of mud salinity, density, and filter cake properties is important in achieving optimal shale stability and drilling efficiency with water-based drilling mud (WBM).

Kinetics of the Swelling of Clays

Basic studies on the kinetics of swelling have been performed (Suratman, 1985). Pure clays (montmorillonite, illite, and kaolinite) with polymeric inhibitors were investigated, and phenomenologic kinetic laws were established.

Hydrational Stress

Stresses caused by chemical forces, such as hydration stress, can have a considerable influence on the stability of a wellbore (Chen et al., 1995). When the total pressure and the chemical potential of water increase, water is absorbed into the clay platelets. This results either in the platelets moving farther apart (swelling) if they are free to move, or the generation of hydrational stress if the swelling is constrained (Tan et al., 1997). Hydrational stress results in an increase in pore pressure and a subsequent reduction in effective mud support, which leads to a less stable wellbore condition.

Borehole Stability Model

A borehole stability model has been developed that takes into account both the mechanical and chemical aspects of the interactions between drilling fluid and shale (Mody and Hale, 1993). Chemically induced stress alteration, based on the thermodynamics of differences in water molar free energies of the drilling fluid and shale is combined with mechanically induced stress. Based on this model, it should be possible to obtain the optimal mud weight and salt concentration for drilling fluids.

Further stability models based on surface area, equilibrium water-content–pressure relationships, and electric double-layer theory can successfully characterize borehole stability problems (Wilcox, 1990). The application of surface area, swelling pressure, and water requirements of solids can be integrated into these models, and mud process control approaches can be derived, which improve the design of WBM in active or older shales.

Shale Inhibition with Water-based Muds

One potential mechanism by which polymers may stabilize shales is by reducing the rate of water invasion into the shale. This is not the only mechanism involved in shale stabilization (Ballard et al., 1993); there is also an effect of the polymer additive.

Inhibiting Reactive Argillaceous Formations

Argillaceous formations are very reactive in the presence of water. Such formations can be stabilized by bringing them in contact with a polymer solution that contains hydrophilic and hydrophobic links (Audibert et al., 1997). The hydrophilic portion consists of polyoxyethylene, with hydrophobic end groups based on isocyanates. The polymer is capable of inhibiting the swelling or dispersion of argillaceous rock because of its adsorptive and hydrophobic capacities.

Thermal Treatment to Increase the Permeability

To increase the permeability of a certain region of the reservoir, the liquid-absorbed water is evaporated by heating the portion to above the boiling point of water, taking into account the ambient pressure (Jamaluddin and Nazarko, 1994;

Reed, 1993). The liquid water is evaporated by injecting a water-undersaturated gas, such as heated nitrogen, into the reservoir.

Formation Damage by Fluids

Formation damage due to invasion by drilling fluids is a well-known problem in drilling. This is caused by the differential pressure between the hydrostatic column and the formation pressure, especially in low-pressure or depleted zones (Whitfill et al., 2005).

Invasion is also caused by openings in the rock, and the ability of fluids. When drilling depletes sands under overbalanced conditions, the mud will penetrate progressively into the formation unless there is an effective flow barrier present at the wellbore wall.

Horizontal drilling may also drill across highly fractured or permeable, low-pressure or depleted zones, which increases the probability of the drill pipe getting stuck due to it lying on the low side of the borehole. The exposure of numerous fractures or openings with low formation pressures will increase the problems of lost circulation and formation invasion (Whitfill et al., 2005).

Formation Damage in Gas Production Shut-in

Sometimes it may become necessary to shut-in a gas well when the demand for gas is low. In such instances, the well is shut-in for an indefinite period, after which it is reopened and production is resumed. It has often been found that the production rate of gas from the reopened well is substantially less than before the shut-in.

During production, the inner wall of the production tubing will be coated with a film of condensed fresh water because of the geothermal gradient. This water flows down when production is interrupted, and can cause formation damage, because clays are normally saturated with brine and not with fresh water. This swelling can be prevented with the injection of some additive, for example, sodium chloride, potassium chloride, calcium chloride, or an alcohol or a similar organic material (Wilson and Miller, 2001).

SWELLING INHIBITORS

Inhibitors of swelling act by a chemical mechanism, rather than in a mechanical manner. They change the ionic strength and the transport behavior of the fluids into the clays. Both the cations and the anions are important for the efficiency of the inhibition of swelling of clays (Doleschall et al., 1987).

Salts

Swelling can be inhibited by the addition of KCl in relatively high amounts. Other swelling inhibitors are both uncharged polymers and polyelectrolytes (Anderson et al., 2010).

Quaternary Ammonium Salts

Choline salts are effective anti-swelling drilling fluid additives for underbalanced drilling operations (Kippie and Gatlin, 2009). Choline is a quaternary ammonium salt containing the *N*,*N*,*N*-trimethylethanolammonium cation, often present as the chloride.

Preparation 3–1: Triethanol amine methyl chloride can be prepared by adding methyl chloride in excess to triethanol amine in aqueous solution and heating for several hours. Upon completion of the reaction, the excess of methyl chloride is evaporated.

Choline formate is prepared from an aqueous solution of choline hydroxide by the reaction with formic acid simply by stirring. ■

Argillaceous formations contain clay particles. If a water-based drilling fluid is used in such formations, ion exchange, hydration, etc., will take place. These reactions cause swelling, crumbling, or dispersion of the clay particles. Ultimately, washout and even complete collapse of the borehole may occur (Eoff et al., 2006). Certain quaternized polymer additives may prevent these unfavorable reactions.

Such polymers have been shown in laboratory testing to vastly reduce shale erosion. Quaternized polymers can be synthesized by Eoff et al. (2006):

1. Quaternization of an AA based amine derivative with an alkyl halide, and subsequent polymerization, or
2. First polymerization and afterwards quaternization of the polymeric moieties.

Preparation 3–2: A quaternized monomer can be prepared by mixing dimethyl amino ethyl methacrylate with hexadecyl bromide. The mixture is heated to 43°C and stirred for 24 h. Then, the mixture is poured into petroleum ether, whereby the quaternized monomer precipitates (Eoff et al., 2006). The reaction is shown in Figure 3.3. ■

A copolymer can be prepared using the quaternized monomer described above and dimethyl amino ethyl methacrylate. The aqueous solution is neutralized with sulfuric acid and radically polymerized with 2,2′-azobis (2-amidinopropane) dihydrochloride, c.f., Figure 3.4. This initiator is water soluble. The polymerization is carried out at 43°C for 18 h (Eoff et al., 2006).

The quaternization of a polymer from dimethyl amino ethyl methacrylate has been described. To an aqueous solution of a homopolymer from dimethyl amino ethyl methacrylate sodium hydrochloride is added to adjust the pH to 8.9. Then again some water is added and hexadecyl bromide as alkylation agent, further benzylcetyldimethyl ammonium bromide as emulsifier. This mixture is then heated, with stirring, to 60°C for 24 h (Eoff et al., 2006).

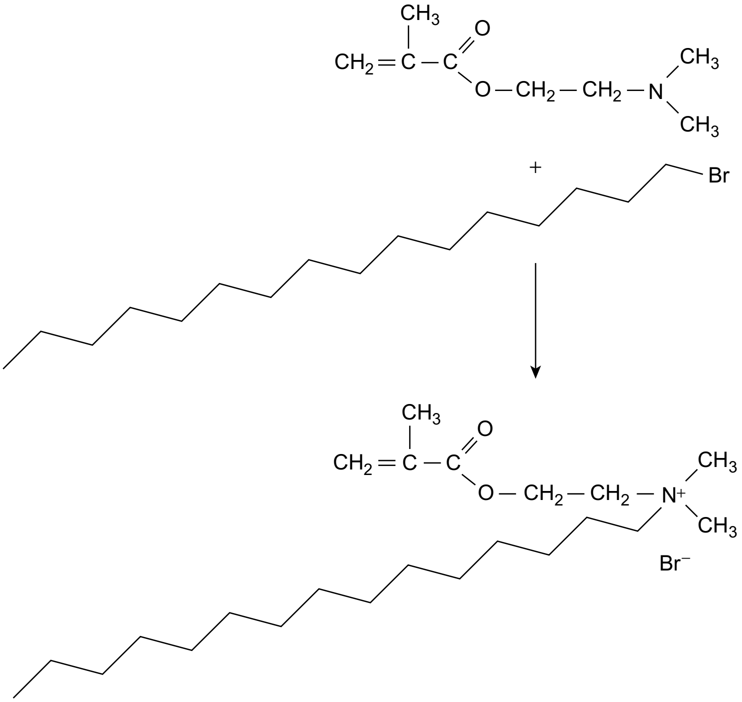
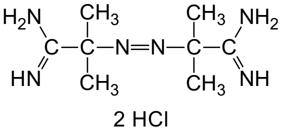


FIGURE 3.3 Quaternization reaction of dimethyl amino ethyl methacrylate with hexadecyl bromide.



2,2′-Azobis (2-amidinopropane) dihydrochloride

FIGURE 3.4 Water-soluble radical initiator.

Potassium Formate

Clay is stabilized in drilling and treatment operations by adding potassium formate to the drilling fluid along with a cationic formation control additive. Potassium formate can be generated in situ from potassium hydroxide and formic acid. The cationic additive is basically a polymer containing quaternized amine units, e.g., polymers of dimethyl diallyl ammonium chloride or acrylamide (Smith, 2009).

In the clay pack flow test, where the higher volumes at a given time indicate better clay stability, the addition of a small amount of potassium formate increases the volume throughput for a given polymer concentration.

For example, 0.1% polydimethyl diallyl ammonium chloride added to the formulation had a volume at 10 min of 112 ml.

The same polymer, when combined with potassium formate and treated at 0.05% of the polymer, i.e., half the original polymer concentration, had a volume of 146 ml, indicating better clay stability and a possible synergistic effect from the addition of the potassium formate (Smith, 2009).

Saccharide Derivatives

The reaction product of methyl glucoside and alkylene oxides such as ethylene oxide (EO), propylene oxide (PO), or 1,2-butylene oxide is a drilling fluid additive that acts as a clay stabilizer. It is soluble in water at ambient conditions, but becomes insoluble at elevated temperatures (Clapper and Watson, 1996). Because of this insolubility, these compounds concentrate at important surfaces, such as the drill bit cutting surface, the borehole surface, and the surfaces of the drilled cuttings.

Sulfonated Asphalt

Asphalt is a solid, black-brown to black, bitumen fraction, which softens when heated and re-hardens upon cooling. It is not water soluble and difficult to disperse or emulsify in water.

Sulfonated asphalt can be obtained by reacting asphalt with sulfuric acid and sulfur trioxide. By neutralization with alkaline hydroxides, such as NaOH or NH_3, sulfonate salts are formed. Only a limited portion of the sulfonated product can be extracted with hot water, but the fraction thus obtained, which is water soluble, is crucial for quality.

Sulfonated asphalt is predominantly used in water-based drilling fluids but also for those based on oil (Huber et al., 2009). It is reduced filtrate loss, improved filter cake properties, good lubrication of the drill and decreased formation damage (Huber et al., 2009).

The mechanism of action of sulfonated asphalt as a clay inhibitor in a drilling fluid is due to the electronegative sulfonated macromolecules attaching to the electropositive ends of the clay platelets. This creates a neutral barrier, which suppresses the absorption of water into the clay.

In addition, because the sulfonated asphalt is partially lipophilic, and therefore water repellent, the water influx into the clay is restricted by purely physical means. As mentioned already, the solubility in water of the sulfonated asphalt is crucial for proper application. By the introduction of a water-soluble and an anionic polymer component, the proportion of water-insoluble asphalt can be markedly reduced.

In other words, the proportion of the water-soluble fraction is increased by introducing the polymer component. Especially suitable are lignosulfonates as well as sulfonated phenol, ketone, naphthalene, acetone, and amino plasticizing resins (Huber et al., 2009).

Grafted Copolymers

The clay stabilization of copolymers of styrene and MA grafted with polyethylene glycol (PEG) has been investigated (Smith and Balson, 2004).

The amounts of shale recovery from bottle rolling tests have been used to measure the shale inhibition properties. The tests were done using Oxford Clay cuttings, a water-sensitive shale, sieved to 2–4 mm. Swelling was performed in 7.6% aqueous KCl.

The grafted copolymer used is an alternating copolymer of styrene and MA. It is grafted with polyethylene glycol (PEG) of varying molecular weights. The amount of shale recovery with various PEG types is shown in Table 3.2.

It seems that there is an optimum, with respect to the molecular weight of the grafted PEG. Further, the results in the lower part of Table 3.2 indicate that increasing the amount of styrene in the backbone increases the amount of shale that is recovered.

Polyoxyalkylene Amines

One method for reducing clay swelling is to use salts in drilling fluids. Salts generally reduce the swelling of clays, but they flocculate the clays resulting in both high fluid losses and an almost complete loss of thixotropy. Further, increasing the salinity often decreases the functional characteristics of drilling fluid additives (Patel et al., 2007).

Another method for controlling clay swelling is to use organic shale inhibitor compounds. It is believed that they are adsorbed onto the surfaces of clays where they compete with water molecules for clay reactive sites and thus serve to reduce clay swelling.

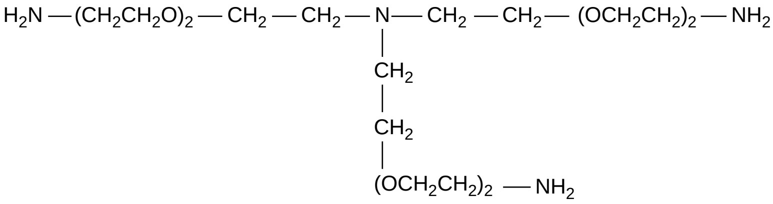
Polyoxyalkylene amines are a class of compound that contains primary amino groups attached to a polyether backbone. They are also known as polyether amines. They are available in a variety of molecular weights, ranging up to 5 kDalton.

They are synthesized by the ring opening polymerization of oxirane compounds in the presence of amino compounds. Such compounds were made by reacting Jeffamine® with 2 equivalents of EO. Alternatively, PO is reacted with an oxyalkyldiamine (Patel et al., 2007). The polyether backbone is based either on EO, or PO, or a mixture of these oxirane compounds (Patel et al., 2007).

TABLE 3.2 Amount of Shale Recovery (Smith and Balson, 2004)

Sample	KCl/[%]	Shale Recovery/[%]
KCl only	7.6	25
PEG	7.6	38
SMAC MPEG 200	7.6	54
SMAC MPEG 300	7.6	87
SMAC MPEG 400	7.6	85
SMAC MPEG 500	7.6	72
SMAC MPEG 600	7.6	69
SMAC MPEG 750	7.6	70
SMAC MPEG 1100	7.6	66
SMAC MPEG 1500	7.6	49
KCl only	12.9	27
PEG	12.9	53
SMAC MPEG 500	12.9	85
SMAC 2:1 MPEG 500	12.9	95

SMAC	*Styrene and MA copolymer*
SMAC 2:1	*Styrene and MA copolymer, 2 styrene units for every MA*
MPEG	*Polyethylene glycol monomethyl ethers, the number refers to the molecular weight*



$$H_2N-(CH_2CH_2O)_2-CH_2-CH_2-\underset{\displaystyle \underset{\displaystyle \underset{\displaystyle (OCH_2CH_2)_2-NH_2}{|}}{\underset{\displaystyle CH_2}{|}}}{\underset{\displaystyle CH_2}{\underset{|}{N}}}-CH_2-CH_2-(OCH_2CH_2)_2-NH_2$$

FIGURE 3.5 Polyether amine (Klein and Godinich, 2006).

A typical polyether amine is shown in Figure 3.5. Such products belong to the Jeffamine® product family. A related shale hydration inhibition agent is based on an *N*-alkylated 2,2′-diaminoethylether.

Anionic Polymers

Anionic polymers may act by the long chain with negative ions attaching to the positive sites on the clay particles, or to the hydrated clay surface through hydrogen bonding (Halliday and Thielen, 1987). Surface hydration is reduced as the polymer coats the surface of the clay.

The protective coating also seals, or restricts the surface fractures or pores, thereby reducing or preventing the capillary movement of filtrate into the shale. This stabilizing process is supplemented by PAC. Potassium chloride enhances the rate of polymer absorption onto the clay.

Amine Salts of Maleic Imide

Compositions containing amine salts of the imides of MA polymers are useful for clay stabilization. These types of salts are formed by the reaction of MA with a diamine such as dimethyl aminopropylamine, in ethylene glycol (EG) solution (Poelker et al., 2009). The primary nitrogen dimethyl aminopropylamine forms the imide bond.

In addition, it may add to the double bond of MA. Further, the EG may add to the double bond, but also may condense with the anhydride itself. On repetition of these reactions, oligomeric compounds may be formed. The elementary reactions are shown in Figure 3.6. Finally, the product is neutralized with acetic acid or methanesulfonic acid to a pH of 4.

The performance of this compound was tested in Bandera sandstone, where it was found that the material neutralized with methanesulfonic acid performed somewhat less well then that neutralized with acetic acid. The compositions are particularly suitable for water-based hydraulic fracturing fluids.

Comparative Study

Three different clay inhibitors, a Performatrol® drilling fluid, a Claygrabber® shale stabilizer, and a Clay Sync™ shale stabilizer were compared to 4% glycol, a standard clay inhibitor, for their ability to inhibit the uptake of water by shale cuttings (Valenziano et al., 2009).

Clay Sync is a lowmolecular-weight, non-ionic polyacrylamide (PAM); Claygrabber Clay Sync is a highmolecular-weight, non-ionic PAM; and Performatrol® is poly*N*-vinyl-2-pyrrolidone, a water-soluble polymer. All of these compounds are commercially available from Baroid Fluid Services.

For each clay inhibitor, two types of shale cuttings were used. Each cutting was then placed in a 350 ml solution containing water and the indicated clay inhibitor for 4 h at 27°C. 0.5% Claygrabber®, 2 pounds per barrel Clay Sync,

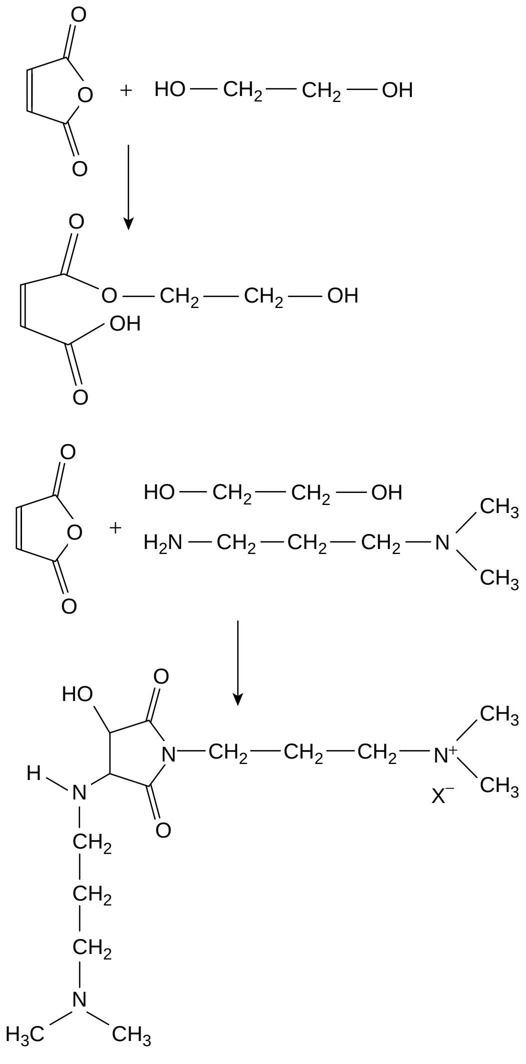


FIGURE 3.6 Start of condensation with ethylene glycol (top) and formation of amine salts of imides (bottom) (Poelker et al., 2009).

and 14 pounds per barrel Performatrol were used. The swelling S in Eq. 3.1 is the relative increase of the volume before V_b and after treatment V_a.

$$S = 100\frac{V_a - V_b}{V_b} \tag{3.1}$$

A summary of the results is shown in Table 3.3.

TABLE 3.3 Swelling Data (Valenziano et al., 2009)

Clay Inhibitor	Cutting	Swelling/[% v/v]
Pure water		
PERFORMATROL drilling fluid	1	48.3
PERFORMATROL drilling fluid	2	95.5
CLAYGRABBER shale stabilizer	1	60.6
CLAYGRABBER shale stabilizer	2	
CLAY SYNC shale stabilizer	1	85.0
CLAY SYNC shale stabilizer	2	72.7
4% Glycol	1	52.4
Water + 5% KCl		
PERFORMATROL drilling fluid	1	33.3
PERFORMATROL drilling fluid	2	13.3
CLAYGRABBER shale stabilizer	1	39.3
CLAYGRABBER shale stabilizer	2	18.8
CLAY SYNC shale stabilizer	1	30.0
CLAY SYNC shale stabilizer	2	18.5
4% Glycol	1	35.0
4% Glycol	2	26.5
Water + 37% NaCl		
PERFORMATROL drilling fluid	1	9.5
PERFORMATROL drilling fluid	2	20.0
CLAYGRABBER shale stabilizer	1	16.7
CLAYGRABBER shale stabilizer	2	17.9
CLAY SYNC shale stabilizer	1	13.3
CLAY SYNC shale stabilizer	2	13.3
4% Glycol	1	0.0
4% Glycol	2	6.8

This demonstrates that the addition of either KCl or NaCl to solutions of clay inhibitors improves their ability to reduce the absorption of aqueous fluid by shale (Valenziano et al., 2009).

TEST METHODS

Shale Erosion Test

A shale erosion test is commonly employed to determine the ability of a drilling fluid plus additives to prevent a shale from eroding in the presence of an aqueous medium such as a drilling fluid (Eoff et al., 2006).

Such erosion, when encountered in actual field conditions in a borehole, and as noted above, can lead to problems ranging from a washout to a complete collapse of the borehole. Various shale erosion tests have been developed based on (Eoff et al., 2006; Reed, 1977):

- Time of total disintegration of the particles, and
- The change of particle size during rolling.

Disintegration of Particles

A shale erosion test has been developed that consists of compressing a known unstable oil field shale into a 0.5 in. diameter by 1 in. The cylinder is then placed into a capped round pint jar, which is two-thirds filled with the test fluid.

This jar is put onto motor driven rollers, which cause the shale cylinder to smoothly roll through the test fluid on the side of the jar. The time taken for the shale pellets to totally disintegrate is recorded (Reed, 1977).

Change of Mesh Size

A typical shale erosion test is conducted by rolling a weighed portion of sized shale particles in an aqueous medium, and then screening the particles to determine the amount of shale that eroded to the point of passing through a selected sized screen.

The shale is crushed and ground into particles that can pass through a 6 mesh screen but are retained on a 14 mesh screen. Thus, particles of a mesh size from 6 to 14 are used for the erosion test.

Portions of 40 g of the shale are placed in a laboratory barrel containing 350 ml of the test fluid and rolled for 16 hrs at the desired temperature, 65°C.

Afterwards, the drilling fluids are again screened through the 14 mesh screen. The retained solids are washed, dried, and weighed. Finally, the percent of erosion is calculated on the basis of the weight loss, corrected for the moisture content of the original sample (Eoff et al., 2006).

Hassler Cell

The effect of drilling fluid additives on reactive shales can be assessed by the Hassler Cell test, which basically measures permeability. For this reason, all effects that cause a change in permeability can be assessed. For example, a shale inhibition can be measured, as the permeability of a core is reduced. Furthermore the change in wettability by chemical treatment has been measured

(Fleury et al., 1999). Hassler developed his method in the 1940 (Hassler, 1944; Hassler and Brunner, 1945).

The cores under investigation are centrifuged and saturated with liquid to establish a pressure gradient. The effluent fluids from the samples are collected in glass tubes. A strobed light source is used to determine the amounts of fluids collected.

The relative permeability of the core to a given fluid F_L can be expressed as

$$F_L = \frac{u_s/dP_s}{u_{100}/dP_{100}} \tag{3.2}$$

Here, u is the rate of flow of the liquid, and dP is the pressure gradient. The indices s mean an arbitrary saturation and 100 means 100% saturation.

Measuring the capillary pressure requires increasing the speed of the centrifuge in increments and measuring the amount of fluid produced from the core sample when the flow has ceased for that particular centrifuge speed (Vinegar et al., 1987).

It has been pointed out that for two-phase flow some problems in the application of this method may arise (Rose, 1980). It is confined to a drainage mode of flow for a water-wet core initially filled with a wetting fluid, which is then invaded by a non-wetting fluid, i.e., oil invading a water-wet core, the method hence, is not useful when a wetting fluid invades a water-wet core containing a non-wetting fluid as the equilibrium level of production of the non-wetting fluid is dependent upon imbibition and not centrifuge speed. However, such measurements are needed in order to design waterflood recovery methods, where the invading fluid is wetting (Vinegar et al., 1987).

Even when developed in 1945, the method was readily automated, and methods have since been developed to determine the saturation of the fluid inside the core. Electromagnetic radiation is used to image a region while it is being centrifuged. From the attenuation coefficients, the fluid saturation may be calculated at several of points within the core. These saturations may be used to calculate capillary pressure or relative permeability (Vinegar et al., 1987).

Nowadays, pressure buildup can be readily established by chromatographic pumps instead of centrifugal forces (Buckley et al., 2007). In this design, a Hassler cell resembles a short chromatographic column.

REFERENCES

Aften, C.W., Gabel, R.K., 1994. Clay stabilizer. US Patent 5 342 530, August 30 1994.

Alford, S.E., 1991. North Sea field application of an environmentally responsible water-base shale stabilizing system. In: Proceedings Volume, SPE/IADC Drilling Conf. (Amsterdam, the Neth, 3/11–14/91), pp. 341–355.

Alonso-Debolt, M.A., Jarrett, M.A., 1994. New polymer/surfactant systems for stabilizing troublesome gumbo shale. In: Proceedings Volume, SPE Int. Petrol. Conf. of Mex (Veracruz, Mex, 10/10–13/94), pp. 699–708.

Alonso-Debolt, M., Jarrett, M., 1995. Synergistic effects of sulfosuccinate/polymer system for clay stabilization. In: Proceedings Volume, Vol. PD-65, Asme Energy-Sources Technol. Conf. Drilling Technol. Symp. (Houston, 1/29/95–2/1/95), pp. 311–315.

Anderson, R.L., Ratcliffe, I., Greenwell, H.C., Williams, P.A., Cliffe, S., Coveney, P.V., 2010. Clay swelling – A challenge in the oilfield. Earth-Sci. Rev. 98 (3–4), 201–216.

Audibert, A., Lecourtier, J., Bailey, L., Maitland, G., 1997. Method for inhibiting reactive argillaceous formations and use thereof in a drilling fluid. US Patent 5 677 266, assigned to Inst. Francais Du Petrole, October 14 1997.

Auerbach, S.M. (Ed.), 2007. Handbook of Layered Materials, reprint from 2004 Edition. CRC Press, Boca Raton.

Aviles-Alcantara, C., Guzman, C.C., Rodriguez, M.A., 2000. Characterization and synthesis of synthetic drilling fluid shale stabilizer. In: Proceedings Volume, SPE Int. Petrol. Conf. in Mex (Villahermosa, 2/1–3/2000).

Bailey, L., Reid, P.I., Sherwood, J.D., 1994. Mechanisms and solutions for chemical inhibition of shale swelling and failure. In: Proceedings Volume, Recent Advances in Oilfield Chemistry, 5th Royal Soc. Chem. Int. Symp. (Ambleside, Engl, 4/13–15/94), pp. 13–27.

Ballard, T., Beare, S., Lawless, T., 1993. Mechanisms of shale inhibition with water based muds. In: Proceedings Volume, IBC Tech. Serv. Ltd Prev. Oil Discharge from Drilling Oper. The Options Conf. (Aberdeen, Scot, 6/23–24/93).

Blachier, C., Michot, L., Bihannic, I., Barrès, O., Jacquet, A., Mosquet, M., 2009. Adsorption of polyamine on clay minerals. J. Colloid Interface Sci. 336 (2), 599–606.

Bragg, J.R., Varadaraj, R., 2006. Solids-stabilized oil-in-water emulsion and a method for preparing same. US Patent 7 121 339, assigned to ExxonMobil Upstream Research Company (Houston, TX), October 17 2006.

Branch, H.I., 1988. Shale-stabilizing drilling fluids and method for producing same. US Patent 4 719 021, January 12 1988.

Buckley, L.J., Carter, M.A., Wilson, M.A., Scantlebury, J.D., 2007. Methods of obtaining pore solution from cement pastes and mortars for chloride analysis. Cement Concr. Res. 37 (11), 1544–1550.

Chen, M., Chen, Z., Huang, R., 1995. Hydration stress on wellbore stability. In: Proceedings Volume, 35th US Rock Mech Symp. (Reno, NV, 6/5–7/95), pp. 885–888.

Chen, X., Tan, C.P., Haberfield, C.M., 1996. Wellbore stability analysis guidelines for practical well design. In: Proceedings Volume, SPE Asia Pacific Oil & Gas Conf. (Adelaide, Australia, 10/28–31/96), pp. 117–126.

Clapper, D.K., Watson, S.K., 1996. Shale stabilising drilling fluid employing saccharide derivatives. EP Patent 702 073, assigned to Baker Hughes Inc., March 20 1996.

Coveney, P.V., Watkinson, M., Whiting, A., Boek, E.S., 1999. Stabilizing clayey formations. WO Patent 9 931 353, assigned to Sofitech NV, Dowell Schlumberger SA, and Schlumberger Canada Ltd., June 24 1999.

Crawshaw, J.P., Way, P.W., Thiercelin, M., 2002. A method of stabilizing a wellbore wall. GB Patent 2 363 810, assigned to Sofitech NV, January 09 2002.

Crowe, C.W., 1990. Laboratory study provides guidelines for selecting clay stabilizers. In: Proceedings Volume, Vol. 1, Cim. Petrol. Soc/SPE Int. Tech. Mtg. (Calgary, Can, 6/10–13/90).

Crowe, C.W., 1991. Laboratory study provides guidelines for selecting clay stabilizers, SPE Unsolicited Pap SPE-21556, Dowell Schlumberger (January 1991).

Doleschall, S., Milley, G., Paal, T., 1987. Control of clays in fluid reservoirs. In: Proceedings Volume, 4th BASF AG et al Enhanced Oil Recovery Europe Symp. (Hamburg, Ger, 10/27–29/87), pp. 803–812.

Durand, C., Onaisi, A., Audibert, A., Forsans, T., Ruffet, C., 1995a. Influence of clays on borehole stability: A literature survey: Pt.1: Occurrence of drilling problems physico-chemical description of clays and of their interaction with fluids. Rev. Inst. Franc. Pet. 50 (2), 187–218.

Durand, C., Onaisi, A., Audibert, A., Forsans, T., Ruffet, C., 1995b. Influence of clays on borehole stability: A literature survey: Pt.2: Mechanical description and modelling of clays and shales drilling practices versus laboratory simulations. Rev. Inst. Franc. Pet. 50 (3), 353–369.

Eoff, L.S., Reddy, B.R., Wilson, J.M., 2006. Compositions for and methods of stabilizing subterranean formations containing clays. US Patent 7 091 159, assigned to Halliburton Energy Services, Inc. (Duncan, OK), August 15 2006.

Evans, B., Ali, S., 1997. Selecting brines and clay stabilizers to prevent formation damage. World Oil 218 (5), 65–68.

Fleury, M., Branlard, P., Lenormand, R., Zarcone, C., 1999. Intermediate wettability by chemical treatment. J. Pet. Sci. Eng. 24 (2–4), 123–130.

Gazaniol, D., Forsans, T., Boisson, M.J.F., Piau, J.M., 1994. Wellbore failure mechanisms in shales: Prediction and prevention. In: Proceedings Volume, Vol. 1, SPE Europe Petrol. Conf. (London, UK, 10/25–27/94), pp. 459–471.

Gazaniol, D., Forsans, T., Boisson, M.J.F., Piau, J.M., 1995. Wellbore failure mechanisms in shales: Prediction and prevention. J. Pet. Technol. 47 (7), 589–595.

Grim, R.E., 1968. Clay Mineralogy, second ed. McGraw-Hill, New York.

Hale, A.H., van Oort, E., 1997. Efficiency of ethoxylated/propoxylated polyols with other additives to remove water from shale. US Patent 5 602 082, February 11 1997.

Halliday, W.S., Thielen, V.M., 1987. Drilling mud additive. US Patent 4 664 818, assigned to Newpark Drilling Fluid In, May 12 1987.

Hassler, G.L., 1944. Method and apparatus for permeability measurements. US Patent 2 345 935, assigned to Dev., April 04 1944.

Hassler, G.L., Brunner, E., 1945. Measurement of capillary pressures in small samples. Pet. Trans. AIME 160, 114–123.

Himes, R.E., 1992. Method for clay stabilization with quaternary amines. US Patent 5 097 904, assigned to Halliburton Co., March 24 1992.

Himes, R.E., Vinson, E.F., 1989. Stabilizing clay-containing formations. EP Patent 308 138, assigned to Halliburton Co., March 22 1989.

Hoffmann, R., Lipscomb, W.N., 1962. Theory of polyhedral molecules. i. physical factorizations of the secular equation. J. Chem. Phys. 36 (8), 2179–2189.

Huber, J., Plank, J., Heidlas, J., Keilhofer, G., Lange, P., 2009. Additive for drilling fluids. US Patent 7 576 039, assigned to BASF Construction Polymers GmbH (Trostberg, DE), August 18 2009.

Jamaluddin, A.K.M., Nazarko, T.W., 1994. Process for increasing near-wellbore permeability of porous formations. US Patent 5 361 845, November 08 1994.

Kippie, D.P., Gatlin, L.W., 2009. Shale inhibition additive for oil/gas down hole fluids and methods for making and using same. US Patent 7 566 686, assigned to Clearwater International, LLC (Houston, TX), July 28 2009.

Klein, H.P., Godinich, C.E., 2006. Drilling fluids. US Patent 7 012 043, assigned to Huntsman Petrochemical Corporation (The Woodlands, TX), March 14 2006.

Kubena Jr., E., Whitebay, L.E., Wingrave, J.A., 1993. Method for stabilizing boreholes. US Patent 5 211 250, assigned to Conoco Inc., May 18 1993.

Mody, F.K., Hale, A.H., 1993. A borehole stability model to couple the mechanics and chemistry of drilling fluid shale interaction. In: Proceedings Volume, SPE/IADC Drilling Conf. (Amsterdam, Neth, 2/23–25/93), pp. 473–490.

Mooney, R.W., Keenan, A.G., Wood, L.A., 1952. Adsorption of water vapor by montmorillonite. II. Effect of exchangeable ions and lattice swelling as measured by X-ray diffraction. J. Am. Chem. Soc. 74 (6), 1371–1374.

Murray, H.H., 2007. Applied Clay Mineralogy: Occurrences, Processing, and Application of Kaolins, Bentonites, Palygorskite-Sepiolite, and Common Clays, Vol. 2. Elsevier, Amsterdam.

Norrish, K., 1954. The swelling of montmorillonite. Discuss. Faraday Soc. 18, 120–134.

Palumbo, S., Giacca, D., Ferrari, M., Pirovano, P., 1989. The development of potassium cellulosic polymers and their contribution to the inhibition of hydratable clays, in: Proceedings Volume, SPE Oilfield Chem. Int. Symp. (Houston, 2/8–10/89), pp. 173–182.

Patel, A.D., McLaurine, H.C., 1993. Drilling fluid additive and method for inhibiting hydration. CA Patent 2 088 344, assigned to M I Drilling Fluids Co., October 11 1993.

Patel, A.D., Stamatakis, E., Davis, E., 2001. Shale hydration inhibition agent and method of use. US Patent 6 247 543, assigned to M I Llc., June 19 2001.

Patel, A.D., Stamatakis, E., Davis, E., Friedheim, J., 2007. High performance water based drilling fluids and method of use. US Patent 7 250 390, assigned to M-I L.L.C. (Houston, TX), July 31 2007.

Poelker, D.J., McMahon, J., Schield, J.A., 2009. Polyamine salts as clay stabilizing agents. US Patent 7 601 675, assigned to Baker Hughes Incorporated (Houston, TX), October 13 2009.

Reed, M.G., 1977. Hydroxy-aluminum based drilling fluid. US Patent 4 045 357, assigned to Chevron Research Company (San Francisco, CA), August 30 1977.

Reed, M.G., 1993. Permeability of fines-containing earthen formations by removing liquid water. CA Patent 2 046 792, January 12 1993.

Rose, W., 1980. Some problems in applying the hassler relative permeability method. J. Pet. Technol. 32 (7), 1161–1163.

Scheuerman, R.F., Bergersen, B.M., 1989. Injection water salinity, formation pretreatment, and well operations fluid selection guidelines. In: Proceedings Volume, SPE Oilfield Chem. Int. Symp. (Houston, 2/8–10/89), pp. 33–49.

Sloat, B.F., 1989. Nitrogen stimulation of a potassium hydroxide wellbore treatment. US Patent 4 844 169, assigned to Marathon Oil Co., July 04 1989.

Sloat, B.F., 1991. Nitrogen stimulation of a potassium hydroxide wellbore treatment. CA Patent 1 291 419, October 29 1991.

Smith, K.W., 2009. Well drilling fluids. US Patent 7 576 038, assigned to Clearwater International, L.L.C. (Houston, TX), August 18 2009.

Smith, C.K., Balson, T.G., 2000. Shale-stabilizing additives. GB Patent 2 340 521, assigned to Sofitech NV and Dow Chemical Co., February 23 2000.

Smith, C.K., Balson, T.G., 2004. Shale-stabilizing additives. US Patent 6 706 667, March 16 2004.

Smith, K.W., Thomas, T.R., 1997. Method of treating shale and clay in hydrocarbon formation drilling. US Patent 5 607 902, assigned to Clearwater Inc., March 04 1997.

Stowe, C., Bland, R.G., Clapper, D., Xiang, T., Benaissa, S., 2002. Water-based drilling fluids using latex additives. GB Patent 2 363 622, assigned to Baker Hughes Inc., January 02 2002.

Suratman, I., 1985. A study of the laws of variation (kinetics) and the stabilization of swelling of clay (contribution a l'etude de la cinetique et de la stabilisation du gonflement des argiles), Ph.D. thesis. Malaysia.

Tan, C.P., Richards, B.G., Rahman, S.S., Andika, R., 1997. Effects of swelling and hydrational stress in shales on wellbore stability. In: Proceedings Volume, SPE Asia Pacific Oil & Gas Conf. (Kuala Lumpur, Malaysia, 4/14–16/97), pp. 345–349.

Tshibangu, J.P., Sarda, J.P., Audibert-Hayet, A., 1996. A study of the mechanical and physicochemical interactions between the clay materials and the drilling fluids: Application to the boom clay

(Belgium) (etude des interactions mecaniques et physicochimiques entre les argiles et les fluides de forage: Application a l'argile de boom (Belgique)). Rev. Inst. Franc. Pet. 51 (4), 497–526.

Valenziano, R., Harris, K.L., Dixon, M.D., 2009. Servicing a wellbore with an aqueous based fluid comprising a clay inhibitor. US Patent 7 549 474, assigned to Halliburton Energy Services, Inc. (Duncan, OK), June 23 2009.

Van Oort, E., 1997. Physico-chemical stabilization of shales, in: Proceedings Volume, SPE Oilfield Chem. Int. Symp. (Houston, 2/18–21/97), pp. 523–538.

Vinegar, H.J., O'Meara Jr., D.J., Rohan, J.A., 1987. Method and apparatus for determining distribution of fluids. US Patent 4 671 102, assigned to Shell Oil Company (Houston, TX), June 9 1987.

Westerkamp, A., Wegner, C., Mueller, H.P., 1991. Borehole treatment fluids with clay swelling-inhibiting properties (ii) (bohrloch- behandlungsfluessigkeiten mit tonquellungsinhibierenden eigenschaften (ii)). EP Patent 451 586, assigned to Bayer AG, October 16 1991.

Whitfill, D.L., Pober, K.W., Carlson, T.R., Tare, U.A., Fisk, J.V., Billingsley, J.L., 2005. Method for drilling depleted sands with minimal drilling fluid loss. US Patent 6 889 780, assigned to Halliburton Energy Services, Inc. (Duncan, OK), May 10 2005.

Wilcox, R.D., 1990. Surface area approach key to borehole stability. Oil Gas J. 88 (9), 66–80.

Wilson, S.J., Miller, M.E., 2001. Treatment for shut-in gas well. US Patent 6 302 206, assigned to Vastar Resources Inc. and Atlantic Richfield Co., October 16 2001.

Zaitoun, A., Berton, N., 1990. Stabilization of montmorillonite clay in porous media by high-molecular-weight polymers. In: Proceedings Volume, 9th SPE Formation Damage Contr. Symp. (Lafayette, LA, 2/22–23/90), pp. 155–164.

Zaltoun, A., Berton, N., 1992. Stabilization of montmorillonite clay in porous media by high-molecular-weight polymers. SPE Prod. Eng. 7 (2), 160–166.

Zhou, Z.J., Gunter, W.D., Jonasson, R.G., 1995. Controlling formation damage using clay stabilizers: A review. In: Proceedings Volume-2, no. CIM 95-71, 46th Annu. Cim. Petrol. Soc. Tech. Mtg. (Banff, Can, 5/14–17/95).

TRADENAMES

TABLE 3.4 Tradenames in References

Tradename Description	Supplier
Aerosil® Fumed silica (Bragg and Varadaraj, 2006)	Degussa AG
Barasil™ –S Shale stabilizer (Valenziano et al., 2009)	Baroid Fluid Services
Baromega™ Aqueous-based silicate containing resilient graphitic carbon (Whitfill et al., 2005)	Halliburton Energy Services, Inc.
Carbolite™ Sized ceramic proppant (Kippie and Gatlin, 2009)	Carbo Corp.

TABLE 3.4 Tradenames in References–Cont'd

Tradename Description	Supplier
Clay Sync™ Shale stabilizer (Valenziano et al., 2009)	Baroid
ClaySeal® Shale stabilizer (Valenziano et al., 2009)	Baroid Fluid Services
Dacron® Polyethylene terephtthalate (Kippie and Gatlin, 2009)	DuPont
EZ-Mud® Shale stabilizer (Valenziano et al., 2009)	Baroid
GEM™ 2000 Shale stabilizer (Valenziano et al., 2009)	Baroid
Grabber® Flocculant (Valenziano et al., 2009)	Baroid
Hydro-Guard® Inhibitive water-based-fluid (Valenziano et al., 2009)	Halliburton Energy Services, Inc.
Jeffamine® (Series) Amine capped polyalkoxylene glycol (Patel et al., 2007)	Huntsman Petrochemical Corp.
Jeffamine® D-230 Polyoxypropylene diamine (Klein and Godinich, 2006)	Huntsman
Jeffamine® EDR-148 Triethyleneglycol diamine (Klein and Godinich, 2006)	Huntsman
Jeffamine® HK-511 Polyoxyalkylene amine (Klein and Godinich, 2006)	Huntsman
Performatrol® Shale stabilizer (Valenziano et al., 2009)	Baroid
Shale Guard™ NCL100 Shale anti-swelling agent (Kippie and Gatlin, 2009)	Weatherford Int.
Steelseal® Resilient graphitic carbon (Whitfill et al., 2005)	Halliburton Energy Services, Inc.

Chapter 4

Lubricants

One of the greatest challenges in the formulation of specialty lubricants for drilling applications is the prevention of drill bit bearing wear in subterranean formations. In such applications, lubrication takes place in an abrasive environment of mud and rock particles deep below the earth's surface.

The journal bearings are subject to extremely high loads, because the bit generally turns at slow speeds and has the weight of the drill string on top of it. Furthermore, there is shock loading due to the bouncing and vibrating of the drill string (Willey et al., 2007).

SYNTHETIC GREASES

There are monographs on the issues of synthetic greases, including their application in petroleum industries (Rudnick, 2006). Synthetic greases have considerable advantages over conventional hydrocarbon-based greases including (Willey et al., 2007):

- High viscosity with good pumpability,
- Lower torque,
- Ability to function at lower operating temperatures, and
- Excellent thermal and oxidative stability.

Many of these advantages arise from the use of controlled synthesis, which yields products with exact properties. These benefits have led to the development of many commercial synthetic types of grease for a variety of uses.

Rock bit bearings are generally lubricated with greases to assist the seals in keeping out the drilling muds. These greases are prepared by adding a thickener to a lubricating oil.

Thickeners consist mostly of metal soaps, formed by the saponification of fatty oils into the corresponding fatty acids then subsequent neutralization

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with a metal hydroxide. A grease formulation typically includes various additives (Willey et al., 2007):

- Extreme pressure,
- Anti-wear,
- Corrosion,
- Solubility,
- Anti-seize protection, and
- Oxidation protection.

Base Fluids

Synthetic base fluids are low molecular weight poly-α-olefins (PAOs) with a high viscosity index (Willey et al., 2007). Preferred blends typically combine a high viscosity and a low viscosity component. Preferably, the high viscosity index PAO is the high viscosity component and the low viscosity component is an alkylated naphthalene.

So-called unconventional base stocks can be used as additional base fluids. These fluids are hydroprocessed, highly refined paraffinic base stocks, containing extremely low amounts of aromatic compounds, and sulfur and nitrogen levels relative to conventional hydroprocessed and solvent refined base stocks. They exhibit a high resistance to oxidation and thermal degradation, very high viscosity indices, superior viscosity and film strength at high temperatures, substantially reduced volatility, and improved lubricity (Willey et al., 2007).

Dibasic acid esters also exhibit good thermal stability, but are usually used in combination with additives to enhance the resistance to hydrolysis and oxidation. Polyol esters contain two or more alcohol moieties, such as trimethylolpropane, neopentylglycol, and pentaerythritol esters. They are the reaction product of a fatty acid derived from either animal or plant sources and a synthetic polyol and have excellent thermal stability, and generally resist hydrolysis and oxidation better than other base stocks.

Naturally occurring triglycerides or vegetable oils are in the same chemical family as polyol esters. However, polyol esters tend to be more resistant to oxidation than such oils, and thus tend to function better under severe conditions and high temperatures. The instability normally associated with vegetable oils is generally due to their high content of linoleic and linolenic fatty acids, both of which are unsaturated compounds. As the degree of unsaturation in the fatty acids in vegetable oils increases, the resulting esters tend to be less thermally stable (Willey et al., 2007). Ester-based lubricants have some advantages over oil-based lubricants (Rudnick, 2006, p. 71) in that they:

- Can tolerate faster and deeper drilling,
- Exhibit lower toxicity,
- Contain no polycyclic hydrocarbons,
- Exhibit good biodegradability,

- Produce less drilling waste, and
- Incur reduced drilling costs.

Extreme Pressure Agents

Extreme pressure agents (EPs) are additives for lubricants that decrease the wear on parts gears that are exposed to very high pressures. They modify the surface of the exposed parts under high pressure conditions by a chemical reaction. EPs include:

- Sulfurized fatty compounds and hydrocarbons,
- Chlorinated hydrocarbons,
- Chlorendic acid esters,
- Polymeric esters,
- Polysulfides, and
- Molybdenum compounds.

There are two types of EP (Willey et al., 2007); firstly compounds that become active at high temperatures, such as lead dithiocarbamate, organosulfur compounds, and organophosphorus sulfur compounds, and secondly inorganic EPs such as molybdenum disulfide, graphite, metal oxides, and powered metals such as copper and lead. The particles of solid EPs act by forming layers between the two bearing surfaces, and so protect them under load by sliding against each other in a way that is similar to cards in a stack sliding against each other. Solid EPs improve the load carrying capacity, but they contribute to excessive seal and hub wear and drill bit seal failure.

Drill bit lubricant compounds containing a copper EP caused seal failures due to copper that was deposited close to the seal area. This accumulated near the seal area until it became abraded by the contact with the copper deposit. Eventually, the grease composition is ejected from the journal area, and a metal-to-metal contact occurs between the roller cone and the journal, which causes a drill bit failure.

On the other hand, lubricants that reduce seal and hub wear do not have a sufficient film strength, i.e., load carrying capacity, to be used as drill bit lubricants. In general, any additives made up from heavy metal complexes exhibit an adverse environmental impact.

Alteratively, zirconium 2-ethylhexanoate or bismuth 2-ethylhexanoate can be added in amounts up to 20% as an additive. These compounds are non-toxic, which gives easier handling in the storage, use, and final deposit of the lubricant.

In addition, zirconium compounds impart some corrosion resistance to metal surfaces, which contributes to reducing the hub wear, and improves the sealing properties. Seals may also wear out more slowly when a zirconium-based lubricant is used.

Zirconium compounds also modify the viscosities of the base stock, which will extend the range of operating temperatures.

Anti-seize Agents

Anti-seize compounds are used to mitigate damage from high bearing stresses by providing a dissimilar metal or other material between like substrates. Such a compound inhibits the welding that may otherwise occur from the temperatures, pressures, and stresses normally incurred during proper make-up (Oldiges and Joseph, 2003).

Conventional anti-seize thread compounds include greases, which contain substantial amounts of heavy metals or their oxides, carbonates, or phosphates. The metals include (Oldiges and Joseph, 2003):

- Copper,
- Zinc,
- Lead,
- Nickel,
- Molybdenum, and
- Aluminum.

However, environmental regulations have begun to discourage or prohibit the use of anti-seize compounds that contain such materials. Organic fluid additives containing antimony, zinc, molybdenum, barium, and phosphorus have also become the subject of environmental scrutiny, partly because of the way that they are used.

Oil field threaded connections are usually coated with an excess amount of the thread compound to ensure complete connection coverage. The excess compound is sloughed off and ends up downhole, where it is then included with the other materials pumped out of the wellhole and into a containment area. From there, materials contaminated with heavy metals must be removed and deposited to a hazardous waste disposal site.

Alternatively, threaded connections can be protected by coating the threads, prior to their make-up, with a solvent-thinned, resin-based coating and bonding composition, composed of a suspending agent, a bonding agent, a thinning agent, and a metallic flake. The coated threads are dried to bond the coating and the bonding composition to the threads. Prior to their make-up, the threads are coated with an excess of an environmentally friendly lubricating composition. A typical formulation is shown in Table 4.1.

Using such a method, the anti-seize metallic film adheres to the thread surface to provide an anti-seize protection while minimizing the amount of metal emitted, since only thread wear discharges metal into the environment. Thus the metal contamination is substantially reduced in comparison to conventional methods.

In summary, the use of anti-seize metallic films, in conjunction with environmentally friendly lubricating compositions reduces the potential for environmental damage, while still providing an optimum protection in critical operations.

TABLE 4.1 Anti-seize Composition (Oldiges and Joseph, 2003)

Ingredient	Amount/[%]
Suspending agent, ethyl cellulose	2
Bonding agent, silicone thermoset	6
Thinning agent (xylene/trichloroethane)	84
Seizing-agent, copper flakes	8

TABLE 4.2 Grease Compositions (Oldiges et al., 2006)

Ingredient	Amount/[%]	Examples
Thixotropic base material	40–90	Metal salt complex greases
Metal complex grease	50–90	Lithium complex grease, aluminum calcium complex grease
Anti-seize agents	5–50	Metal fluorides
Boundary lubricant	5–50	Metal borates, molybdates, carbonates, acetates, stearates, etc.
Friction adjusters	0–12	polytetrafluoroethylene (PTFE), graphitic materials, natural or powders and synthetic fibers, molybdenum disulfide, fibers etc.
Anti-wear additives	0–5	Sulfurized isobutylene, phosphate esters, dithiocarbamates, dithiophosphates, naphthanates, or the like
Anti-degradant additives	0–2	Antioxidants and antiozonants

Fluorides of alkaline or earth alkaline metals such as CaF_2 have been proposed as anti-seize agents for nickel and chrome ferrous alloys that are prone to galling under high contact stress (Oldiges et al., 2006). Typical grease compositions are formulated as shown in Table 4.2.

Anti-wear Additives

Anti-wear additives are divided into two categories (Willey et al., 2007): those activated at a lower temperature than EPs, such as zinc dialkyl dithiophosphate, sorbitan monoleate, chlorinated hydrocarbons, and phosphate esters, and those that become active at lower loads than EPs, PTFE, and antimony trioxide.

Metal Deactivators

Metal deactivators protect against nonferrous corrosion and in some cases also against ferrous corrosion. Common metal deactivators are based on benzotriazole. Ferrous corrosion inhibitors include organic acids and esters, phenolates, and sulfonates (Willey et al., 2007).

Solubility Aids

Solubility aids make the additives dissolve in the oil or the soap. Common solubility aids include esters, such as trimellitic acid esters (Willey et al., 2007).

Antioxidants

Common antioxidants used in grease formulations include zinc dialkyl dithiophosphates, amine phosphates, aromatic amines, phenothiazine, or hindered phenols, such as *tert*-butylhydroxytoluene.

It is generally preferred not to employ a zinc dialkyl dithiophosphate antioxidant in the lubricating grease if the rock bit comprises an incompatible metal. They are, however, used in other lubricating applications (Willey et al., 2007).

Base stocks

A wide variety of grease compositions are known and often made from refined petroleum or hydrocarbon base stock, which gives them a low viscosity, and provides the base lubricity of the composition. The base stock may constitute about three-quarters of the total grease composition.

This base stock is thickened with a conventional metal soap or a metal complex soap. Light base stocks with low viscosity are used for low temperature greases, and heavier, higher viscosity base stocks are used for high temperature greases (Denton et al., 2007). In order to enhance the film lubricating capacity of base stocks, solid additives such as molybdenum disulfide, copper, lead, or graphite can be added (Newcomb, 1982).

Synthetic polymer EPs and high viscosity synthetic polymers may also be used. Such materials enhance the ability of the lubricant base stock to form a friction-reducing film between the moving metal surfaces under conditions of extreme pressure, and to increase the load carrying capacity of the lubricants.

LUBRICANT COMPOSITIONS

Molybdenum disulfide

Molybdenum disulfide is used traditionally in greases for bit lubrication. In addition, polymers of 2-methylpropene (i.e., isobutene) and metal soaps are used to formulate synthetic greases (Denton and Fang, 1996).

A viscosity of 600–750 cP at 120°C is desirable. However, in the severe environment of a rock bit bearing, the viscosity of the composition should be at least 200 cP at 100°C (Delton and Hooper, 1994). Other heavy-duty greases based on molybdenum sulfide also contain calcium fluoride (Landry and Koltermann, 1991a,b) and metal soaps as thickeners.

Specialized lubricating greases have been developed for the bearing assemblies of roller bits. They are prepared from petroleum oils thickened with alkali and alkaline earth metal soaps (Lyubinin et al., 1995). The greases contain additives and fillers, such as synthetic dichalcogenides of refractory metals, which exhibit the necessary service characteristics. Tests have shown that such greases out perform the initial grease by 7 to 12 times (Table 4.3).

Polarized Graphite

Because of environmental concerns, molybdenum disulfide, regarding alternative compositions for solid lubricants have been developed. These compositions

TABLE 4.3 Compounds Suitable as Lubricants

Compound	References
Carbon black, fatty acid esters	Runov et al. (1992)
Sodium ethyl siliconate based compositions[a]	Goncharov et al. (1993)
Polyacrylamide, carboxymethyl cellulose, gypsum[b]	Kalashnikov (1994)
Olefins[c]	Halliday and Schwertner (1997); Koltermann and Willey (1999, 2000)
2,4,8,10-tetra-oxaspiro-5, 5-undecane[d]	Frolov et al. (1993)
Phosphatides or phospholipids[e]	Garyan et al. (1998)
Polypropylene glycol[f]	Enright et al. (1991); Fang et al. (1998); Sano (1997)
Fluoropolymers and zinc dioctyl phenyl dithiophosphate[g]	Chanshev et al. (1992)

a) Sealing lubricant down to −40°C
b) Sealing lubricant
c) With metal soaps and Aerosil® as thickener
d) Reaction product from pentaerythrite and paraformalehyde
e) Environmentally safe lubricating additives
f) As mud additive for lubrication
g) Antioxidizing and anticorrosion additive to lubricating oils

consist of graphite, sodium molybdate, and sodium phosphate (Holinski, 1995; Zaleski et al., 1998), or, more recently, polarized graphite.

Polarized graphite can be used as a lubricant additive for rock bits, since it exhibits extremely good load carrying ability and anti-wear performance.

Graphite consists of carbon in a layered structure, and its lack of polarity prevents graphite powder from forming a lubricant film and adhering to metal surfaces. The polarization of graphite results allows it to adhere to metal and thus form a lubricant film that can carry extremely high loads without failure.

Ordinary graphite has a laminar hexagonal crystal structure and the closed rings of carbon atoms do not normally have any electrical polarization. Hence, graphite has good lubricity because the layers may slip or shear readily, but the lack of polarity leads to a poor adhesion to metal surfaces.

Graphite can be treated with alkali molybdates or tungstenates to impart a polarized layer at its surface. Alternating positive and negative charges are formed. The treated graphite shows an extremely good load carrying capacity and anti-wear performance, somewhat similar to molybdenum disulfide, as well as a good adhesion of particles on metal surfaces and good film-forming properties (Denton and Lockstedt, 2006).

Ellipsoidal Glass Granules

The use of ellipsoidal glass granules instead of spherical glass beads increases the contact surface of antifrictional particles, reduces their ability to penetrate deeply into the mud cake, and increases their breaking strength (Kurochkin et al., 1990; Kurochkin et al., 1992a,b; Kurochkin and Tselovalnikov, 1994).

Calcium-Sulfonate-based Greases

Drilling muds have been changed significantly over the last few years due to environmental pressures and the increase in drilling operations in more extreme environments, where conventional grease formulations cannot withstand the enhanced demands. For these reasons, new materials have appeared that (Oldiges et al., 2007):

- Adhere more effectively to the threaded connections,
- Do not degel at elevated temperatures and higher pH levels, and
- Impart galling resistance and corrosion resistance.

Typical grease thickeners are calcium acetate, lithium stearate, lithium 12-hydroxystearate, anhydrous and hydrous calcium soaps, sodium soaps, organophilic clays, and silica. It is important for a grease to be stable over a range of pHs, since the pH of drilling mud increases as oil well depths increase.

During drilling operations, the threaded connections are exposed to drilling fluids, which include drilling muds and shavings from the drilling operations. These fluids and shavings tend to dissolve, erode, or ablate the grease compounds thus removing their protection and increasing the likelihood of damage to the threaded connections.

Calcium-sulfonate-based grease formulations are a suitable alterative to conventional greases. These high performance sulfonate greases are superior carriers for controlled friction properties in oil field drilling and production thread compounds.

By reducing the thickener content, a cost-competitive calcium sulfonate grease can be formulated. Preferred base stocks include PAOs, polybutenes, polyol esters, vegetable oils, and animal oils (Oldiges et al., 2007). Thixotropic greases or grease-like overbased calcium sulfonate compositions have corrosion inhibiting properties (Olson et al., 1994).

When a drill bit is used in hard, tough formations, high pressures and temperatures are encountered. The total useful life of a drill bit in such severe environments is in the order of 20–200 h for bits of 6–28 in diameter, at depths of about 1,500–6000 m. Useful lifetimes of about 65–150 h are typical. When a drill bit wears out or fails as a borehole is being drilled, it is necessary to withdraw the drill string to replace the bit, which is a very expensive process. Prolonging the lives of drill bits minimizes the lost time in round tripping the drill string for replacing them (Denton et al., 2007).

The replacement of a drill bit can be required for a number of reasons, including wearing out or breakage of the structure contacting the rock formation. The journal bearings on which the roller cones are mounted may fail or wear severely. These bearings are lubricated with special formulations so that they may survive the severe conditions. A lubrication failure can sometimes be attributed to misfit of bearings or seal failure, as well as a problem with the grease itself (Denton et al., 2007).

Paraffins

Purified paraffins are non-toxic and biodegradable (Halliday and Clapper, 1998) and may be used as lubricants, rate of penetration enhancers, or spotting fluids for water-based drilling mud (WBM).

Olefins

Olefin isomers containing 8–30 carbon atoms are suitable, but isomers having fewer than 14 carbon atoms are more toxic, and isomers having more than 18 carbon atoms are more viscous. Therefore olefin isomers having 14–18 carbon atoms are preferred (Halliday and Schwertner, 1997).

Phospholipids

In aqueous drilling fluids, phospholipids are effective lubricating agents (Patel et al., 2006). They are naturally occurring compounds, for example,

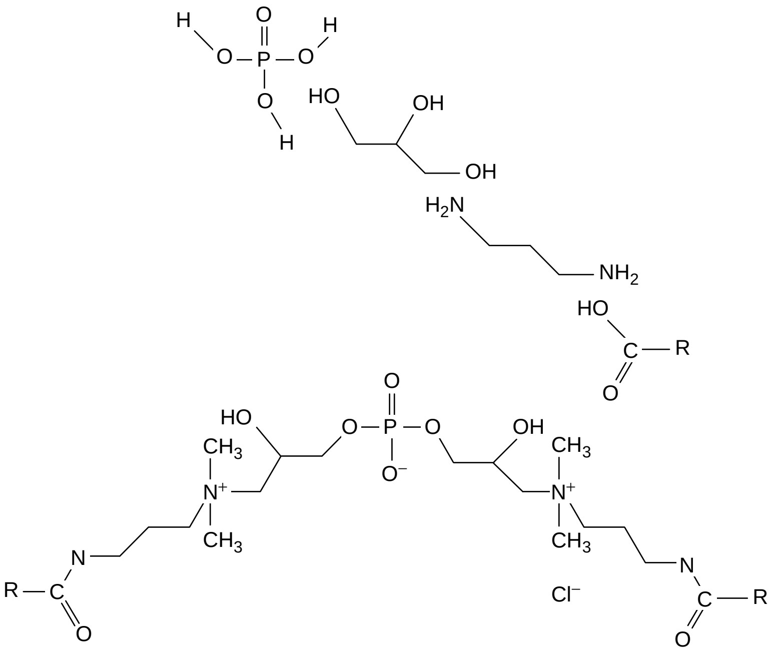


FIGURE 4.1 Structural units of a phospholipid (up) and the phospholipid formed from them (bottom).

lecithin belongs to the class of phospholipids. An introduction to phospholipid chemistry was given by Hanahan (1997). They also find use as polymers (Nakaya and Li, 1999). The structural units of a phospholipid are shown in Figure 4.1.

Because of their ionic nature, some phospholipids are soluble in water. A preferred compound as lubrication additive for aqueous drilling fluids is cocoamidopropyl propylene glycol diammonium chloride phosphate (Patel et al., 2006). Phosphatides or phospholipids are environmentally safe lubricating additives (Garyan et al., 1998).

Alcohols

Alcohol Glucoside Mixture

Many oil-based fluids, or additives for such fluids, have caused environmental concerns and tend to be more costly than aqueous-based fluids, so aqueous-based fluids are often preferred (Fisk et al., 2006). However, these fluids tend to have more lubricity problems and adverse effects on the subterranean formation, such as causing swelling of clays, than encountered with oil-based fluids.

Silicate-based aqueous drilling fluids have long been known to inhibit the formation damage caused by water, but are also known to have poor lubricity

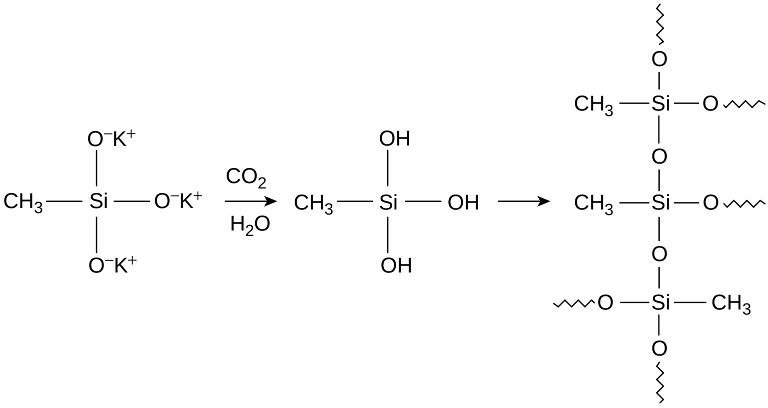


FIGURE 4.2 Polymerization of silic acid Fleury et al. (1999).

properties. Lubricants commonly known and used in WBMs do not provide good lubricity in silicate muds (Fisk et al., 2006).

Recently, silicic-acid-based drilling fluids have been found to provide a membrane-efficient WBM, but they have high torque and drag values. Moreover, traditional mud lubricants show little to no effect in a high pH, silicic-acid-based mud.

The reaction mechanism for the polymerization of silicic acids derivatives is shown in Figure 4.2. A lubricant composition has been developed for silicic-acid-based drilling fluids (Fisk et al., 2006), comprising 2-octyldodecanol, and 2-ethylhexylglucoside (Fisk et al., 2006). Alternative alcohols include oleyl alcohol, stearyl alcohol, and polyetherglycols.

It is believed that the alcohol serves as the more active lubricant, and the alkylglucoside serves primarily as a wetting agent. These compounds exhibit their wetting properties even at high pH. Summarizing, the lubricant compositions is effective in a high pH environment, has low toxicity, and is environmentally acceptable.

Partial Glycerides

Historically, pure water-based systems are the oldest in the development of drilling fluids. However, their use is attended by such serious disadvantages that only limited application has been possible in technically demanding drilling operations. Most importantly, the interaction of the water-based drilling fluids with the water sensitive layers of rock, especially the layers of clay, leads to unacceptable interference with the drilling process (Müller et al., 2004a).

It has, however, been observed that, even in highly sensitive shale formations, adequate stability can be obtained in the case of purely water-based drilling fluids if soluble alkali metal silicates, i.e., water-glasses are used.

However, using water-based drilling fluids requires the addition of lubricants including mineral oils, animal and vegetable oils, and esters. Regulations with regard to the biodegradability of drilling fluids and their constituents are gradually restricting the use of otherwise particularly suitable mineral oils.

Fatty acid partial glycerides have been found to be lubricants suitable for both water-based and oil-based drilling muds (OBMs) for use at low temperatures. Basic WBMs and OBMs that have been used for testing the lubricants are given in Table 4.4.

The effectiveness of the lubricants can be measured by the Almen-Wieland test (Buyanovskii, 1994), the Falex pin and vee block method (ASTM, 2009), the Timken wear and lubricant test (ASTM, 2008), and the four ball test (Totten et al., 2003). The effect of various lubricants has been measured as shown in Figure 4.3.

Aminoethanols

High pH values affect the stability of lubricating products, in particular those based on conventional esters, which hydrolyze at high pHs and temperatures, so instead of alcohols, amino alcohols can be used. For example, a lubricating composition has been synthesized by the reaction of polymerized linseed oil with diethanol amine at 160°C. A product with a viscosity of around 2,700 mPa s at 40°C is obtained (Argillier et al., 2004), or this can be reduced by adding some methyl oleate to the reaction product.

When added to a silicate mud, good lubricating properties are obtained, even up to a pH of 12. Tests revealed that the addition of 3% of a lubricant to a base mud reduced the torque readings by 50%.

Polymeric Alcohols

Synthetic PAOs are non-toxic and effective in marine environments when used as lubricants, return-of-permeability enhancers, or spotting fluid additives for WBMs.

TABLE 4.4 Water-Based and Oil-Based Drilling Muds (Müller et al., 2004a)

Water-based		Oil-based	
Water	4 l	Mineral oil	675 ml
Xanthan gum	20 g	Water	225 ml
Bentonite	56 g	$CaCl_2$	95 g
Carboxymethyl cellulose	40 g	Emulsifier	35 g
Barite	1.8 g	Fluid loss additive	10 g
		Viscosifier	25 g
		Lime	17 g
		Barite	360 g

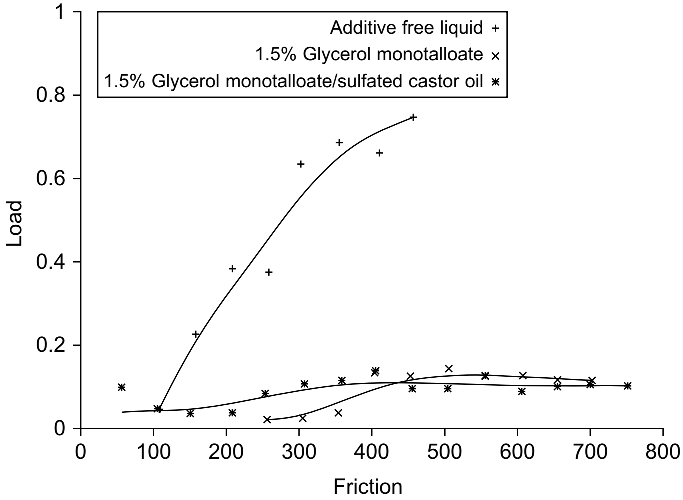


FIGURE 4.3 Effect of various lubricants (arbitrary units) (Müller et al., 2004a).

Both polyalkylene glycol (Alonso-Debolt et al., 1999) and side chain polymeric alcohols such as polyvinyl alcohol (PVA) have been suggested. These substances are comparatively environmentally safe (Penkov et al., 1999; Sano, 1997).

PVAs may be applied as they are, or in crosslinked form (Audebert et al., 1996). Crosslinkers can be aldehydes, e.g., formaldehyde, acetaldehyde, glyoxal, and glutaraldehyde, to form acetals, maleic acid or oxalic acid to form crosslinked ester bridges, or dimethylurea, polyacrolein, diisocyanate, and divinylsulfonate (Audebert et al., 1994, 1998).

An amine-terminated polyoxyalkylene with an average molecular weight of 600–10,000 Dalton can be acylated with a succinic acylating agent, e.g., hexadecenyl succinic anhydride or a Diels-Alder diacid, obtained from an unsaturated fatty acid (Forsberg and Jahnke, 1993a,b). Similarly, alkyl-aryl sulfonate salts can be used in lubrication (Naraghi and Rozell, 1996).

The pendant hydroxy groups of ethylene oxide-propylene oxide copolymers of dihydroxy and trihydroxy alcohols may be sulfurized to obtain a sulfurized alcohol additive. This is effective as a lubricant when used in combination with oils and fats (Clark and Dye, 1997; Dye et al., 1995). The sulfurized alcohols may be obtained by the reaction of sulfur with an unsaturated alcohol.

Fatty alcohols and their mixtures with carboxylic acid esters have also been proposed as lubricant components (Müller et al., 1999a).

Ethers

2-Ethylhexanol can be epoxidized with 1-hexadecene epoxide. This additive also helps reduce or prevent foaming. By eliminating the need for traditional, oil-based components, the composition is non-toxic to marine life, biodegradable, environmentally acceptable, and capable of being disposed of at the drill site without the need for costly disposal procedures (Alonso-Debolt et al., 1995).

Esters

Esters are compounds of interest, as alternatives with better biodegradability. Some are listed in Table 4.5.

The use of esters in water-based systems, particularly under highly alkaline conditions, can lead to considerable difficulties. Ester cleavage can result in the formation of components with a marked tendency to foam, which then introduces unwanted problems into the fluid systems.

Sulfonates of vegetable oils, in particular soya oil sulfonate, are also used as lubricants. Soya oil sulfonate can be used in water- and oil-based systems, but shows significant foaming, especially in water-based fluids, which restricts its usefulness (Müller et al., 2004a).

A lubricating composition that comprises components that can be obtained from by-products of manufacturing processes, so providing a use for them would also be advantageous (Breeden and Meyer, 2005).

A lubricating composition has been proposed that is obtained by reacting glycerol component comprising glycerol, glycerol oligomers, and a fatty acid component. The reaction product is neutralized with potassium hydroxide or ammonium hydroxide. The composition of the glycerol component is shown in Table 4.6.

The fatty acid component can be obtained from vegetable oils, wood pulp processing, animal fats processing, etc.

Catalysts for esterification include sulfuric acid, hydrochloric acid, nitric acid, and *p*-toluene sulfonic acid, although concentrated sulfuric acid is preferred (Breeden and Meyer, 2005). The composition can also be subjected to chain extension using diacids, such as maleic acid, succinic acid, or glutaric acid (Breeden and Meyer, 2005).

TABLE 4.5 Esters as Lubricants

Ester Compound	References
2-Ethylhexyl oleate	Chapman and Ward (1997)
Triglyceride oil	Chapman and Ward (1997)
Soya oil sulfonate	Müller et al. (2004a)
Glycerol monotalloate	Müller et al. (2004a)
Sulfonated castor oil	Müller et al. (2004a)

TABLE 4.6 Composition of the Glycerol Component (Breeden and Meyer, 2005)

Compound	%
Glycerine	10–13
Diglycerine	16–23
Triglycerine	5–7
Tetraglycerine	4–6
Pentaglycerine	3–4
Heavier polyglycerines	15
NaCl	2–4
Na_2CO_3	0.3–1
Water	22–28
Carboxylic acid salt	11–14

Ester-based Oils

Several ester-based oils are suitable as lubricants (Durr et al., 1994; Genuyt et al., 2001), as are branched chain carboxylic esters (Senaratne and Lilje, 1994). Tall oils can be transesterified with glycols (Runov et al., 1991) or condensed with monoethanolamine (Andreson et al., 1992). The ester class also comprises natural oils, such as vegetable oil (Argillier et al., 1999), spent sunflower oil (Kashkarov et al., 1998, 1997; Konovalov et al., 1993a,b), and natural fats, for example, sulfonated fish fat (Bel et al., 1998). In WBM systems no harmful foams are formed from partially hydrolyzed glycerides of predominantly unsaturated C_{16} to C_{24} fatty acids.

The partial glycerides can be used at low temperatures and are biodegradable and non-toxic (Müller et al., 2000). A mixture of long chain polyesters and polyamides (PAs) is suitable for high temperature applications (Wall et al., 1995a).

In the case of esters from, for example, neopentylglycol, pentaerythrite, and trimethylolpropane with fatty acids, tertiary amines, such as triethanol amine, together with a mixture of fatty acids, improve the efficiency (Argillier et al., 1997).

Ester Alcohol Mixtures

In addition to esters, mixtures of fatty alcohols with carboxylic acid esters have been proposed as lubricating additives in WBMs. The alcohols include guerbet and oleyl alcohols with oleyl oleate or isotridecyl stearate as the ester component (Müller et al., 2004b). Fatty alcohols exhibit a foam-suppressing effect.

Phosphate Esters

It has been found that including polyether phosphate esters and polyethylene glycol (PEG) can give aqueous drilling fluids, which provide good lubricating properties in a wide range of drilling fluids (Dixon, 2009).

Typical synthetic routes to such esters involve the reaction of the polyether with a phosphating agent such as phosphorus pentoxide or polyphosphoric acid. The use of polyphosphoric acid in the synthesis gives higher proportions of the monoester, which is preferred. The optimal molecular weight of the PEG is 400 Dalton (Dixon, 2009). The compatibility of the lubricant may be adversely affected by other components of the drilling fluid, particularly by divalent cations such as calcium (Dixon, 2008, 2009).

Biodegradable Compositions

A biodegradable lubricating composition has been proposed, based on an aliphatic hydrocarbon oil and a fatty acid ester (Genuyt et al., 2006). It is important that the hydrocarbon is not aromatic because petroleum cuts with a high aromatic compound content present a risk to marine life due to their toxicity.

The composition is used as a continuous oil phase in an invert emulsion in a petroleum drilling fluid or mud. It is particularly useful in offshore drilling in deep water, or in inclined or long-range drilling. In the case of deep water drilling, the temperature of the water is around 4°C, hence the viscosity of drilling fluids needs to be controlled.

Triglyceride esters of animal or plant fatty acids are biodegradable, but the use of these compounds in invert emulsion drilling fluids shows them to be extremely susceptible to hydrolysis, which results in unwanted changes in the viscosity of emulsions.

Esters of saturated or unsaturated monocarboxylic acids, e.g., isononanic acid and of longer chain alcohols, e.g., isoheptanol, 2-ethyl hexanol, or *n*-octanol (Müller et al., 1990) are less sensitive to hydrolysis. However, they retain some susceptibility, particularly at temperatures above 160°C, as are encountered in rock drilling and deep offshore drilling.

Esters that have been condensed from rapeseed fatty acids and 2-ethyl hexanol Finagreen® BMDF (Totalfina) claim to have even better properties (Genuyt et al., 2006). Rapeseed oil consists mainly of oleic and linoleic acids. Mineral hydrocarbon cuts with different properties have been used to which the esters have been added. Some properties of these cuts are given in Table 4.7.

The kinematic viscosity as a function of temperature of cuts A and E, and of a mixture consisting of 70% of these cuts and 30% of Finagreen® BMDF are given in Table 4.8.

Inspection of the table reveals that cut A has a viscosity of 8.4 $mm^2 s^{-1}$ at 0°C, which is suitable for use in the low temperature conditions encountered

TABLE 4.7 Properties of Mineral Oil Cuts (Genuyt et al., 2006)

Property	Cut A	Cut E
Typical chain length	C13–C15	C14–C18
Flash point/[°C]	101	116
Flow point/[°C]	−51	−15
Aromatics/[%]	<0.01	0.9
n-Paraffins/[%]	3	27
i-Paraffins/[%]	44	19
Naphthenes/[%]	53	53
Aromatics /[%]	0	0.9

TABLE 4.8 Viscosity of Biodegradable Compositions as a Function of Temperature (Genuyt et al., 2006)

	Temperature/[°C]				
	0	10	20	30	40
Composition	Viscosity/[mm^2s^{-1}]				
Cut A	5.92	4.6	3.5	2.8	2.28
Cut E	10.3	7.2	5.3	3.9	3.2
Cut A + ester[a]	8.4	6.1	4.6	3.7	3.0
Cut E + ester[a]	13.5	9.25	6.8	5.1	4.07

a) 30% Finagreen® BMDF

in deep water drilling. Here, the maximum kinematic viscosity threshold at a temperature of 0°C must be less than 10 mm^2s^{-1} for a drilling fluid.

An Arrhenius plot of the data in Table 4.8 is presented in Figure 4.4. Here the viscosities are normalized to those measured at 0°C.

Polymers

Synthetic and natural polymers suitable for drilling muds are listed in Tables 4.9 and 4.10, respectively. The structures of morpholine and methylenebisacrylamide are drawn in Figure 4.5.

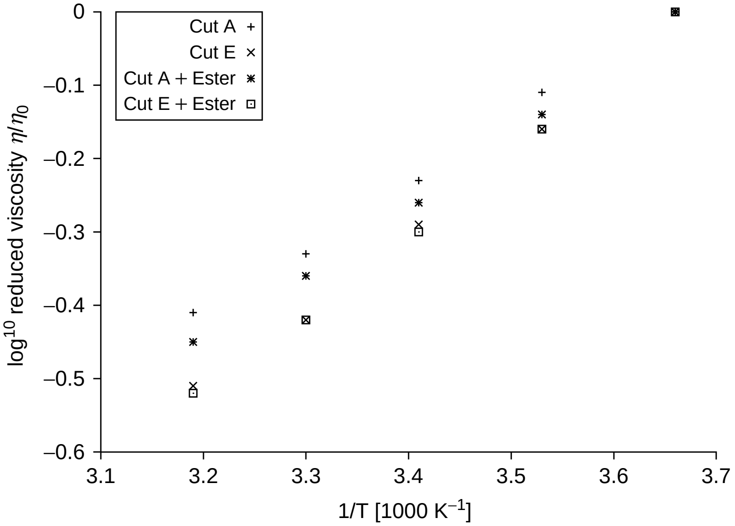


FIGURE 4.4 Arrhenius plot of the reduced viscosities.

Polyacrylamides (PAMs) are eventually hydrolyzed over time and temperature, leading to a lack of tolerance toward electrolyte contamination and to rapid degradation. Modifications of PAM structures have been proposed to retain thermal stability at higher temperatures. Monomers such as 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) or sulfonated styrene/maleic anhydride can be used to prevent acrylamide (AAm) comonomer from hydrolyzing (Audibert and Argillier, 1995).

Starch

Starch is a high molecular weight, natural polymer composed of repeating 1,4-α-D-glucopyranosyl units. It is typically a mixture of linear and branched polymers. Amylose is the linear component with a molecular weight of around 200 kDalton, and amylopectin is the branched component with a molecular weight of around 1 MDalton (Fanta et al., 2002).

Normal dent cornstarch contains about 25% amylose, and commercial cornstarch varieties are available that range in amylose content from 0% (waxy cornstarch) to about 70% (high amylose cornstarch).

Starch, as isolated in its native state, is insoluble in water at room temperature because of hydrogen bonding between polysaccharide macromolecules and areas of crystallinity within the starch granule. When a solution of starch is heated, granules initially take up water with limited swelling, then, at a definite temperature, typically about 70°C, the granules swell rapidly and irreversibly, and areas of crystallinity within the granule are lost. The temperature at which this occurs is referred to as the gelatinization temperature.

TABLE 4.9 Synthetic Copolymers

Polymer	References
2-Acrylamido-2-methyl-1-propane sulfonic acid AMPS, diallyldimethylammonium chloride, *N*-vinyl-*N*-methylacetamide, AAms and acrylates[a]	Hille et al. (1996); Li et al. (1996); Oswald et al. (2000)
AMPS/AAm/vinyl acetate copolymer	Matz et al. (2001) and Wang (1999)
AAm styrene sulfonate copolymer[b]	Patel and McLaurine (1991)
AAm, vinylpyrrolidone, *N*-vinyl lactam	Patel (2000)
Copolymer from AAm and AMPS, with methylenebisacry-lamide as the crosslinker	Patel (1998)
Copolymer from acryloylmorpholine and ammonium AMPS	Udarbe et al. (2000)
Styrene-butadiene copolymer latex and styrene-acrylate-methacrylate terpolymer latex	Bailey (2001a,b)
Polymers of amido sulfonic acid	Sopko and Lorentz (1991)
Acrylic polymer	Selikhanovich et al. (1997)
N-Vinyl-2-pyrrolidone, acrylamidopropane sulfonic acid, AAm, and acrylic acid copolymer	Stephens and Swanson (1992)
AMPS and *N*-vinyl amides of acrylics and methacrylics, or *N*-vinylcaprolactam	Heier et al. (2002)
Sulfonated chromium humate	Tan (1990)
Sulfonated phenolic resin and hydrolytic ammonium polyacrylate	Tan (1990)
PA and polyimide	Wall et al. (1995b)
Hydrolyzed polyacrylonitrile and cyan-ethylate carboxymethyl cellulose[c]	Liu et al. (1996)
PAOs[d]	Mensa-Wilmot et al. (1997)
Polymers of hydroxy carboxylic acids as a rheologic additive	Müller et al. (1999b)
Dimethyl silicone fluids	Patel (1997)

a) Deep-drilling additives
b) The polymer additive is characterized by increased viscosity at low shear rates and enhanced fluid loss control
c) Salt tolerance (above 10%)
d) The additive also reduces drill string drag

TABLE 4.10 Natural and Natural Modified Polymers

Polymer	References
Amylopectin[a]	Kok et al. (1999a,b)
Polyanionic cellulose sulfonate-containing polymer[b]	Hen (1991)
Hydroxyethyl and hydroxypropyl cellulose	Plank (1993)
Hydroxyethyl cellulose, hydrophobically modified	Audibert et al. (1995, 2000)
Carboxymethyl cellulose	Ryzhov et al. (1996)
Gellan	Dreveton et al. (1995)
Diutan	Navarrete et al. (2001); Navarrete and Shah (2001)
Cornstarch, carboxylated methyl, crosslinked hydroxypropyl cornstarch	Anderson et al. (1991) and Bernu (1998)
Graft copolymer of starch, AAm, and PVA	Gao et al. (1993)
Waxy maize starch, epichlorohydrin, crosslinked	Estes and Bernu (1999)
Crosslinked starches	Cobianco et al. (2001); Sifferman et al. (1999)
Amine-derivatized potato starch	Anderson et al. (1991)
Sulfonated chromium humate, sulfonated phenolic resin, and hydrolytic ammonium polyacrylate	Tan (1990)
Gellan, scleroglucan, xanthan gum	Dreveton et al. (1998)
Hydrophobically modified guars	Audibert and Argillier (1998)
Hydroxypropyl guar gum, hydrophobically modified	Audibert and Argillier (1996)
Deacetylated xanthan gum	Langlois (1999)
Vinyl grafted lignite[c]	Huddleston and Williamson (1990, 1991)

a) *The amylopectin starch may be crosslinked with epichlorohydrin to stabilize the starch molecule. The molecule may also be stabilized by hydroxypropylation, carboxymethylation, or both.*
b) *Combination for high temperature/high pressure.*
c) *For example, with dimethyl aminopropyl methacrylamide, methacrylamido propyltrimethyl ammonium chloride, N-vinylformamide, N-vinylacetamide, diallyl dimethyl ammonium chloride, and diallylamine.*

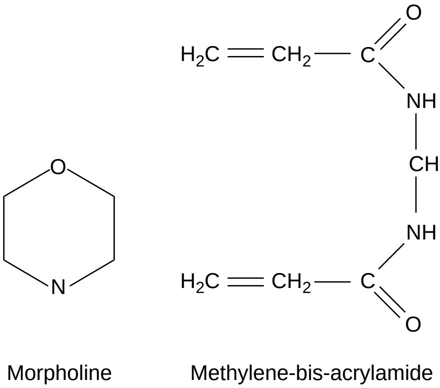


FIGURE 4.5 Morpholine, methylenebisacrylamide.

Near this temperature, the amylose component becomes soluble and diffuses out of the granule matrix. As the temperature is increased beyond about 70°C, a greater percentage of the starch becomes soluble. The granules become highly swollen, until, at a temperature of about 90–100°C, a viscous dispersion of starch in water is obtained. However, despite the overall apparent solubility, the starch is only partially soluble in water and usually occurs as highly swollen granules, thus granule fragments that may be easily separated from such a starch solution by centrifuging.

True solutions of starch in water are difficult to prepare using conventional cooking techniques, and require the application of specialized methods, such as autoclaving at elevated temperatures and pressures.

Steam jet cooking is another technique for preparing starch solutions. This is simpler and more economical than autoclaving, and is suitable for continuous processing. Because of these processing advantages, jet cooking has been used for decades to prepare starch solutions for commercial applications. The method involves pumping a water slurry of starch through an orifice located in a heating chamber, i.e., a hydroheater, where the starch slurry contacts a jet of high temperature, high pressure steam (Fanta et al., 2002). The amount of steam is carefully controlled in the process to achieve complete steam condensation. This means that only little or no excess steam passes through the cooker.

In the excess steam jet cooking technique, the steam entering the hydroheater exceeds the amount required to achieve the required cooking temperature and pressure, thus allowing considerable amounts of excess steam to pass through the cooker along with the cooked starch solution. The intense turbulence caused by the passage of this excess steam promotes mechanical shearing and degradation of starch molecules, especially those having the highest molecular weight, and produces starch solutions with a reduced viscosity (Fanta et al., 2002, 1999b).

The high degree of turbulence and mechanical shear of the excess steam jet cooking process also converts the water-immiscible lubricant phase to a homogeneous aqueous dispersion of micrometer-sized oleaginous droplets. These unique, aqueous, starch-oil dispersions form the basis for lubricant compositions that are suitable for oil field applications.

An inherent property of starch pastes and solutions is their tendency to form gels on cooling, and this property is commonly referred to as retrogradation. The phenomenon is caused by aggregation of starch molecules through hydrogen bonding and crystallization. The tendency of starch solutions to retrograde and form gels increases with its amylose content, because amylose is a straight chain polymer with little or no branching.

Although retrogradation has also been observed in amylopectin solutions, it is much slower here, and is generally observed only after such solutions have been allowed to stand for prolonged periods of time (Fanta et al., 2002). The starch can be crosslinked with epichlorohydrin or phosphorus oxychloride (Sifferman et al., 2001, 2002).

Starch-oil compositions are prepared by mixing starch, water, and lubricating oil at room temperature, and then passing this mixture through an excess steam jet cooker. Alternatively, mixtures of starch and water are precooked in the steamcooker, and, after admixing the lubricating oil, the composition is again guided in a steamcooker.

For lubricant oils, a base olefin, a high molecular weight base olefin, a high molecular weight base olefin with ester, olefin blends with ester, or a viscous, liquid polybutene are used (Fanta et al., 2002). The resulting jet cooked compositions are stable with respect to separation and coagulation of oil droplets and are comprised of microscopic droplets of oil, about 1–10 μ in diameter, which are uniformly distributed in the starch-water phase (Fanta et al., 2002).

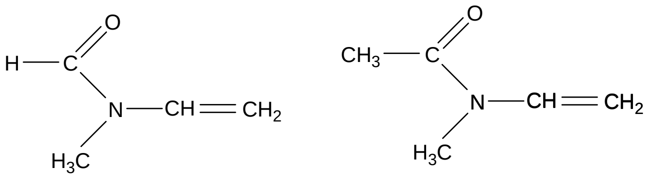
No emulsifying agents, dispersing agents, or surface active agents are used in the process. If the oil content is held within the preferred range of 20–40 phr, jet cooked compositions can be easily dried by drum drying. Outwardly dry, flake like products are obtained that can be easily reduced in size by milling. No separation of the oil from the dried starch matrix is observed.

These compositions can be easily dispersed in water to form smooth, stable, lump-free dispersions. Water dispersions do not phase separate into their oil and aqueous components on prolonged standing because of a thin layer or shell of starch that spontaneously forms around each oil droplet during the jet cooking process (Fanta et al., 1999a).

Preparation 4–1: The crosslinking of starch is achieved as follows (Sifferman et al., 2002): At room temperature, 1000 g of waxy maize starch is slurried in 1500 g of water. To the slurry, sodium hydroxide, as a 3% solution, is slowly added to reach a pH of 12. Then, 0.13% epichlorohydrin is added to the slurry. The reaction mixture is allowed to react at 40°C for completion, then cooled to room temperature, and neutralized to a pH of 6.0 with aqueous hydrochloric acid. Eventually the starch is filtered, washed, and dried to provide an ungelatinized dry powder. ■

TABLE 4.11 **Coefficients of Friction and Fluid Loss Values of Drilling Fluids Containing Starch Lubricant Composites (Fanta et al., 2002)**

	Friction		Fluid Loss	
Composition	**coeff. k**	**Reduction %**	**API ml**	**HTHP ml**
Base mud	0.3126	–	8.0	26
Field mud + 3% lubricant	0.2981	4.6	4.4	14
Base mud + starch composite with 0.5% high MW olefin	0.2732	12.6	3.1	12
Base mud + starch composite with 0.5% base olefin	0.2653	15.1	3.4	11
Base mud + starch composite with 0.5% high MW olefin + ester	0.2551	18.4	3.0	13
Base mud + starch composite with 0.5% base olefin + ester olefin copolymer	0.2473	20.9	3.2	12
Base mud + starch composite with 0.5% polybutene	0.1672	46.5	2.7	10


N-Vinylformamide

N-Vinyl-N-methylacetamide

FIGURE 4.6 Vinyl amide monomers.

Laboratory tests indicated that starch lubricant compositions lower both API and high temperature/high pressure fluid loss values. Results are represented in Table 4.11. The coefficients of friction are up to 45% lower than those of the untreated base muds; similar to those of OBMs. Only 0.5% of starch lubricant need be added to get satisfactory results (Sifferman et al., 2003).

Amides

This group of nitrogen-containing additives comprises phenolic Mannich bases, phosphoric acid (Umutbaev et al., 1993), and oxalkylated alkyl phenols with nitrogen containing additives (Koshelev et al., 1993). Vinyl amide monomers for synthetic muds are shown in Figure 4.6.

SPECIAL ISSUES

Side Reactions

Extensive laboratory work has been carried out to determine the performance of a number of lubricants including tests to determine the potential for formation damage of several types of drilling fluids, as well as the reduction in the friction coefficient.

Certain polymer additives are also effective as lubrications as a side effect, but in many cases, additional lubricants must be added for the fluid to be successful in drilling to the total intended depth (Knox and Jiang, 2005).

Lubricants for water-based drilling are primarily chosen for their technical performance and environmental acceptability. Hydrocarbons and fatty acids were used mostly in the past, but nowadays a trend to more environmentally acceptable alternatives can be seen, in particular to esters and naturally occurring vegetable oils.

These chemicals are highly lubricating materials as they significantly reduce the coefficients of friction of both metal/metal and metal/rock contacts in water-based fluid environments, by up to 70%. Clearly, effective additives exhibit a high degree of surface activity. This property improves their adhesion to the metal casing or the drilling mud solids. On the other hand, this surface activity makes the lubricants more prone to reacting with other components of the mud.

Lubricants may act as an emulsifier in the presence of even small quantities of oil. Such a composition may turn into an invert emulsion, with the consistency of cottage cheese (Knox and Jiang, 2005). Of course, such events are highly undesirable as the formation of a highly viscous material is definitely a drilling hazard, and the production zone may be damaged.

Apart from this, the lubricant may react with divalent or multivalent ions, forming the ionic bonds as found in ionomers. This reaction results in the formation of a grease-like precipitate, which may formed at concentrations of calcium or magnesium ions as low as 1000 ppm, depending on the chemical nature of the lubricant. Such ionic concentrations are frequently observed even in fresh water. All these issues must be taken into account in the selection of suitable lubricants for water-based drilling fluids (Knox and Jiang, 2005).

Silicate-Based Muds

Silicate-based muds are notorious for their high coefficient of friction against rock or metal in comparison to oil or synthetic-based muds. However, the latter cause environmental concerns, and in certain locations it is not allowed to drill using lower friction muds. Thus, silicate-based muds are preferred for environmental reasons (Albrecht et al., 2008).

Synthetic muds are also more expensive than silicate-based muds. So it is desirable to lower the coefficients of friction of these muds in order to increase the drilling rates.

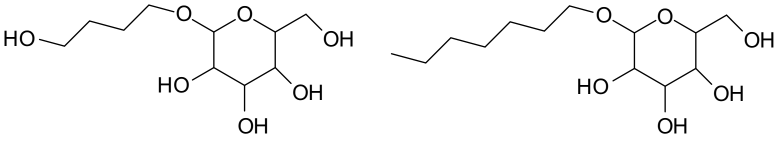
Suitable lubricants can be selected from glycosides, which may be functionalized. The amount of lubricant is typically in the range of 1–15%. Specific examples of glycosides are listed in Table 4.12, and the structure of glucopyranosides is shown in Figure 4.7.

Preparation 4–2: The preparation of alkylated an glucoside is basically an etherification. It can be performed by dissolving dry HCl in the respective alcohol. To this mixture, the glucose is added and allowed to react for 12 h (Brown et al., 1970). Then the glucoside is extracted with ethyl acetate. After drying, the major portion of the solvent is removed. The glucoside is somewhat reluctant to crystallize. ■

Alkylated polyglucosides act as surfactants in microemulsions (Ryan and Kaler, 2001). Microemulsions are thermodynamically stable, isotropic mixtures containing water, oil, and surfactant. They are utilized in a variety of industrial applications besides oil field applications, e.g., in solvent delivery, and polymerization techniques (Hill et al., 1997; Kjellin and Johansson, 2010; Ryan and Kaler, 2001).

TABLE 4.12 Glycoside Lubricants for Silicate-based Muds (Albrecht et al., 2008)

Glycoside
4-Hydroxybutyl-*D*-glucopyranoside
4-Aminobutyl-glycosides-*D*-glucopyranoside
Hexadecylphosphato-*D*-glucopyranoside
Trimethylammoniumcarboxymethyl-*D*-glucopyranoside
Triethylene-oxynonyl-*D*-glucopyranoside
4-Hydroxy propylcarboxy-*D*-glucopyranoside
Stearyl-*D*-glucopyranoside



4-Hydroxybutyl-glucopyranoside

n-Heptyl-glucopyranoside

FIGURE 4.7 Glucopyranosides.

Studies on Pipe Sticking

A study of the effect of various additives on pipe sticking is available (Pandey and Joshi, 1995), which investigates the effect of various available oil field additives in reducing downhole friction and their optimal concentration. As previously mentioned, the frictional forces present at the string-borehole interface are of prime importance. The friction at the string-borehole interface can be reduced through various chemicals incorporated in the drilling fluid system.

To obtain a mud cake in which sensitivity of various chemicals could be studied, a highly sticky cake was prepared from mud containing gypsum, kaolinite, sand, and shale powder. The ability of various mud additives to minimize friction at the string borehole interface, and thereby reduce the sticking tendency, was evaluated systematically with time. The study was extended to several mud systems.

Differential Sticking Reducer

Various additives have been proposed to assist in freeing a stuck drill pipe, the most common of which is diesel oil, added directly to the drilling mud as a spotting fluid. However, this is not always successful.

An additive comprising an oil-in-water microemulsion has been proposed. Sodium dodecyl benzene sulfonate may be used as a surfactant. Ethylene glycol or diethylene glycol act as cosurfactants (Davies et al., 1997).

REFERENCES

Albrecht, M.S., Cowan, K.M., McNeil III, R.I., Van Oort, E., Rock Sr. R.L., 2008. Silica-based drilling mud comprising glycoside lubricants with amino-linked alkyl chains. US Patent 7 320 951, assigned to Shell Oil Company, Houston, TX, January 22, 2008.

Alonso-Debolt, M.A., Bland, R.G., Chai, B.J., Eichelberger, P.B., Elphingstone, E.A., 1995. Glycol and glycol ether lubricants and spotting fluids. WO Patent 9 528 455, assigned to Baker Hughes Inc., October 26, 1995.

Alonso-Debolt, M.A., Bland, R.G., Chai, B.J., Elchelberger, P.B., Elphingstone, E.A., 1999. Glycol and glycol ether lubricants and spotting fluids. US Patent 5 945 386, assigned to Baker Hughes Inc., August 31, 1999.

Andreson, B.A., Abdrakhmanov, R.G., Bochkarev, G.P., Umutbaev, V.N., Fryazinov, V.V., Kudinov, V.N., Valiakhmetov, F.M., 1992. Lubricating additive for water-based drilling solutions – contains products of condensation of monoethanolamine and tall oils, kerosene, monoethanolamine and flotation reagent. SU Patent 1 749 226, assigned to Bashkir Oil Ind. Res. Inst. and Bashkir Oil Proc. Inst., July 23, 1992.

Anderson, C.P., Blenkinsopp, S.A., Cusack, F.M., Costerton, J.W., 1991. Drilling mud fluid loss – an alternative to expensive bulk polymers. In: Proceedings Volume, 4th Institute of Gas Technology, Gas, Oil, & Environmental Biotechnology International Symposium, Colorado Springs, CO, December 9–11, 1991, pp. 481–489.

Argillier, J.F., Audibert, A., Marchand, P., Demoulin, A., Janssen, M., 1997. Lubricating composition including an ester-use of the composition and well fluid including the composition. US Patent 5 618 780, assigned to Inst. Francais Du Petrole, April 8, 1997.

Argillier, J.F., Demoulin, A., Audibert-Hayet, A., Janssen, M., 1999. Borehole fluid containing a lubricating composition – method for verifying the lubrification of a borehole fluid–application with respect to fluids with a high ph (fluide de puits comportant une composition lubrifiante – procede pour controler la lubrification d'un fluide de puits - application aux fluides a haut ph). WO Patent 9 966 006, assigned to Inst. Francais Du Petrole and Fina Research SA, December 23, 1999.

Argillier, J.-F., Demoulin, A., Audibert-Hayet, A., Janssen, M., 2004. Borehole fluid containing a lubricating composition–method for verifying the lubrification of a borehole fluid–application with respect to fluids with a high ph. US Patent 6 750 180, assigned to Institut Francais du Petrole, Rueil-Malmaison Cedex, FR, Oleon NV, Ertvelde, BE, June 15, 2004.

Audebert, R., Janca, J., Maroy, P., Hendriks, H., 1994. Chemically crosslinked polyvinyl alcohol (pva), process for synthesizing same and its applications as a fluid loss control agent in oil fluids. GB Patent 2 278 359, assigned to Sofitech NV, November 30, 1994.

Audebert, R., Janca, J., Maroy, P., Hendriks, H., 1996. Chemically crosslinked polyvinyl alcohol (pva), process for synthesizing same and its applications as a fluid loss control agent in oil fluids. CA Patent 2 118 070, assigned to Schlumberger Canada Ltd., April 14, 1996.

Audebert, R., Maroy, P., Janca, J., Hendriks, H., 1998. Chemically crosslinked polyvinyl alcohol (pva), and its applications as a fluid loss control agent in oil fluids. EP Patent 705 850, assigned to Sofitech NV, September 2, 1998.

Audibert, A., Argillier, J.F., 1995. Thermal stability of sulfonated polymers. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, San Antonio, February 14–17, 1995, pp. 81–91.

Audibert, A., Argillier, J.F., 1996. Process and water-based fluid utilizing hydrophobically modified guar gums as filtrate (loss) reducer (procede et fluide a base d'eau utilisant des guars modifies hydrophobiquement comme reducteur de filtrat). EP Patent 722 036, assigned to Inst. Francais Du Petrole, July 17, 1996.

Audibert, A., Argillier, J.F., 1998. Process and water-base fluid utilizing hydrophobically modified guars as filtrate reducers. US Patent 5 720 347, assigned to Inst. Francais Du Petrole, February 24, 1998.

Audibert, A., Argillier, J.F., Bailey, L., Reid, P.I., 1995. Procedure and water-based fluid utilizing hydrophobically modified cellulose derivatives as filtrate reducer (fluide de traitement de puits de forage utilisant des derives cellulosiques modifies hydrophobiquement comme reducteur de filtrat, et procede d'utilisation). EP Patent 670 359, assigned to Inst. Francais Du Petrole and Sofitech NV, September 6, 1995.

Audibert, A., Argillier, J.F., Bailey, L., Reid, P.I., 2000. Process and water-base fluid utilizing hydrophobically modified cellulose derivatives as filtrate reducers. US Patent 6 040 276, assigned to Inst. Francais Du Petrole, March 21, 2000.

Bailey, L., 2001a. Latex additive for water-based drilling fluids. GB Patent 2 351 986, assigned to Sofitech NV, January 17, 2001.

Bailey, L., 2001b. Latex additive for water-based drilling fluids. WO Patent 0 104 232, assigned to Sofitech NV, January 18, 2001.

Bel, S.L.A., Demin, V.V., Kashkarov, N.G., Konovalov, E.A., Sidorov, V.M., Bezsolitsen, V.P., Gorjacheva, M.V., Gorlov, S.G., Ivchenko, A.M., Mal, T.L.S., Mojsa, Y.N., 1998. Lubricating composition – for treatment of clayey drilling solutions, contains additive in form of sulphonated fish fat. RU Patent 2 106 381, assigned to Shchelkovsk Agro Ent St C and Fakel Res. Prod. Assoc., March 10, 1998.

Bernu, C.J., 1998. High temperature stable modified starch polymers and well drilling fluids employing same. EP Patent 852 235, assigned to Chemstar Products Co., July 8, 1998.

Breeden, D.L., Meyer, R.L., 2005. Ester-containing downhole drilling lubricating composition and processes therefor and therewith. US Patent 6 884 762, assigned to Newpark Drilling Fluids, L.L.C., Houston, TX, April 26, 2005.

Brown, G.M., Dubreuil, P., Ichhaporiaa, F.M., Desnoyers, J.E., 1970. Synthesis and properties of some α-*D*-alkyl glucosides and mannosides: Apparent molal volumes and solubilization of nitrobenzene in water at 25°C. Can. J. Chem. 48, 2525–2531.

Buyanovskii, I.A., 1994. Tribological test methods and apparatus. Chem. Technol. Fuels Oils 30 (3), 133–147.

Chanshev, R.F., Kovtunenko, S.V., Tsikunkov, F.D., Ismakov, R.A., Konesev, G.V., Mulyukov, R.A., 1992. Lubricant for cutter bit bearings – contains ethylene-propylene synthetic rubber, zinc dioctyl- phenyl dithio-phosphate, polytetrafluoroethylene and mineral oil. SU Patent 1 778 162, November 30, 1992.

Chapman, J., Ward, I., 1997. Lubricant for drilling mud. EP Patent 0 770 661, assigned to Mud B W Ltd., May 2, 1997.

Clark, D.E., Dye, W.M., 1997. Environmentally safe lubricated well fluid method of making a well fluid and method of drilling. US Patent 5 658 860, assigned to Baker Hughes Inc., August 19, 1997.

Cobianco, S., Bartosek, M., Guarneri, A., 2001. Non-damaging drilling fluids. EP Patent 1 104 798, assigned to Eni SPA and Enitecnologie SPA, June 6, 2001.

Davies, S.N., Meeten, G.H., Way, P.W., 1997. Water based drilling fluid additive and methods of using fluids containing additives. US Patent 5 652 200, assigned to Schlumberger Technol. Corp., July 29, 1997.

Delton, R.M., Hooper, M., 1994. Rock bit grease composition. GB Patent 2 276 884, assigned to Smith International Inc., October 12, 1994.

Denton, R.M., Fang, Z., 1996. Rock bit grease composition. US Patent 5 589 443, assigned to Smith International Inc., December 31, 1996.

Denton, R.M., Lockstedt, A.W., 2006. Rock bit with grease composition utilizing polarized graphite. US Patent 7 121 365, assigned to Smith International, Inc., Houston, TX, October 17, 2006.

Denton, R., Lockstedt, A.W., White, A.C. 2007. Drill bit lubricant with enhanced load carrying/anti wear properties. US Patent 7 267 183, assigned to Smith International, Inc., Houston, TX, September 11, 2007.

Dixon, J., 2008. Drilling fluids. US Patent 7 343 986, assigned to Croda International PLC, Goole, East Yorkshire, GB, March 18, 2008.

Dixon, J., 2009. Drilling fluids. US Patent 7 614 462, assigned to Croda International PLC, Goole, East Yorkshire, GB, November 10, 2009.

Dreveton, E., Lecourtier, J., Ballerini, D., Choplin, L., 1995. Process utilizing gellan as filtrate reducer for water-based drilling fluids (procede utilisant le gellane comme reducteur de filtrat pour les fluides de forage a base d'eau). EP Patent 662 563, assigned to Inst. Francais Du Petrole, July 12, 1995.

Dreveton, E., Lecourtier, J., Ballerini, D., Choplin, L., 1998. Process using gellan as a filtrate reducer for water-based drilling fluids. US Patent 5 744 428, assigned to Inst. Francais Du Petrole, April 28, 1998.

Durr Jr., A.M., Huycke, J., Jackson, H.L., Hardy, B.J., Smith, K.W., 1994. An ester base oil for lubricant compounds and process of making an ester base oil from an organic reaction by-product. EP Patent 606 553, assigned to Conoco Inc., July 20, 1994.

Dye, W., Clark, D.E., Bland, R.G., 1995. Well fluid additive. EP Patent 652 271, assigned to Baker Hughes Inc., May 10, 1995.

Enright, D.P., Dye, W.M., Smith, F.M., Perricone, A.C., 1991. Drilling fluid methods and composition. US Patent 5 007 489, assigned to Baker Hughes Inc., April 16, 1991.

Estes, B.L., Bernu, C.J., 1999. New and improved drilling fluids and additives therefor. WO Patent 9 951 701, assigned to Dresser Industries Inc., October 14, 1999.

Fang, Z., Peterson, S., Denton, R., 1998. O-ring seal with lubricant additives for rock bit bearings. GB Patent 2 318 139, assigned to Smith International Inc., April 15, 1998.

Fanta, G.F., Felker, F.C., Eskins, K., Baker, F.L., 1999a. Aqueous starch-oil dispersions prepared by steam jet cooking. Starch films at the oil-water interface. Carbohydr. Polym. 39 (1), 25–35.

Fanta, G.F., Muijs, H.M., Eskins, K., Felker, F.C., Erhan, S.M., 2002. Starch-containing lubricant systems for oil field applications. US Patent 6 461 999, assigned to The United States of America as represented by the Secretary of Agriculture (Washington, DC) Shrieve Chemical Products, The Woodlands, TX, October 8, 2002.

Fanta, G.F., Shogren, R.L., Salch, J.H., 1999b. Steam jet cooking of high-amylose starch-fatty acid mixtures. An investigation of complex formation. Carbohydr. Polym. 38 (1), 1–6.

Fisk Jr., J.V., Kerchevile, J.D., Pober, K.W., 2006. Silicic acid mud lubricants. US Patent 6 989 352, assigned to Halliburton Energy Services, Inc. Duncan, OK, January 24, 2006.

Fleury, M., Branlard, P., Lenormand, R., Zarcone, C., 1999. Intermediate wettability by chemical treatment. J. Pet. Sci. Eng. 24 (2–4), 123–130.

Forsberg, J.W., Jahnke, R.W., 1993a. Methods of drilling well boreholes and compositions used therein. US Patent 5 260 268, assigned to Lubrizol Corp., November 9, 1993.

Forsberg, J.W., Jahnke, R.W., 1993b. Methods of drilling well boreholes and compositions used therein. WO Patent 9 302 151, assigned to Lubrizol Corp., February 4, 1993.

Frolov, M.A., Molyavko, I.V., Spivak, A.I., Rakhmankulov, D.L., Rakhmatullin, V.R., Romanov, N.A., 1993. Lubricant for friction pairs working under heavy loads – contains mineral oil and additive in form of 2,4,8,10-tetra-oxaspiro-(5,5)-undecane, to improve anti-wear and antiscratch properties. SU Patent 1 817 788, assigned to Borehole Drill Constr. Tech., May 23, 1993.

Gao, J., Guo, D., Li, J., Qiu, Z., 1993. The synthesis and properties of high temperature filtrate reducer, aps. Drill. Fluid Completion Fluid 10 (1), 21–23,74.

Garyan, S.A., Kuznetsova, L.P., Moisa, Y.N., 1998. Experience in using environmentally safe lubricating additive fk-1 in drilling muds during oil and gas well drilling. Stroit Neft Gaz Skvazhin Sushe More (10), 11–14.

Genuyt, B., Janssen, M., Reguerre, R., Cassiers, J., Breye, F., 2001. Biodegradable lubricating composition and uses thereof, in particular in a bore fluid [composition lubrifiante biodegradable et ses utilisations, notamment dans un fluide de forage]. WO Patent 0 183 640, assigned to Total Raffinage Dist SA, November 8, 2001.

Genuyt, B., Janssen, M., Reguerre, R., Cassiers, J., Breye, F., 2006. Biodegradable lubricating composition and uses thereof, in particular in a bore fluid. US Patent 7 071 150, assigned to Total Raffinage Distribution S.A., Puteaux, FR, July 4, 2006.

Goncharov, S.V., Neradovskij, V.V., Zevakov, M.E., Babets, M.A., Bektimirov, E.I., Bezdenezhnykh, V.I., Shmavonyants, V.S., 1993. Sealing lubricant for profiled joints of e.g. casing strings – contains silico-organic liquid, diethylene glycol, graphite powder, mixture of derivatives of synthetic fatty acids and solution of polyacrylamide. SU Patent 1 796 648, February 23, 1993.

Halliday, W.S., Clapper, D.K., 1998. Purified paraffins as lubricants, rate of penetration enhancers, and spotting fluid additives for water-based drilling fluids. US Patent 5 837 655, November 17, 1998.

Halliday, W.S., Schwertner, D., 1997. Olefin isomers as lubricants, rate of penetration enhancers, and spotting fluid additives for water-based drilling fluids. US Patent 5 605 879, assigned to Baker Hughes Inc., February 25, 1997.

Hanahan, D.J., 1997. A Guide to Phospholipid Chemistry. Oxford University Press, New York.

Heier, K.H., Morschhaeuser, R., Tardi, A., Weber, S., Botthof, G., 2002. Copolymers and their use as drilling aids. US Patent 6 380 137, assigned to Clariant GmbH, April 30, 2002.

Hen, J., 1991. Sulfonate-containing polymer/polyanionic cellulose combination for high temperature/high pressure filtration control in water base drilling fluids. US Patent 5 008 025, assigned to Mobil Oil Corp., April 16, 1991.

Hill, K., Rybinski, W., Stoll, G., 1997. Alkyl Polyglycosides: Technology, Properties, and Applications. Wiely VCH, New York.

Hille, M., Wittkus, H., Tonhauser, J., Engelhardt, F., Riegel, U., 1996. Water-soluble copolymers useful in drilling fluids. US Patent 5 510 436, assigned to Hoechst AG, April 23, 1996.

Holinski, R., 1995. Solid lubricant composition. US Patent 5 445 748, assigned to Dow Corning GmbH, Wiesbaden, DE, August 29, 1995.

Huddleston, D.A., Williamson, C.D., 1990. Vinyl grafted lignite fluid loss additives. US Patent 4 938 803, assigned to Nalco Chemical Co., July 3, 1990.

Huddleston, D.A., Williamson, C.D., 1991. Vinyl grafted lignite fluid loss additives. US Patent 5 028 271, assigned to Nalco Chemical Co., July 2, 1991.

Kalashnikov, Y.T., 1994. Lubricant-sealer for profiled joints of casing pipes - contains soap plastic lubricant, polyacrylamide or carboxymethyl cellulose and additionally gypsum or cement powder, to increase sealing rate. RU Patent 2 007 438, February 15, 1994.

Kashkarov, N.G., Konovalov, E.A., Vjakhirev, V.I., Gnoevykh, A.N., Rjabokon, A.A., Verkhovskaja, N.N., 1998. Lubricant reagent for drilling muds - contains spent sunflower oil, and light tall oil and spent coolant-lubricant as modifiers. RU Patent 2 105 783, assigned to Tyumen Nat Gases Res. Inst., February 27, 1998.

Kashkarov, N.G., Verkhovskaya, N.N., Ryabokon, A.A., Gnoevykh, A.N., Konovalov, E.A., Vyakhirev, V.I., 1997. Lubricating reagent for drilling fluids – consists of spent sunflower oil modified with additive in form of aqueous solutions of sodium alkylsiliconate(s). RU Patent 2 076 132, assigned to Tyumen Nat Gases Res. Inst., March 27, 1997.

Kjellin, M., Johansson, I. (Eds.), 2010. Surfactants from Renewable Resources. Wiley, Chichester, West Sussex.

Knox, D., Jiang, P., 2005. Drilling further with water-based fluids – selecting the right lubricant. In: Proceedings Volume, no. 92002-MS, International Symposium on Oilfield Chemistry, Society of Petroleum Engineers, Inc., The Woodlands, TX, 2005.

Kok, S.J., Guns, J., Kraan, L.C., Schuringa, G.E., Kesselmans, R.P.W., 1999a. Drilling fluids. WO Patent 9 952 990, assigned to Coop Verkoop Prod. Aard De, October 21, 1999.

Kok, S.J., Kraan, L.C., Schuringa, G.E., Guns, J., Kesselmans, R.P.W., 1999b. Drilling fluids. EP Patent 949 311, assigned to Coop Verkoop Prod. Aard De, October 13, 1999.

Koltermann, T.J., Willey, T.F., 1999. Lubricating grease. US Patent 5 891 830, assigned to Baker Hughes Inc., April 6, 1999.

Koltermann, T.J., Willey, T.F., 2000. Lubricating grease. US Patent 6 056 072, assigned to Baker Hughes Inc., May 2, 2000.

Konovalov, E.A., Ivanov, Y.A., Shumilina, T.N., Pichugin, V.F., Komarova, N.N., 1993a. Lubricating reagent for drilling solutions – contains agent based on spent sunflower oil, water, vat residue from production of oleic acid, and additionally water glass. SU Patent 1 808 861, assigned to Moscow Gubkin Oil Gas Inst., April 15, 1993.

Konovalov, E.A., Rozov, A.L., Zakharov, A.P., Ivanov, Y.A., Pichugin, V.F., Komarova, N.N., 1993b. Lubricating reagent for drilling solutions – contains spent sunflower oil as active component, water, boric acid as emulsifier, and additionally water glass. SU Patent 1 808 862, assigned to Moscow Gubkin Oil Gas Inst., April 15, 1993.

Koshelev, V.N., Krezub, A.P., Ponomarev, D.M., Mojsa, Y.N., Frolova, N.V., Penkov, A.I., Vasilchenko, S.V., 1993. Drilling solution with improved lubricating and rheology – contains additionally oxyalkylated alkylphenol with nitrogen-containing additive, in aromatic solvent. SU Patent 1 797 617, assigned to Borehole Consolidation Mu., February 23, 1993.

Kurochkin, B.M., Kolesov, L.V., Biryukov, M.B., 1990. Use of ellipsoidal glass granules as an antifriction mud additive. Neft Khoz (12), 61–64.

Kurochkin, B.M., Kolesov, L.V., Masich, V.I., Stepanov, N.V., Tselovalnikov, V.F., Alekperov, V.T., Kerimov, I.N., Ibragimov, O.N., Bulanov, B.M., 1992a. Solution for drilling gas and oil wells – contains ellipsoidal glass beads as additive reducing friction between walls of well and casing string. SU Patent 1 740 396, assigned to Drilling Tech. Res. Inst., June 15, 1992.

Kurochkin, B.M., Simonyan, E.A., Simonyan, A.A., Khirazov, E.F., Ozarchuk, P.A., Voloshinivskii, V.O., Glushakov, A.Y., 1992b. New technology of drilling with the use of glass granules. Neft Khoz (7), 9–11.

Kurochkin, B.M., Tselovalnikov, V.F., 1994. Use of ellipsoidal glass granules for drilling under complicated conditions. Neft Khoz (10), 7–13.

Landry, D.K., Koltermann, T.J., 1991a. Bearing grease for rock bit bearings. CA Patent 2 018 779, assigned to Hughes Tool Co., March 18, 1991.

Landry, D.K., Koltermann, T.J., 1991b. Bearings grease for rock bit bearings. US Patent 5 015 401, assigned to Hughes Tool Co., May 14, 1991.

Langlois, B., 1999. Fluids useful for oil mining comprising de- acetylated xanthane gum and at least one compound increasing the medium ionic strength (fluides utilisables dans l'exploitation du petrole comprenant de la gomme xanthane desacetylee et au moins un compose augmentant la force ionique du milieu). WO Patent 9 903 948, assigned to Rhodia Chimie, January 28, 1999.

Li, Y.G., Li, S.L., Wang, Z.L., 1996. New high temperature filtration reducer fla for drilling fluid. Drill. Fluid Completion Fluid 13 (3), 33–35.

Liu, Y.Y., Hou, W.G., Sun, D.J., Wu, T., Zhang, C.G., 1996. Study on function mechanism of filtration reducer: Research and development of new filtration reducer. Drill. Fluid Completion Fluid 13 (4), 12–14.

Lyubinin, I.A., Gubarev, A.S., Butovets, V.V., Torgashov, A.V., 1995. Modern lubricants for roller bit bearings. Stroit Neft Gaz Skvazhin Sushe More (3), 14–25.

Matz, G.F., Melby, A.L., Loeffler, R.J., Vozza, N.F., Chen, S.R.T., 2001. Water soluble polymer composition and method of use. WO Patent 0 105 365, assigned to Calgon Corp., January 25, 2001.

Mensa-Wilmot, G., Garrett, R.L., Stokes, R.S., 1997. Pao (polyalphaolefin) lubricant inhibits bit balling, speeds drilling. Oil Gas J. 95 (16), 68–70.

Müller, H., Herold, C.P., Bongardt, F., Herzog, N., von Tapavicza, S., 2000. Lubricants for drilling fluids (schmiermittel fuer bohrspuelungen). WO Patent 0 029 502, assigned to Cognis Deutschland GmbH, May 25, 2000.

Müller, H., Herold, C.P., von Tapavicza, S., 1999a. Use of selected fatty alcohols and their mixtures with carboxylic acid esters as lubricant components in water-based drilling fluid systems for soil exploration (verwendung ausgewaehlter fettalkohole und ihrer abmischungen mit carbonsaeureestern als schmiermittelkomponente in wasserbasierten bohrspuelsystemen zum erdreichaufschluss). EP Patent 948 576, assigned to Henkel KG Auf Aktien, October 13, 1999.

Müller, H., Podubrin, S., Herold, C.P., Heidbreder, A., 1999b. Dispersions containing homopolymers or copolymers of hydroxy carboxylic acids as a rheological additive (dispersionen enthaltend homo- oder copolymere von hydroxycarbonsaeuren als rheologisches additiv). WO Patent 9 952 623, assigned to Cognis Deutschland GmbH, October 21, 1999.

Müller, H., Herold, C.-P., Bongardt, F., Herzog, N., von Tapavicza, S., 2004a. Lubricants for drilling fluids. US Patent 6 806 235, assigned to Cognis Deutschland GmbH & Co. KG, Duesseldorf, DE, October 19, 2004.

Müller, H., Herold, C.-P., von Tapavicza, S., 2004b. Use of selected fatty alcohols and their mixtures with carboxylic acid esters as lubricant components in water-based drilling fluid systems for soil exploration. US Patent 6 716 799, assigned to Cognis Deutschland GmbH & Co. KG, Duesseldorf, DE, April 6, 2004.

Müller, H., Herold, C.-P., von Tapavicza, S., Neuss, M., Zoellner, W., Burbach, F., 1990. Esters of medium chain size carboxylie acids as components of the oil phase of invert emulsion drilling fluids. EP Patent 0 386 636, assigned to Henkel KGAA, September 12, 1990.

Nakaya, T., Li, Y.-J., 1999. Phospholipid polymers. Prog. Polym. Sci. 24 (1), 143–181.

Naraghi, A.R., Rozell, R.S., 1996. Method for reducing torque in downhole drilling. US Patent 5 535 834, assigned to Champion Technologies, July 16, 1996.

Navarrete, R.C., Seheult, J.M., Coffey, M.D., 2001. New biopolymers for drilling, drill-in, completions, spacer, and coil-tubing fluids: Pt. 2. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, Houston, TX, February 13–16, 2001.

Navarrete, R.C., Shah, S.N., 2001. New biopolymer for coiled tubing applications. In: Proceedings Volume, SPE/International Coiled Tubing Association, Coiled Tubing Roundtable, Houston, TX, March 7–8, 2001.

Newcomb, A.L., 1982. Composite grease for rock bit bearings. US Patent 4 358 384, assigned to Smith International Inc., Newport Beach, CA, November 9, 1982.

Oldiges, D.A., Joseph, A.W., 2003. Methods for using environmentally friendly antiseize/lubricating systems. US Patent 6 620 460, assigned to Jet-Lube, Inc., Houston, TX, September 16, 2003.

Oldiges, D., McDonald, H., Blake, T., 2007. Use of calcium sulfonate based threaded compounds in drilling operations and other severe industrial applications. US Patent 7 294 608, assigned to Jet-Lube, Inc., DE, November 13, 2007.

Oldiges Jr., D.A., McDonald, H., Blake, T., Stroup, K., Oldiges III, D.A., 2006. Non-metallic thread sealant and anti-seize compound having improved anti-galling properties for metal alloys. US Patent 7 091 161, assigned to Jet-Lube, Inc., Houston, TX, August 15, 2006.

Olson, W.D., Muir, R.J., Eliades, T.I., Steib, T., 1994. Sulfonate greases. US Patent 5 308 514, assigned to Witco Corporation, New York, May 3, 1994.

Oswald, R.J., Morschhaeuser, R., Heier, K.H., Tardi, A., Tonhauser, J., Kayser, C., Patterson, D., 2000. Water-soluble copolymers and their use for the exploration and recuperation of oil and gas. EP Patent 1 059 316, assigned to Clariant GmbH, December 13, 2000.

Pandey, A.K., Joshi, N.P., 1995. Effectivity of additives in reducing down hole friction and preventing sticking. In: Proceedings Volume, Vol. 3, 1st India Oil & Natural Gas Corporation Ltd et International Petroleum Conference, Petrotech 95, New Delhi, India, January 9–12, 1995, pp. 45–54.

Patel, A.D., 1997. Silicone based fluids for drilling applications. EP Patent 764 709, assigned to M I Drilling Fluids LLC., March 26, 1997.

Patel, A.D., 1998. Water-based drilling fluids with high temperature fluid loss control additive. US Patent 5 789 349, assigned to M I Drilling Fluids LLC., August 4, 1998.

Patel, B.B., 2000. Drilling fluid additive and process therewith. WO Patent 0 020 527, assigned to Phillips Petroleum Co., April 13, 2000.

Patel, A.D., Davis, E., Young, S., Stamatakis, E., 2006. Phospholipid lubricating agents in aqueous based drilling fluids. US Patent 7 094 738, assigned to M-I L.L.C., Houston, TX, August 22, 2006.

Patel, A.D., McLaurine, H.C., 1991. Drilling fluid additive. EP Patent 427 107, assigned to M I Drilling Fluids Co., May 15, 1991.

Penkov, A.I., Vakhrushev, L.P., Belenko, E.V., 1999. Characteristics of the behavior and use of polyalkylene glycols for chemical treatment of drilling muds. Stroit Neft Gaz Skvazhin Sushe More (1–2), 21–24.

Plank, J., 1993. Drilling mud composition and process for reducing the filtrate of metal hydroxide mixtures containing drilling mud compositions. WO Patent 9 312 194, assigned to Skw Trostberg AG, June 24, 1993.

Rudnick, L.R., (Ed.), 2006. Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology, Vol. 111 of Chemical Industries. Taylor & Francis, Boca Raton.

Runov, V.A., Mojsa, Y.N., Subbotina, T.V., Pak, K.S., Krezub, A.P., Pavlychev, V.N., Istomin, N.N., Evdokimova, Z.A., Borzenko, V.I., 1991. Lubricating additive for clayey drilling solution - is obtained by esterification of tall oil or tall pitch with hydroxyl group containing agent, e.g. low mol. wt. glycol or ethyl cellulose. SU Patent 1 700 044, assigned to Volgo Don Br. Sintez Pav and Burenie Sci Prod. Assoc., December 23, 1991.

Runov, V.A., Subbotina, T.V., Mojsa, Y.N., Krezub, A.P., Samotoj, A.K., Morgunov, A.N., 1992. Lubricant additive for clayey drilling muds – contains chalk, carbon black or graphite as mineral component, and glycol ester(s) of synthetic higher fatty acids as organic component. SU Patent 1 726 491, assigned to Volgo Don Br. Sintez Pav and Burenie Sci Prod. Assoc., April 15, 1992.

Ryan, L.D., Kaler, E.W., 2001. Alkyl polyglucoside microemulsion phase behavior. Colloids Surf. A 176 (1), 69–83.

Ryzhov, V.M., Mironyuk, V.S., Mazepa, T.Y., Muravev, V.V., 1996. Controlling water absorption of drilling solution – based on carboxymethyl cellulose, involves introduction of sodium and-or potassium chloride into aqueous solution of carboxymethyl cellulose. RU Patent 2 066 684, September 20, 1996.

Sano, M., 1997. Polypropylene glycol (PPG) used as drilling fluids additive. Sekiyu Gakkaishi 40 (6), 534–538.

Selikhanovich, A.M., Chuprina, G.A., Olejnikov, A.N., 1997. Reagent for treating drilling muds – contains acrylic polymer, sodium hydroxide, additional diethylene glycol, and water. RU Patent 2 087 515, assigned to Volgo Urals Hydrogen Gas, August 20, 1997.

Senaratne, K.P.A., Lilje, K.C., 1994. Preparation of branched chain carboxylic esters. US Patent 5 322 633, assigned to Albemarle Corp., June 21, 1994.

Sifferman, T.R., Muijs, H.M., Fanta, G.F., Felker, F.C., Erhan, S.M., 2003. Starch-lubricant compositions for improved lubricity and fluid loss in water-based drilling muds. In: Proceedings Volume, no. 80213-MS, International Symposium on Oilfield Chemistry, Society of Petroleum Engineers, Inc., Houston, TX, 2003.

Sifferman, T.R., Swazey, J.M., Skaggs, C.B., Nguyen, N., Solarek, D.B., 1999. Fluid loss control additives and subterranean treatment fluids containing the same. WO Patent 9 905 235, assigned to Monsanto Co. and Natl. Starch Chem. Inv. Corp., February 4, 1999.

Sifferman, T.R., Swazey, J.M., Skaggs, C.B., Nguyen, N., Solarek, D.B., 2001. Fluid loss control additives and subterranean treatment fluids containing the same. US Patent 6 180 571, assigned to Monsanto Company, St. Louis, MO, National Starch and Chemical Investment Holding Corporation, Wilmington, DE, January 30, 2001.

Sifferman, T.R., Swazey, J.M., Skaggs, C.B., Nguyen, N., Solarek, D.B., 2002. Method of controlling loss of a subterranean treatment fluid. US Patent 6 492 305, assigned to CP Kelco U.S., Inc., Wilmington, DE, National Starch and Chemical Investment Holding Corporation, Wilmington, DE, December 10, 2002.

Sopko, T.M., Lorentz, R.E., 1991. Method of using polymers of amido-sulfonic acid containing monomers and salts as drilling additive. US Patent 5 039 433, assigned to Lubrizol Corp., August 13, 1991.

ASTM, 2009. Standard test methods for measurement of extreme pressure properties of fluid lubricants (falex pin and vee block methods). ASTM Standard, Book of Standards, Vol. 5.01 ASTM D 3233(93). ASTM International, West Conshohocken, PA.

ASTM, 2008. Standard test method for measurement of extreme-pressure properties of lubricating fluids (timken method). ASTM Standard, Book of Standards, Vol. 5.01 ASTM D 2782-02. ASTM International, West Conshohocken, PA.

Stephens, M., Swanson, B.L., 1992. Drilling mud comprising tetrapolymer consisting of *N*-vinyl-2-pyrrolidone, acrylamidopropanesulfonic acid, acrylamide, and acrylic acid. US Patent 5 135 909, assigned to Phillips Petroleum Co., August 4, 1992.

Tan, D., 1990. Test and application of drilling fluid filtrate reducer polysulfonated humic acid resin. Oil Drill. Prod. Technol. 12 (1), 27–32, 97–98.

Totten, G.E., Westbrook, S.R., Shah, R.J. (Eds.), 2003. Fuels and Lubricants Handbook: Technology, Properties, Performance, and Testing, Vol. 37 of ASTM Manual Series. American Society for Testing & Materials (ASTM), West Conshohocken, PA.

Udarbe, R.G., Hancock-Grossi, K., George, C.R., 2000. Method of and additive for controlling fluid loss from a drilling fluid. US Patent 6 107 256, assigned to Fritz Industries Inc., August 22, 2000.

Umutbaev, V.N., Kamaletdinov, M.G., Andreson, B.A., Abdrakhmanov, R.G., Sharipov, A.U., Utyaganov, I.V., 1993. Lubricant additive for water-based drilling muds – contains a mixture of phenolic mannich bases, additional phosphoric acid and water. SU Patent 1 799 895, assigned to Bashkir Oil Ind. Res. Inst., March 7, 1993.

Wall, K., Martin, D.W., Zard, P.W., Barclay-Miller, D.J., 1995a. Temperature stable synthetic oil. WO Patent 9 532 265, assigned to Burwood Corp. Ltd., November 30, 1995.

Wall, K., Zard, P.W., Barclay-Miller, D.J., Martin, D.W., 1995b. Amide and imide compounds and their use as lubricant oils. WO Patent 9 530 643, assigned to Burwood Corp. Ltd., November 16, 1995.

Wang, Z., 1999. Synthesis of AMPS/AM (acrylamide)/VAC (vinyl acetate) copolymer – a filtration reducer of drilling fluid. Drill. Prod. Technol. 22 (4), 55–56, 4A.

Willey, T.F., Willey, R.J., Willey, S.T., 2007. Rock bit grease composition. US Patent 7 312 185, assigned to Tomlin Scientific Inc. Santa Ana, CA, December 25, 2007.

Zaleski, P.L., Derwin, D.J., Weintritt, D.J., Russell, G.W., 1998. Drilling fluid loss prevention and lubrication additive. US Patent 5 826 669, assigned to Superior Graphite Co., October 27, 1998.

TRADENAMES

TABLE 4.13 Tradenames in References

Tradename Description	Supplier
Aldacide® G Biocide, glutaraldehyde (Fisk et al., 2006)	Halliburton Energy Services, Inc.
AquaPAC® Polyanionic cellulose (Sifferman et al., 2001, 2002)	Aqualon Corp.
BARASIL® S Sodium silicate shale stabilizer (Fisk et al., 2006)	Halliburton Energy Services, Inc.
BIOZAN® Heteropolysaccaride (Fisk et al., 2006)	Merck
COLALIPID™ (Series) Quaternized amines (Patel et al., 2006)	Colonial Chemical, Inc.
COLALIPID™ RC Ricinoleamidopropyl PG-dimonium chloride phosphate (Patel et al., 2006)	Colonial Chemical, Inc.
Finagreen® BMDF 2-ethyl hexanol fatty acid esters (Genuyt et al., 2006)	Petrofina S.A.
Hatcol™ 2372 Polyol ester of dipentaerythritol (Willey et al., 2007)	Hatco Corp. of Fords, N.J.
Hatcol™ 2926 Polyol ester of dipentaerythritol (Willey et al., 2007)	Hatco Corp. of Fords, N.J.
Kopr-Kote® Aluminum complex lubricant with copper flakes (Oldiges et al., 2007)	Jet-Lube, Inc.
Lucant® HC-2000 Hydrocarbon-based nonpolar synthetic oil (Denton et al., 2007)	Mitsui Chemicals America, Inc.
Lucant® HC-600 Hydrocarbon-based nonpolar synthetic oil (Denton et al., 2007)	Mitsui Chemicals America, Inc.

TABLE 4.13 Tradenames in References–Cont'd

Tradename Description	Supplier
Retsch® ZM-1 Grinding mill (Fanta et al., 2002)	Retsch GmbH
Rev Dust Artificial drill solids (Fisk et al., 2006)	Milwhite, Inc.
Seppic SIMULSOL AS-48™ Alkylglucoside (Fisk et al., 2006)	Seppic
Spectrasyn ULTRA™ Grease formulation (Willey et al., 2007)	Exxon Mobil
Supersyn™ (Series) Lubricating oil (Willey et al., 2007)	Mobil Oil Corp., Union Carbide Corp.
Synalox® PB-200 Chain alcohols (Fisk et al., 2006)	Dow Chemical Comp.
Unirex S2® Zirconium 2-ethylhexanoate grease (Denton et al., 2007)	Exxon Mobil
XAN-PLEX™ D Polysaccharide viscosifying polymer (Fanta et al., 2002)	Baker Hughes INTEQ

Chapter 5

Bacterial Control

Major problems in oil and gas operations result from the biogenic formation of hydrogen sulfide (H_2S) in the reservoir, which results in increased corrosion and iron sulfide formation leading to higher operating costs and reduced revenue. The gas also constitutes a serious environmental and health hazard.

In secondary oil recovery, which involves waterflooding of the oil-containing formation, biofilms can plug the oil-bearing formation, and severe corrosion can result from the production of acids associated with the growth of certain bacterial biofilms. These biofilms are often composed of sulfate-reducing bacteria, which grow anaerobically in water, often in the presence of oil and natural gases. Once biofilms are established, it is extremely difficult to regain biological control of the system.

When biofilms are formed on metallic surfaces, they can seriously corrode oil production facilities. Microbiologically influenced corrosion represents the most serious form of that degradation, and it is estimated that this type of corrosion may be responsible for 15–30% of failures caused by corrosion across all industries.

Effective control of bacteria is therefore mandatory. Several biocides and together with nonbiocidal techniques are available, and procedures and techniques to detect bacteria have been developed.

MECHANISMS OF GROWTH

Growth of Bacteria Supported by Oil Field Chemicals

Growth experiments have been conducted using bacteria from oil installations with several chemicals normally used in injection water treatments. These studies have revealed that some chemicals utilized as nitrogen, phosphorus, or carbon sources by those bacteria (Sunde et al., 1990). Therefore, it was concluded that the growth potential of water treatment additives may be substantial and this aspect should be investigated during their selection.

Petroleum Engineer's Guide to Oil Field Chemicals and Fluids. DOI: 10.1016/B978-0-12-383844-5.00005-2

In other experiments it was established that the cultures of sulfate-reducing bacteria isolated from the waters around several oil fields have a greater capacity to form H_2S than the standard collection culture. The stimulating effect of a given chemical product can vary considerably, depending on the species, activity, and adaptation of bacteria to the chemical in question.

Cultures of sulfate-reducing bacteria acquire relative resistance to toxic compounds, as a result of adaptation, which require higher doses of bactericide than those calculated for laboratory collection cultures to suppress the vital activity of sulfate-reducing bacteria in the bottom hole zone and reservoir (Kriel et al., 1993).

It has been shown that sulfidogenic bacteria injected into a reservoir with floodwater may survive high temperatures in the formation and can be recovered from producing well fluids (Salanitro et al., 1993). These organisms may colonize cooler zones and sustain growth by degrading fatty acids in the formation waters.

Mathematical Models

A mathematical model for reservoir souring, as caused by the growth of sulfate-reducing bacteria, is available. The model is a one-dimensional numerical transport model based on conservation equations, and includes bacterial growth rates and the effect of nutrients, water mixing, transport, and adsorption of H_2S in the reservoir formation. The adsorption of H_2S by the rock has been considered. Two basic concepts for microbial H_2S production were tested with field data (Sunde et al., 1993):

- H_2S production in the mixing zone between formation water and injection water (mixing zone model), and
- H_2S production caused by the growth of sulfate-reducing bacteria in a biofilm in the reservoir rock close to the injection well (biofilm model).

Field data obtained from three oil producing wells on the Gullfaks field correlated with H_2S production profiles obtained using the biofilm model but could not be explained by the mixing zone model (Sunde et al., 1993).

Model of Colony Growth

The growth of bacteria with time in the presence of various amounts of copper sulfate is shown in Figure 5.1. The diameter of the colonies was used as an indicator of growth.

A simplified model of colony growth has been presented (Rodin et al., 2005). According to this model, during growth, a colony passes successively through exponential and linear phases of growth, with the exponential phase persisting unless the concentration of nutritious substrates becomes limited. The increase of colony diameter *d* during the exponential phase can be described as:

$$d = d_0 \exp\left(\frac{\mu'_m}{2} t\right). \tag{5.1}$$

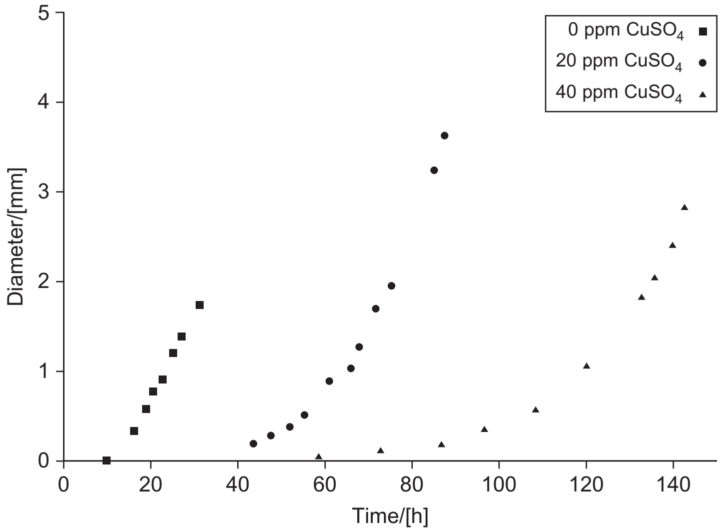


FIGURE 5.1 Effect of copper sulfate on the growth of *S. marcescens* colonies (Rodin et al., 2005).

Here d is the diameter of the colony at the incubation time t, d_0 is the effective diameter of the individual cell, the colony progenitor, and μ'_m is the maximal growth rate.

In contrast, the linear phase of growth occurs under conditions of limited nutrients; beginning at a time t_l, after which the colony diameter increases at a constant rate k_d according to:

$$d = d_{t_l} + k_d(t - t_l). \tag{5.2}$$

Eq. 5.1 and Eq. 5.2 can be combined to give:

$$t = \frac{d}{k_d} + \frac{2}{\mu'_m}\left[\ln\left(\frac{2k_d}{d_0\,\mu'_m}\right) - 1\right]. \tag{5.3}$$

Eq. 5.3 relates the key parameter of the exponential growth phase of an invisible microcolony with the parameters of the linear growth phase of the visible macrocolony. This property essentially simplifies the experimental determination of the parameter μ'_m (Rodin et al., 2005).

Detection of Bacteria

In oil field systems, the detection of living bacteria is necessary to evaluate the potential for microbially influenced corrosion, biogenic souring, and to evaluate the effectiveness of biocide treatment programs (Cowan, 2005). If methods of measurement of the bacteria present is insufficient then the dosages of biocide will be too low or too high.

Uncontrolled growth and activity of sulfate-reducing bacteria can create safety, environmental, and operational problems, such as microbially influenced corrosion, solids production, and biogenic hydrogen sulfide generation. Rapid enumeration of living bacteria would allow quick biocide treatments, so optimizing bacterial control and minimizing, the environmental impact of the chemical treatment.

Microbiologically influenced souring (MIS) is the production of H_2S through the metabolic activities of microorganisms. This problem is easier to control by using biocides if the problem is detected early in the souring process (Morris et al., 1994). However, if allowed to spread into the subsurface regions that are less accessible to biocides, i.e., profuse-stage MIS, the problem becomes more difficult to mitigate by conventional means.

API Serial Dilution Method

This is the most widely used method for the detection of microorganisms. Field test methods for estimating bacterial populations have been standardized, and a standard method dealing with the dose-response (time-kill) testing for evaluating biocides has been established. Effective sampling is essential to any successful analysis.

Enzymatic Assay

The enzymatic (luciferase) assay for adenosine triphosphate (ATP) is one method applied to biocidal control in oil production (Prasad, 1988). Measuring the bioluminescence produced by the luciferin luciferase system is known to be a reliable method for the determination of ATP.

Electrochemical Determination

An electrochemical method has been developed to allow on-line monitoring of biofilm activity in aqueous environments.

Colorimetry

Laboratory data concerning the persistence of biocides formulated in glutaraldehyde and acrolein are available (Morris and Pope, 1994). A colorimetric, general aldehyde detection method, based on *m*-phenylenediamine, was used. Such studies follow the demand for a better understanding of ecological systems for environmental protection.

In another study, a mathematical model was constructed, incorporating experimentally determined glutaraldehyde persistence, rates of water production, and other factors. The model was used to calculate levels of glutaraldehyde in a specified environment (lagoons) as a function of time, based on the amount of glutaraldehyde applied downhole (Derr et al., 1994).

Most Probable Number Technique

The traditional method for bacterial enumeration is the most probable number technique (Barton and Hamilton, 2007; Oblinger and Koburger, 1975; Postgate, 1979). Serial dilution into bacterial culture media is the most common method that is used to enumerate viable oil field bacteria, but this method takes up to 4 weeks to obtain results for slow growing sulfate-reducing bacteria.

Direct microscopy is an alternative, faster method, but it does not differentiate between living and dead bacteria. A method for the rapid enumeration of living sulfate-reducing bacteria has been developed, based on the rehydration of dried nutrients with system water. This method gives results in 1–7 days (Cowan, 2005).

DNA Sequencing

Bacterial enumeration and identification in diesel and naphtha pipelines located in northwest and southwest India has been reported. Traditional cultivation techniques and 16S rDNA gene sequencing was used, the latter using a Genetic Analyzer from PE Applied Biosystems.

The study included the phylogenetic analysis of 16S rRNA sequences of the isolated species. The sequences obtained were analyzed with BLAST search and 11 bacterial species were identified, as summarized in Table 5.1.

Sulfate-reducing bacteria were not detected in the samples. The dominant species were *Bacillus cereus* and *Serratia marcescens*.

It has been concluded that several types of bacteria may be involved in biocorrosion from natural biofilms in pipelines. Further localized pitting was

TABLE 5.1 Bacterial Species Found in Pipelines (Rajasekar et al., 2010)

Species
Serratia marcescens ACE2
Bacillus subtilis AR12
Bacillus cereus ACE4
Pseudomonas aeruginosa AI1
Klebsiella oxytoca ACP
Pseudomonas stutzeri AP2
Bacillus litoralis AN1
Bacillus sp.
Bacillus pumilus AR2
Bacillus carboniphilus AR3
Bacillus megaterium AR4

observed by analysis with scanning electron microscopy (Rajasekar et al., 2010).

Sulfate-reducing Bacteria

Sulfate-reducing bacteria are chemolithotrophic bacteria (Barton and Fauque, 2009), of which 220 species in 60 genera are known. All use sulfate as a terminal electron acceptor. This makes them a unique physiological group of microorganisms, which couple anaerobic electron transport to ATP synthesis.

These bacteria can use a wide variety of compounds as electron donors, including proteins with metal groups that can be oxidized or reduced. In particular, they act on soluble electron transfer proteins and via transmembrane redox complexes. Their ability to utilize hydrocarbons offers the possibility to use them for the bioremediation of soils, which are contaminated with aromatic hydrocarbons.

Some strains of sulfate-reducing bacteria can even reduce chlorinated compounds, e.g., 3-chlorobenzoate, chloroethenes, and nitroaromatic compounds. Sulfate-reducing bacteria can also reduce some heavy metals, hence, several procedures have been proposed for using these strains in the bioremediation of materials contaminated with toxic metals.

High levels of hydrogen sulfide are produced by the metabolism, which contributes to the souring of the oil fields of these organisms, and the corrosion of casings and concrete (Barton and Fauque, 2009).

New strains of sulfate-reducing bacteria are being discovered all the time (Agrawal et al., 2010; Miranda-Tello et al., 2003; Youssef et al., 2009). For example in 2003, a new spirilloid sulfate-reducing bacterium, designated strain MET2T, was isolated from a Mexican oil field separator (Miranda-Tello et al., 2003).

Issues in the Oil field

Mesophilic and thermophilic sulfate-reducing bacteria are common inhabitants of oil field facilities. They may penetrate into oil reservoirs with the injection water, and so contaminate the well. Their sulfide production and hydrogen oxidation are responsible for serious and costly biocorrosion problems in the oil industry (Sarioglu et al., 1997). They are most often controlled in situ by biocides (Barton and Hamilton, 2007; Hamilton, 1983; Miranda-Tello et al., 2003; Postgate, 1979).

The effect of temperature and pressure on a strain of sulfate-reducing bacteria isolated from an oil reservoir in Alaska has been investigated (Cheung et al., 1994). The highest bacterial growth rate was found at 37°C at 100 atm. The temperature has a greater influence on the bacterial proliferation than the pressure.

The effect of various concentrations of biocides, i.e., isothiazolone and formaldehyde, has been tested. Both biocides are similarly effective, but formaldehyde is more effective at high pressures (Cheung et al., 1994).

Bacterial Corrosion

Bacterial corrosion is often referred to as *microbiologically influenced corrosion.* The metabolic products of microorganisms appear to affect most engineering materials, but the more commonly used corrosion-resistant alloys, such as stainless steel, seem to be particularly susceptible.

Its importance has been underestimated because most occurs as a localized, pitting-type attack. In general, it results in relatively low rates of weight loss, changes in electrical resistance, and changes in total area affected. This makes it difficult to detect and to quantify using traditional methods of corrosion monitoring (Pope et al., 1992).

To adequately address microbiologically influenced corrosion problems, interdisciplinary cooperation of specialists in microbiology, metallurgy, corrosion, and water chemistry is required; a single technique cannot provide all the answers in terms of corrosion mechanisms.

The problem of and importance of microbiologically influenced corrosion was not fully realized until recently. Even in the mid-1980s the statement was made that

> *The major problem encountered by the petroleum microbiologist working in the North Sea oil fields is that of convincing the oil field engineer that bacterial corrosion is a subject worthy of serious attention. (Maxwell, 1986)*

A reference guide on recognizing, evaluating, and alleviating corrosion problems caused by microorganisms has been compiled (Anonymous, 1990). This manual provides a guide, training manual, and reference source for field and engineering personnel that deal with corrosion problems caused by microorganisms. Trends seen in the 1990s for dealing with microbiologically influenced corrosion have been reviewed in the literature (Farquhar, 1990). The basic goal of a practicing corrosion engineer should be not to identify, count, or even kill the microorganisms, but to effectively control corrosion in an oil field.

Mechanisms of Microbial Corrosion

The role of microorganisms can be visualized directly in microbially induced corrosion in an electrochemical cell. Alternatively, the role can be indirect, in that it maintains a preexisting electrochemical cell by stimulating either the cathodic or the anodic reaction (Hamilton, 1986).

Various microorganisms and mechanisms are thought to be involved, but most commonly, a differential aeration cell is built where concentrations of oxygen are low shielded beneath slime or colony growth, as compared with the high concentration externally in the bulk environment.

Under these conditions, the surface of the metal in the low concentration area becomes an anode due to the dissolution of metal, while the electrons react at the cathodic region with the high concentration of oxygen, giving rise to hydroxidious. Ultimately, metal oxides and hydroxides are characteristic for aerobic corrosion. Microbes influence the corrosion rate by the following mechanisms (Pope et al., 1990):

1. Cathodic depolarization,
2. Formation of occluded area on metal surface,
3. Fixing the anodic sites, and
4. Underdeposit acid attack.

Simultaneous Mechanisms of Corrosion

Microbiologically influenced corrosion almost always acts in concert with other corrosion mechanisms and may, at times, appear to be crevice corrosion, underdeposit acid attack, oxygen concentration cell corrosion, ion concentration cell corrosion, and CO_2 corrosion (Pope, 1997).

If microbiologically influenced corrosion is found on external surfaces, it is usually associated with disbonded coatings or other areas that are shielded from the potentially protective action of cathodic protection. Furthermore, pipelines are often in contact with wet clays, which have little scaling potential.

pH Regulation

Bacterial metabolism produces weak acids. Sulfate-reducing bacteria regulate the pH of their environment at levels that depend on potential secondary reactions, which are:

- Precipitation of iron sulfide,
- Oxidation of sulfide ions to thiosulfate by traces of oxygen, and
- Metabolism of this thiosulfate or of other sulfur compounds.

Biocide Enhancers

In order to effectively treat water against bacterial contamination, a fast-acting biocide is needed. This may be even more important for on-the-fly treatments, where biocides have a very short contact time with the water before other treating chemicals are added and the fluids are pumped downhole. In some instances it is believed to be helpful to include a biocide enhancer, to aid the biocide treatment or work synergistically with the biocide in order to kill the bacteria rapidly (Bryant et al., 2009).

Quaternary surfactants may act as biocide enhancers, for example, 19N™ is a cationic surfactant that also is a biocide enhancer. When used in combination with biocides such as sodium hypochlorite or glutaraldehyde, bacterial problems may sometimes be treated in times as short as 5 min.

Some quaternary surfactants may, however be fundamentally incompatible with anionic friction reducers, which are also used in subterranean operations. It is believed that this incompatibility may arise from charges present on both molecules that may cause the two to react and eventually form a precipitate. Some biocides, such as oxidizers, may also degrade certain friction reducers (Bryant et al., 2009).

Corrosion Monitoring

A critical review of the literature of monitoring techniques for microbiologically influenced corrosion has been presented (Borenstein and Licina, 1994). The monitoring techniques in this review include measurements of electrochemical properties, measurements of physical metal loss, and enumeration of sessile organisms. The procedures for the study of microbiologically influenced corrosion, as well as the advantages and the disadvantages of each technique, are discussed.

Microbiologically influenced corrosion can be misdiagnosed as attack caused by conventional chloride crevice, or as pitting corrosion unless specialized techniques are used during the failure analysis (Borenstein and Lindsay, 1994). These techniques include in situ sampling of residual water, bacterial analysis of corrosion products using analytical chemistry, culture growth, and scanning electron microscopy, as well as nondestructive examination using ultrasonic and radiographic techniques. Metallographic examination can reveal microbiologically influenced corrosion characteristics, such as dendritic corrosion attack in weld metal.

Bacterial Hydrogenase

Theoretical and experimental studies have shown that the removal of molecular hydrogen from cathodic surfaces is a primary driving force in microbiologically influenced corrosion. A rapid (1–4 h) test has been developed for the presence of bacterial hydrogenase that detects the presence of a wide range of corrosion-causing bacteria in water, sludge, and adherent bacterial biofilms (Boivin et al., 1989).

This test can be used to monitor oil and gas systems for the development of potentially corrosive bacterial populations, and to assess the efficacy of control measures, including biocide treatment, because the hydrogenase test yields negative results when this pivotal, corrosion-causing enzyme has been denatured.

Lipid Biomarkers

Microbes of differing physiological types, acting in consortia, appear to be more destructive than monocultures. Methods for examining consortia are based on the detection of lipid biomarkers that are characteristic for different classes of microbes. These can be analyzed by gas chromatography coupled with mass spectrometry (Dowling et al., 1986).

Electron Microscopy

Side stream sampling devices can be used to collect biofilm and corrosion samples. The biofilm, inorganic passive layers, and metal attacked samples can be characterized with scanning electron microscopy and energy dispersive X-ray analysis. Results of one such study showed a correlation between biofouling and corrosion attack of carbon steel samples (Videla et al., 1991).

Electrochemical Impedance Spectroscopy

Electrochemical impedance, weight loss, and potentiodyne techniques can be used to determine the corrosion rates of carbon steel, and the activities of both sulfate-reducing and acid-producing bacteria in water injection field tests. One such study revealed that the corrosion rates as determined by the potentiodyne technique did not correlate with the bacterial activity, but those obtained by electrochemical impedance spectroscopy were comparable with the rates obtained by weight loss measurements (Elboujdaini and Sastri, 1995).

Other electrochemical techniques that have been used include the measurements of the corrosion potential, redox potential, polarization resistance, electrochemical impedance, electrochemical noise, and polarization curves, including pitting scans. A critical review of the literature concerned with the application of electrochemical techniques in the study of microbiologically influenced corrosion is available (Mansfeld and Little, 1990).

Assessment of the Activity of Biocides

Quantitative methods that use indirect parameters of the growth of cells have been developed. Initially, only a few rapid techniques were available. Although some disk diffusion techniques have been described that generated results within 4–6 h, most techniques required an incubation time of 18–24 h before a result was available (Wheat, 2001).

One of the more rapid methods is based on impedance microbiology (Zhou and King, 1995). It uses a double-layer API agar medium, together with sodium thioglycolate as reducing agent. In comparison to the conventional API procedure (API, 1975), which requires 28 days, this technique takes only 1 day to obtain test results.

Another rapid method for estimating the biocide potential of various chemicals toward certain microbes has been developed, based on the redox potential of live microbial cells. A water-soluble organic redox indicator, blue in the oxidized form and pink in the reduced form, was used as an indicator of the reducing potential of microbial cells (Novikov et al., 2001).

Turbidimetry can be also used to assess the growth of bacteria (Piddock, 1990). The microcalorimetric measurement of microbial activity of biofilm samples allows easy testing of the efficacy of biocides (von Rège and Sand, 1998). Experiments with biofilm samples consisting of sulfate-reducing bacteria and chemo-organotrophic bacteria have been performed. Further, biofilms were produced in continuous culture on the surface of a flow-through gold tubing in the measuring cylinder of a calorimeter.

In separate experiments, the biofilm samples were treated with biocides, including formaldehyde, tetramethylammonium hydroxide, 1,8-dihydroxyanthraquinone, and glutaraldehyde at varying concentrations and incubation times. The heat produced in a typical experiment is illustrated in Figure 5.2.

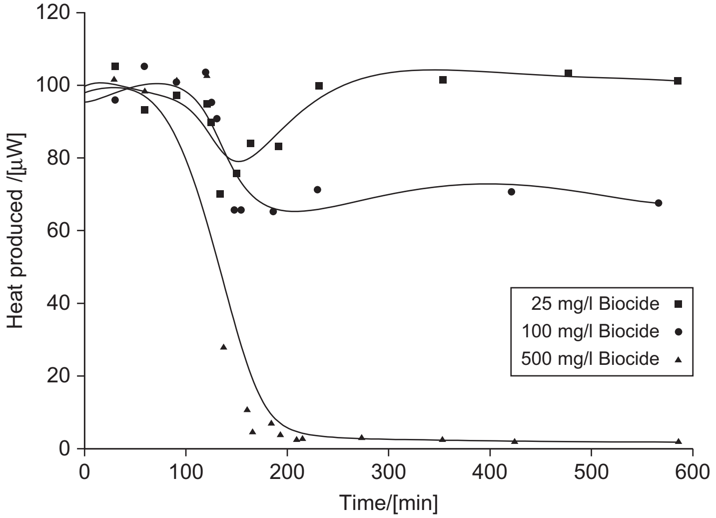


FIGURE 5.2 Heat production by bacteria, biocide added at 2 h (von Rège and Sand, 1998).

In the experiment, a pure culture biofilm with *Vibrio natriegens* was used. A glutaraldehyde-based biocide was added after 120 min, at which time a reduction in the heat produced is observed. Obviously the activity is lost only at the highest concentration of biocide.

Synergistic Action of Biocides

The synergistic effects of biocides can be evaluated. A bacillus together with dehydrated nutrients and a growth indicating dye is put on a plastic strip, and strip then dipped into a fluid of interest. The medium is thereby rehydrated and the spores are activated. Incubation for 24 h should yield a visible growth in the absence of biocides, but in the presence of biocides, growth is inhibited.

The concentration of the biocide in the fluid can be adjusted by making a range of dilutions, which enables one to evaluate which concentration of biocide just inhibits bacterial growth. If more than one biocide is present, it is possible to distinguish between additive effects, antagonism, and enhancement. In many cases, it is possible to determine exact dosing of large systems from the first trial (Hill et al., 1989).

The method has been used to determine the synergistic effects of copper sulfate and kathon, (2-*N*-octyl-4-isothiazolin-3-one) on *S. marcescens* (Rodin et al., 2005). Amino alcohols are not biocides themselves, but they enhance the performance of a wide range of biocides, which are used in water-based fluids (Coburn et al., 2010).

TREATMENTS WITH BIOCIDES

Previously Fractured Formations

A particular problem is the refracturing of a previously fractured formation that is contaminated with bacteria. In such a case, the fracturing fluid must be mixed with an amount of biocide that is sufficient to reach and to kill the bacteria contained in the formation. The refracturing of the formation causes the bactericide to be distributed throughout the formation and to contact and kill bacteria contained therein (McCabe et al., 1991).

Intermittent Addition of Biocide

The intermittent addition technique consists of Hegarty and Levy (1996):

- The addition of a slug dose of a biologically effective amount of a quick-kill biocide.
- Further, intermittent addition of biologically effective amounts of a control biocide.
- This means that the control biocide is dosed for a certain period of time, followed by a period of much lower or zero dosing. This cycle is repeated throughout the treatment.

This process reduces the amount of control biocide employed in the control of contamination of oil production system waters by sessile bacteria. The biocide may be applied at intervals of 2–15 d. The duration of biocide application is preferably 4–8 h (Moody and Montgomerie, 1996).

Nonbiocidal Control

Chemical treatments for bacteria control represent a significant cost and environmental liability. Because the regulatory pressure on the use of toxic biocides is increasing, more environmentally acceptable control measures are being developed.

Biocompetitive Exclusion Technology

Besides adding biocides to wells, modifying the reservoir ecology also appears to be a promising approach to bacterial control. The production of sulfide can be decreased, and its concentration is reduced by the establishment and growth of an indigenous microbial population that replaces the population of sulfate-reducing bacteria.

Low concentrations of a water-soluble nutrient solution are added, which selectively stimulate the growth of an indigenous microbial population, thereby inhibiting the detrimental, sulfate-reducing bacteria population that generate H_2S. This deliberate and controlled modification of the microflora and reservoir ecology has been termed *biocompetitive exclusion* (Hitzman and Dennis, 1997; Sandbeck and Hitzman, 1995).

Inhibitors for Bacterial Films

Laboratory tests with quaternary amine additives showed a very low surface colonization and lower corrosion rates (Enzien et al., 1996). On the other hand, the biocidal effect of quaternary amines in the test fluids appeared to be minimal. These results suggest that quaternary amines may prevent microbiologically influenced corrosion by mechanisms other than killing bacteria and that treatments preventing colonization on the surface may persist longer than most biocides.

Periodic Change in Ionic Strengths

For effective control of microorganisms, it is necessary to take into account the mechanism of formation of bacteria and the ecologic factors affecting it. The process of vital activity of bacteria begins with their adsorption onto the enclosing rocks and their adaptation to the new habitat conditions. Pure cultures of sulfate-reducing bacteria are not active in crude oil.

Population development in oil reservoirs depends entirely on hydrocarbon-oxidizing bacteria, which are the primary cause of oil breakdown. If the ecological conditions in the reservoir change during formation of the microorganisms, the established food chains are disrupted and the active development of microflora ceases. It was experimentally established periodically injecting waters markedly differing in mineralization, taking into account the ecologic characteristics of the formation of the microorganisms, makes it possible to control the biogenic processes in an oil reservoir without disturbing the surrounding environment (Blagov et al., 1990).

BIOCIDES

Various biocides have been used successfully in water treatment applications for many years. These include oxidizers, such as chlorine and bromine products, and non-oxidizing biocides, including isothiazolones, quats, organobromines, and glutaraldehyde.

Biocides are often misapplied in the petroleum industry, particularly if the characteristics of the biocides are not considered before use. Some guidelines for biocide selection are outlined in a review in the literature (Boivin, 1994). Early detection of microbiologic problems is imperative, and reparative actions must be taken as soon as possible.

Remedial measures should include changes in operating methods to prevent degradation of the operating environment. This might include the rejection of untreated waters for cleaning deposits in vessels and lines. In general, biocides are needed to control the activity of the bacteria in a system, but biocides alone usually will not solve a microbiologic problem.

Five requirements for bactericide selection are emphasized (Zhou, 1990):

1. Wide bacteria-killing ability and range,
2. Non-corrosive properties, good inhibiting ability, and convenience of transportation and application,

3. Non-toxic or low toxicity causing no damage to humans and within environmental control regulations,
4. Good miscibility, with no damage or interference to the drilling fluid or its chemical agents, and
5. Bacteria killing effect that is not affected by environmental adaptation of the bacteria.

Various Biocides

In Table 5.2 some biocides proposed for bacteria control are listed. Other aldehydes and hydroxy compounds are summarized in Table 5.3, and *o*-phthalaldehyde is shown in Figure 5.3.

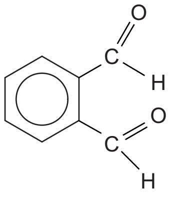
TABLE 5.2 Biocides Proposed for Bacteria Control

Biocide	References
Zinc slurry[d]	Trushevskaya et al. (1992)
Formaldehyde, Glutaraldehyde	Kriel et al. (1993)
Nitrate[b]	Sears et al. (1996)
Monochloroamine	Boivin et al. (1992)
3-Diazaspiro(4,5)decane	Austin (1987)
o-Phthalaldehyde	Theis and Leder (1992)
2-Bromo-4-hydroxyacetophenone	Oppong and King (1995)
Methyl tetrahydrophthalic acid[c]	Khanlarova et al. (1993)
Diammonium salts of tetrahydrophthalic acid	Khanlarova et al. (1993)
2,6-Dimethyl-*m*-dioxan-4-ol acetate	Smith et al. (2008)
Bis[tetrakis(hydroxymethyl)phosphonium] sulfate	Macleod et al. (1995)
Thiocyanomethylthio-benzothiazole[a]	Oppong and Hollis (1995)
1-(2-Hydroxyethyl)-2-methyl-5-nitroimidazole=(metronidazole)	Littmann and McLean (1987)
Di-(tri-*N*-butyl)-(1,4-benzodioxan-6,7-dimethyl) diammonium dichloride	Muganlinskij et al. (1995)
Dimethyl-tetrahydro-thiadiazine-thione	Karaseva et al. (1995)

a) Drilling lubricant
b) 5–50 ppm
c) 25–75 ppm
d) Waste from the production of 1-naphthol-3,6-disulfonic acid

TABLE 5.3 Aldehydes and Hydroxy Compounds

Biocide	References
Glutaraldehyde	Cash et al. (1992), Eagar et al. (1988)
Pentanedial	Lamarre and Martin (1990)
4,4-dimethyl-2-oxazolidinone, glycouril	Sweeny (1996)
Anthraquinones	Weimer et al. (1995), Burger et al. (2001)
Phenoxyethanol	Smith et al. (2008)
Tetrakis-(hydroxymethyl)-phosphonium salts	Bryan et al. (1990), Veale et al. (1990)
o-Phenylphenol	Smith et al. (2008)
p-Chloro-*m*-cresol	Smith et al. (2008)



o-Phthalaldehyde

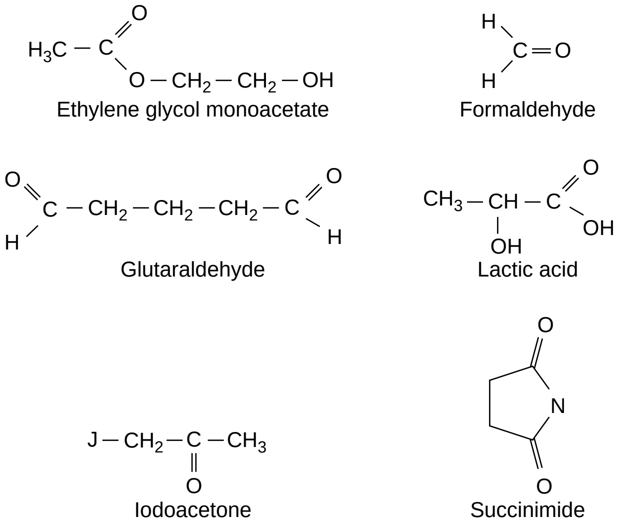
FIGURE 5.3 *o*-Phthalaldehyde.

Formaldehyde

Coreflood experiments were used to evaluate the efficacy of periodic formaldehyde injection for the control of in situ biogenic reservoir souring. Formaldehyde treatments were demonstrated to control souring in both environments; if the formaldehyde can be transported through the reservoir, in situ biogenic souring should be mitigated.

Glutaraldehyde

Glutaraldehyde is a useful antimicrobial agent, but it is dangerous and unpleasant to handle, and is thermally unstable. Despite these disadvantages, it is specified for use against bacteria in cooling towers of air-conditioning systems in buildings and to control anaerobic sulfate-reducing bacteria in oil wells. Some aldehydes and related compounds are shown in Figure 5.4.



Ethylene glycol monoacetate
Formaldehyde
Glutaraldehyde
Lactic acid
Iodoacetone
Succinimide

FIGURE 5.4 Some aldehydes and others.

Bisulfite Adduct

A bisulfite addition complex of an aldehyde or dialdehyde has been proposed for use as an antimicrobial agent (Wrench, 1990, 1991). The complex is less toxic than free glutaraldehyde. In oil wells, its digestion by the sulfate-reducing bacteria releases the free dialdehyde, which in turn controls the bacteria. In this way, a more economic and environmentally safer use of antimicrobial additives is possible.

Combined Chlorine-Aldehyde Treatment

A combined chlorine-aldehyde treatment that has two stages, chlorination and subsequent biocide application, has been suggested. Short-residence–time shock doses of glutaraldehyde have been applied after chlorination (Maxwell et al., 1986). It has been established that a primary chlorination is useful in overall bacterial control.

Green Biocide Enhancer

It is known that ethylene diamine tetraacetic acid (EDTA) is a synergist for biocides (Raad and Sherertz, 2001), but it is only slowly biodegradable, which is a drawback for environmental reasons. For this reason, it has been recommended to replace EDTA with green chelating agents in various industrial applications (Munn et al., 2004).

Ethylene diamine disuccinate is a biodegradable chelating agent. Its structure is shown in Figure 5.5 where it can be seen to contain two chiral carbon atoms (the CH), and has three stereoisomers ([R,R], [R,S]/[S,R], and [S,S]).

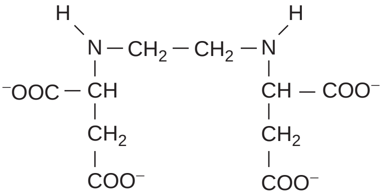


FIGURE 5.5 Ethylene diamine disuccinate anion.

The [S,S]-isomer is rapidly and completely mineralized, in contrast to the other isomers. Thus, the stereospecificity greatly influences biodegradation and metabolite formation (Schowanek et al., 1997).

This chemical has been found to enhance the efficacy of glutaraldehyde in the treatment of sulfate-reducing bacteria. It has a similar chelation ability to EDTA, but produces no persistent metabolites during biodegradation (Schowanek et al., 1997).

It has been demonstrated that the dosage of glutaraldehyde can be considerably reduced by the addition of ethylene diamine disuccinate to inhibit the growth of sulfate-reducing bacteria (Wen et al., 2009).

Glutaraldehyde is hazardous to handle and causes environmental concerns, and it can also deleteriously affect the fluid viscosity of the well treatment fluid at elevated temperatures. This can be problematic in fracturing applications, since higher fluid viscosity downhole could hinder flowback. In addition, glutaraldehyde has been shown to negatively impact the behavior of oxygen scavengers (Starkey et al., 2008).

Chloromethyl methylisothiazolone compounds are biocides with a broad spectrum versus bacteria, algae, and fungi that have been used successfully for microbial control and preventing biofouling in industrial water treatment (Williams, 2007a,b). The most frequently used product is a mixture of 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one in a ratio of 3:1 at a final concentration of 1.5%. 1,2-Benzisothiazolin-3-one (BIT) products have also been used in a limited range of industrial applications, which require long-term preservation for bacterial control.

Understanding their mechanism of action is important for optimizing their use, and combating resistance if encountered. Isothiazolones utilize a two-step mechanism (Williams, 2006):

1. Rapid inhibition of growth and metabolism within minutes and
2. Irreversible cell damage within hours resulting in the loss of viability.

The cells are inhibited by disruption of metabolic pathways involving dehydrogenase enzymes. This means that critical physiological functions are rapidly inhibited, including growth, respiration, and ATP synthesis. The death of the cells results from the destruction of protein thiols and the production of free radicals.

The rate of action and effectiveness may be enhanced by various additives, including the use of surfactants. A technology based on microemulsions has been introduced, using 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one as an algicide.

Oxidizing biocides play a key role in the control of microbial populations and biofouling in industrial cooling water systems. Bromochlorodimethylhydantoin is an oxidizing biocide (Kramer, 2007), which has been evaluated in several excellent field efficacy studies. These studies reveal that its continuous application releases 1–2 ppm of free chlorine, and is effective in reducing the concentration of *Legionella pneumophila* to undetectable levels in recirculating water.

Bromochlorodimethylhydantoin has also been shown to be effective against a mixed bacterial biofilm under laboratory conditions. Studies in dynamic laboratory systems that had been inoculated with a natural microbial flora revealed that it was equally effective against planktonic and biofilm populations of *L. pneumophila*. The literature on these issues has been reviewed (Kramer, 2007).

Benzotriazole and tolyl triazole are corrosion inhibitors for yellow metals. There is a controversy concerning the interaction of azoles with halogenated biocides; it is suspected that their presence may cause halogenated biocides to degrade (Ward and Glaser, 2007). Some researchers claim that the inhibitor is rendered ineffective due to this degradation, others agree that there is an interaction, but state that the products of degradation are still capable of protecting the metal. Laboratory studies have been presented on these open questions, in which it has been shown that azoles are not significantly affected by high concentrations of halogenated biocides bromine, in particular. In fact, azoles still perform well when residual inhibitor is present, even at extremely high dosages of free bromine.

However, azoles have other drawbacks. The triazole moiety is active enough to absorb to the metal, producing a protective film on the copper surface. Even when a protective film is formed, a certain residual level of azole needs to be maintained in the aqueous solution. If this is removed, the protective film starts to break down, causing an almost instantaneous increase in corrosion rates. In such cases, the presence of halogenated biocides only accelerates the rates of corrosion. Protective films formed by tolyl triazole have been found to be more resistant to breakdown in aqueous environments where the methyl group of the tolyl triazole moiety causes a steric hinderance.

2-Propenal (acrolein) is known as biocide, which is commercially available for several applications in the oil and gas industry. However, it has not been widely used on offshore oil production platforms due to safety concerns. However, recent advances allow it a lower level of risk than conventional biocides (Gregg et al., 2006). A case study assessed the risks of using 2-propenal vs. other biocides. 2-Propenal is related to conventional biocides that are applied on an offshore oil production platform with respect to its efficacy, injection hardware requirements, and associated risk elements.

The sea water as well as the sea water injection system was batch treated weekly with tetrakis hydroxyl methyl phosphonium sulfate, prior to sea water breakthrough, and glutaraldehyde, and after sea water breakthrough with 2-propenal, in order to control the biological activity. In later treatments, the biocide batch was supplemented with anthroquinone treatments to prolong the time between the application of glutaraldehyde and 2-propenal, respectively, thereby reducing the costs of treatment. In summary the results of this study looked promising.

The assumed biocidal mechanism of 2-propenal is the attack of sulfhydryl and amine groups on bacterial proteins (Penkala et al., 2004). The reactivity with sulfides renders acrolein effective as an H_2S scavenger and an iron sulfide dissolver. These compounds are byproducts of the metabolism of sulfate-reducing bacteria. A number of case histories have been reviewed on the performance of 2-propenal as biocide, and the results of laboratory studies comparing the efficacy of 2-propenal with other biocides have been compiled.

2-Propenal shows superior performance as biocide against general aerobic and facultative anaerobic bacteria, as well against sulfate-reducing bacteria. It is soluble in oil and penetrates biofilms, hence it is a versatile and effective biocide for use against persistent sessile populations of bacteria. Due to its low minimum inhibitory concentration, 2-propenal is used in batch applications and also in continuous treatment programs (Penkala et al., 2004).

Quaternary Ammonium-based Biocides

Quaternary ammonium-based biocides such as alkyl dimethyl benzyl ammonium chloride and dialkyl dimethyl ammonium chloride compounds have been used for microbiological control in industrial water systems for a long time. They perform well against algae, but they can cause problems with foaming, or can react with anionic additives in an undesired way (Kramer, 2006). In the 1980s, bis[tetrakis(hydroxymethyl)phosphonium] sulfate came on the market. This type of biocide overcame some of these issues: they lack surface activity and are not compatible with halogens.

On the other hand, tributyl tetradecyl phosphonium chloride is unique in that it combines a quaternary phosphonium group with the long alkyl chain moiety of the quaternary ammonium biocides in the same molecule, making it effective at low concentrations. It is also fast acting and effective against a variety of microorganisms, including *L. pneumophila* (Kramer, 2006). Its excellent surface activity makes tributyl tetradecyl phosphonium chloride highly effective for removing biofouling. It remains effective in combination with halogens, and it exhibits low foaming and is compatible with anionic scale and corrosion inhibitors. The structure of bis[tetrakis(hydroxmethyl)phosphonium] sulfate is shown in Figure 5.6.

Tetrakis-hydroxymethyl phosphonium salts have acceptable environmental profiles (Lloyd and Neail, 1993), and they are regarded as a preferred product for bacterial control within the oil production industry.

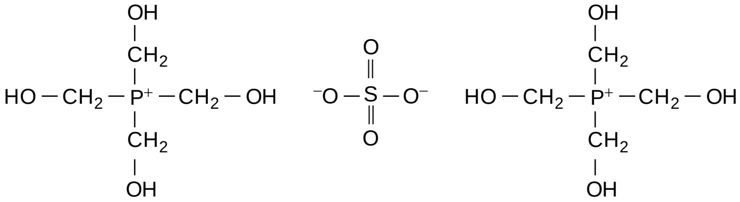


FIGURE 5.6 Bis[tetrakis(hydroxymethyl)phosphonium] sulfate.

Technical developments with respect to its use in oil production applications have been reviewed (Jones et al., 2006). Bis[tetrakis(hydroxymethyl)phosphonium] sulfate was initially applied as an industrial biocide in cooling systems, but it has been used in petroleum production since 1987. In fact, it became the leading biocide where sulfate-reducing bacteria cause problems. The product acts very fast and is effective for the control of free-swimming bacteria.

It is highly effective in downhole applications for controlling biogenic hydrogen sulfide. Treatment results in the dissolution of iron sulfide, which in turn increases oil production.

It has been found that bacteria protect themselves from the bis[tetrakis (hydroxymethyl)phosphonium] sulfate in water by producing a comparatively hydrophobic layer of polysaccharides.

In contrast to conventional quaternary biocides, bis[tetrakis(hydroxymethyl) phosphonium] sulfate does not bear long hydrophobic moieties, so the molecule is not surface active.

A variety of advanced formulations have been developed. The effectiveness of bis[tetrakis(hydroxymethyl)phosphonium] sulfate can be increased by formulating it with surfactants, such as benzalkonium chlorides (Jones et al., 2006).

Thiones for Treatment Fluids

Polymeric additives used in well treatment fluids may encounter an environment conducive to bacterial growth and oxidative degradation. If bacteria grow on these polymers, the physical characteristics of the fluids can be materially altered. For example, bacterial action can degrade the polymer, leading to loss of viscosity, so making the fluid ineffective (Starkey et al., 2008).

Fluids containing polysaccharide and synthetic polymers, such as polyacrylamides (PAM), polyglycosans, and carboxyalkyl ethers are especially susceptible to bacterial degradation. These polymers are also susceptible to oxidative degradation in the presence of free oxygen. This degradation can be directly caused by free oxygen or can be mediated by aerobic microorganisms. This means that biocides and oxygen scavengers are frequently added to well treatment fluids to control bacterial growth and oxygen degradation.

TABLE 5.4 Sulfur Compounds

Biocide	References
n-Butyl benzisothiazolinone	Smith et al. (2008)
1,2-Benzoisothiazolin-3-one	Smith et al. (2008), Morpeth and Greenhalgh (1990)
2-*N*-Octyl-4-isothiazolin-3-one	Hsu (1995)
2-Methyl-4-isothiazolin-3-one	Hsu (1994), Smith et al. (2008)
3-Acetoxy-4-methylthiazol-2(3H)-thione	Austin (1987)
3-Hydroxy-4-methylthiazol-2(3H)-thione	Austin (1987)
3-Hydroxy-4-phenylthiazol-2(3H)-thione	Austin (1987)
Isothiazolin-3-one	Lein (1989), Mattox (1989), Gironda et al. (1995)

The biocide should be selected to have minimal interaction with any of the components in the well stimulation fluid. It should not affect fluid viscosity to any significant extent and should not affect the performance of oxygen scavengers contained within the fluid.

Traditionally, either glutaraldehyde or bis[tetrakis(hydroxymethyl)phosphonium] sulfate is used to control bacterial contamination in well stimulation fluids but more recently, 2,5-dimethyl-1,3,5-thiadiazinane-2-thione has been proposed as an alternative as it is less environmentally harmful (Starkey et al., 2008). Oxygen scavengers are generally chosen from bisulfite salts. Other sulfur containing compounds are summarized in Table 5.4.

Halogen Compounds

Halogen containing compounds are summarized in Table 5.5.

Bromine Chloride

Liquid biocides are popular for the control of microorganisms in industrial water systems. Concentrated formulations of stabilized bromine chloride have been developed as biocides (Nalepa and Azomia, 2006). These are generally used for the treatment of industrial water.

The activity of the formulation approaches that of a fresh bleach, while still delivering the benefits of a stabilized bromine system. In order to achieve a balance of acceptable low temperature performance, i.e., a low freezing point with a good retention of its activity, computer-designed experiments have been performed.

TABLE 5.5 Halogen Compounds

Biocide	References
Chlorine dioxide	Clark and Langley (1990)
Sodium chlorite	Mason (1990)
N,*N*-Dimethyl-*N*′-phenyl-*N*′-fluoro-dichloromethylthiosulfamidesulfamide	Downey et al. (1995)
1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride	Smith et al. (2008)
2,3-Dibromo-1-chloro-4-thiocyanato-2-butene	Austin (1989)
3-(3,4-dichlorophenyl)-1,1-dimethylurea	Morpeth and Greenhalgh (1990)
4,5-Dichloro-2-*N*-octyl-isothiazolin-3-one	Downey et al. (1995)
5-Chloro-2-methyl-4-isothiazolin-3-one	Hsu (1994), Smith et al. (2008)
Chlorothalonil	Smith et al. (2008)
Dichloro-octylisothiazolinone	Smith et al. (2008)
Tributyl tetradecyl phosphonium chloride	Lamarre and Martin (1990)
Dibromo-octylisothiazolinone	Smith et al. (2008)
1,2-Dibromo-2,4-dicyanobutane	Hsu (1995)
1-*N*-Hexadecyl-1,2,4-triazole bromide	Demikhov et al. (1992)
2,2-Dibromo-2-nitroethanol	Leder (1990, 1991)
2,2-dibromo-3-nitrilopropionamide (DBNPA)	Smith et al. (2008)
2-Bromo-2-bromomethylglutaronitrile	Jakubowski (1986)
2-Bromo-2-nitro-1,3-propanediol	Smith et al. (2008)
Bromo-2-nitropropane-1,3-diol (Bronopol)	McLennan et al. (1987)
Iodine	Derr et al. (1995)
Iodoacetone	Rayudu and Pera (1989)
Iodopropynylbutylcarbamate	Smith et al. (2008)
Diiodomethyltolylsulfone	Smith et al. (2008)

Chlorine Dioxide

Chlorine dioxide has been evaluated as a replacement for chlorine (Simpson et al., 1993). Gaseous chlorine is declining in use as a biocide for industrial applications because of safety, environmental, and community impact considerations. Various alternatives have been explored, for example, bromo-chorodimethyl hydantoin, non-oxidizing biocides, ozone, and chlorine dioxide. Chlorine dioxide offers some unique advantages because of its selectivity, effectiveness over a wide pH range, and speed of kill. Safety and cost considerations have restricted its use as a viable replacement.

Nitrogen Containing Compounds

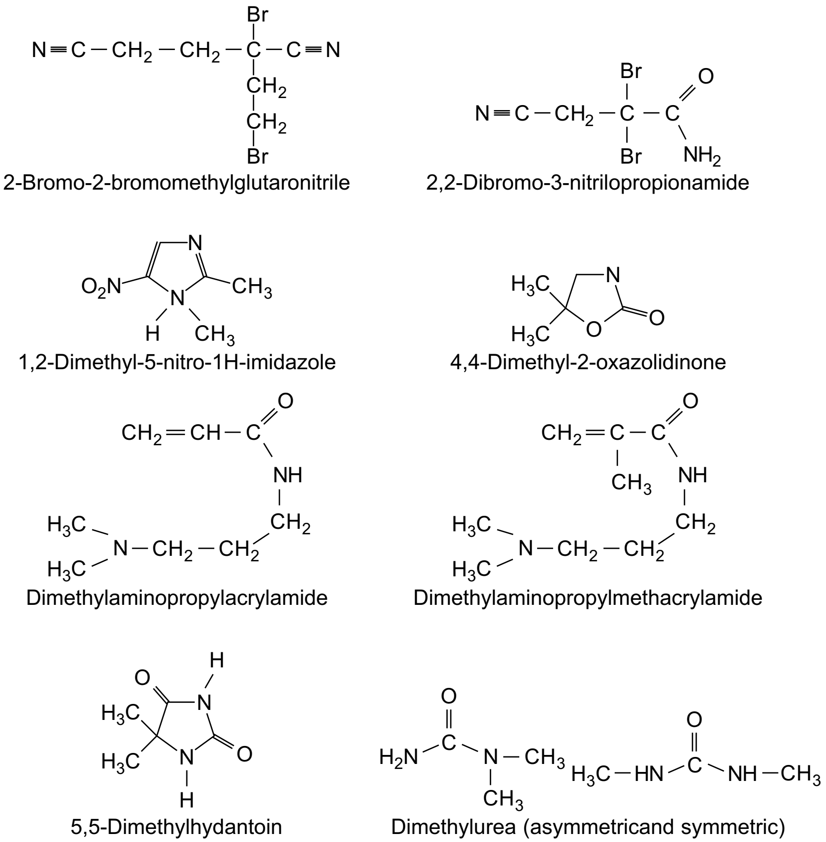
Nitrogen containing compounds are summarized in Table 5.6, and some of their structures some shown in Figures 5.7 and 5.8.

1,2-Dibromo-2,4-dicyanobutane can be prepared by reacting 2-methyleneglutaronitrile with bromine in an alcoholic solvent at 25–65°C and isolating the product without color or odor problems and in high yields (Nigam and Stiffler, 2003). 2-Bromo-2-bromomethylglutaronitrile is used in compositions of personal care and nutritional and pharmaceutical products.

Sodium pyrithione is synthesized by the reaction of 2-halopyridine-*N*-oxide with sodium hydrosulfide and sodium carbonate (Farmer and Katz, 1983). Zinc pyrithione is obtained by reacting the sodium pyrithione with a zinc salt.

TABLE 5.6 Nitrogen Compounds

Biocide	References
1,2-Dimethyl-5-nitro-1H-imidazole	Horstmann and Jones (1990)
1-Hydroxy-5-methyl-4-phenylimidazoline-2-thione	Austin (1987)
N,*N*′-Methylene-bis-morpholine	Smith et al. (2008)
4-(2-nitrobutyl)-morpholine	Smith et al. (2008)
4,4′-(2-ethyl-2-nitrotrimethylene)dimorpholine	Smith et al. (2008)
1,3,5-Tris-(2-hydroxyethyl)-*s*-triazine	Smith et al. (2008)
2-Methylthio-4-*tert*-butylamino-6-cyclopropylamino-S-triazine	Downey et al. (1995)
Trimethyl-1,3,5-triazine-1,3,5-triethanol	Smith et al. (2008)
Tetramethylol acetylene diurea	Smith et al. (2008)
Tris(hydroxymethyl)nitromethane	Smith et al. (2008)
Sodium pyrithione	Smith et al. (2008)
Zinc pyrithione	Smith et al. (2008)
4,4-Dimethyloxazolidine	Smith et al. (2008)
7-Ethyl bicyclooxazolidine	Smith et al. (2008)
Dimethylol-dimethyl-hydantoin	Smith et al. (2008)



2-Bromo-2-bromomethylglutaronitrile

2,2-Dibromo-3-nitrilopropionamide

1,2-Dimethyl-5-nitro-1H-imidazole

4,4-Dimethyl-2-oxazolidinone

Dimethylaminopropylacrylamide

Dimethylaminopropylmethacrylamide

5,5-Dimethylhydantoin

Dimethylurea (asymmetricand symmetric)

FIGURE 5.7 Nitrogen compounds as biocides.

Effervescent Biocide Compositions

Compositions of this kind generally include one or more biocidal ingredients delivered in the form of an effervescent tablet.

It has been discovered that effervescent tablets provide a useful delivery method for delivering biocidal agents to oil field fluids because (Smith et al., 2008):

1. They alleviate problems encountered with the application of dry biocides, i.e., water-soluble bags and
2. The effervescent action of the tablet when it dissolves in the fluid serves to disperse the biocidal agent.

Effervescent compositions are available for 2,2-dibromo-3-nitrilo-propionamide, 1,2-dibromo-2,4-dicyanobutane, 2-bromo-2-nitro-1,3-propanediol, 4,4-dimethyloxazolidine, 1-(3-chloroallyl)-3,5,7-triaza-1-azoniaadamantane chloride, and tris(hydroxymethyl)nitromethane (Smith et al., 2008).

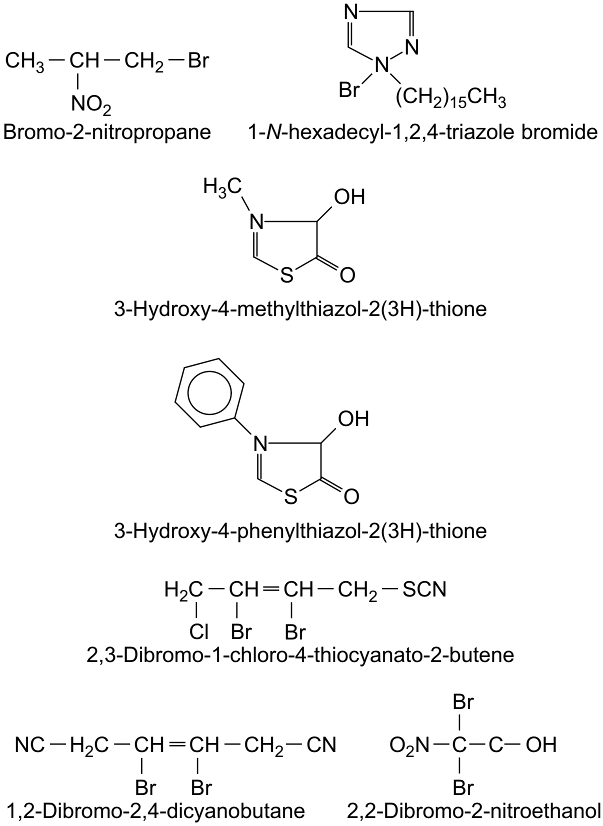


FIGURE 5.8 Nitrogen compounds as biocides.

Citric, malic, tartaric, adipic, and fumaric acid are suitable acids for effervescent tablets. Examples of carbon dioxide delivering compounds include sodium bicarbonate, potassium bicarbonate, sodium carbonate, and potassium carbonate.

REFERENCES

Agrawal, A., Vanbroekhoven, K., Lal, B., 2010. Diversity of culturable sulfidogenic bacteria in two oil-water separation tanks in the north-eastern oil fields of India. Anaerobe 16 (1), 12–18.

Anonymous, 1990. Microbiologically influenced corrosion and biofouling in oilfield equipment. NACE TPC Publication TPC 3.

Austin, P., 1987. Heterocyclic thione compounds and their use as biocides. EP Patent 249 328, December 16, 1987.

Austin, P.W., 1989. Unsaturated, halogenated thiocyanates, the preparation thereof and use as a biocide. EP Patent 316 058, May 17, 1989.

Barton, L., Hamilton, W.A. (Eds.), 2007. Sulphate-Reducing Bacteria: Environmental and Engineered Systems, Cambridge University Press, Cambridge.

Barton, L.L., Fauque, G.D., 2009. Biochemistry, physiology and biotechnology of sulfate-reducing bacteria. In: Laskin, A.I., Sariaslani, S., Gadd, G.M. (Eds.), Advances in Applied Microbiology, vol. 68. Academic Press, New York, ch. 2, pp. 41–98.

Blagov, A.V., Prazdnikova, Z.F., Praporshchikov, V.I., 1990. Use of ecological factors for controlling biogenic sulfate reduction. Neft Khoz (5), 48–50.

Boivin, J., 1994. Oil industry biocides. Mater. Perf. 34 (2), 65–68.

Boivin, J.W., Costerton, J.W., Laishley, E.J., Bryant, R., 1989. A new rapid test for microbial corrosion detection and biocide evaluation. In: Proceedings Volume, 2nd Inst. Gas Technol. Gas, Oil, Coal, & Environmental Biotechnology International Symposium, New Orleans, LA, December 11–13, 1989, pp. 537–547.

Boivin, J.W., Shapka, R., Khoury, A.E., Blenkinsopp, S., Costerton, J.W., 1992. An old and a new method of control for biofilm bacteria. In: Proceedings Volume, Annual NACE Corrosion Conference (Corrosion 92), Nashville, TN, April 27–May 1, 1992.

Borenstein, S.W., Licina, G.J., 1994. An overview of monitoring techniques for the study of microbiologically influenced corrosion. In: Proceedings Volume, 49th Annual NACE International Corrosion Conference (Corrosion 94), Baltimore, MD, February 27–March 4, 1994.

Borenstein, S.W., Lindsay, P.B., 1994. MIC (microbiologically influenced corrosion) failure analysis. Mater. Perf. 33 (4), 43–45.

Bryan, E., Veale, M.A., Talbot, R.E., Cooper, K.G., Matthews, N.S., 1990. Biocidal compositions and treatments. EP Patent 385 801, September 5, 1990.

Bryant, J.E., McMechan, D.E., McCabe, M.A., Wilson, J.M., King, K.L., 2009. Treatment fluids having biocide and friction reducing properties and associated methods. US Patent Application 20090229827, September 17, 2009.

Burger, E.D., Crews, A.B., Ikerd II, H.W., 2001. Inhibition of sulfate-reducing bacteria by anthraquinone in a laboratory biofilm column under dynamic conditions. In: Proceedings Volume, NACE International Corrosion Conference (Corrosion 2001), Houston, TX, March 11–16, 2001.

Cash, H.A., Krupa, A.S., Vance, I., Johnson, B.V., 1992. Laboratory testing of biocides against sessile oilfield bacteria. In: Proceedings Volume, Inst. Gas Technol. Gas, Oil & Environ. Biotechnol. Symposium, Chicago, IL, September 21–23, 1992.

Cheung, C.W.S., Beech, I.B., Campbell, S.A., Satherley, J., Schiffrin, D.J., 1994. The effect of industrial biocides on sulphate-reducing bacteria under high pressure. Int. Biodeterior. Biodegrad. 33 (4), 299–310.

Clark, J.B., Langley, D.E., 1990. Biofilm control. US Patent 4 929 365, May 29, 1990.

Coburn, C.E., Pohlman, J.L., Pyzowski, B.A., Brutto, P.E., Green, G.D., Swedo, R.J., 2010. Aminoalcohol and biocide compositions for aqueous based systems. US Patent Application 20100093736, assigned to Global Technologies Inc., Midland, April 15, 2010.

Cowan, J.K., 2005. Rapid enumeration of sulfate reducing bacteria. In: Corrosion 2005, NACE International, Houston, TX.

Demikhov, V.N., Gilyazov, M.M., Trutneva, E.K., Levin, Y.A., Rakov, A.P., Shermergorn, I.M., 1992. New 1-*n*-alkyl-1,2,4-triazole bromide bactericidal compounds – prepared by alkylation of 1,2,4-triazole with *n*-hexadecyl or *n*-octadecyl. SU Patent 1 776 653, November 23, 1992.

Derr, R., Morris III, E.A., Pope, D.H., 1994. Fate and persistence of glutaraldehyde in a natural gas storage facility. In: Proceedings Volume, 7th Inst. Gas Technol. Gas, Oil, & Environmental Biotechnology International Symposium, Colorado Springs, CO, December 12–14, 1994.

Derr, R.M., Morris, E.A., Pope, D.H., 1995. Applicability and efficacy of iodine as a mitigation strategy for advanced microbiologically influenced souring (MIS). In: Proceedings Volume, 8th Inst.

Gas Technol. Gas, Oil, & Environmental Biotechnology International Symposium, Colorado Springs, CO, December 11–13, 1995.

Dowling, N.J.E., Guezennec, J., White, D.C., 1986. Facilitation of corrosion of stainless steel exposed to aerobic seawater by microbial biofilms containing both facultative and absolute anaerobes. In: Proceedings Volume, Inst. Petrol. Microbiol Comm Microbial Problems in the Offshore Oil Ind. International Conference, Aberdeen, Scotland, April 15–17, 1986.

Downey, A.B., Willingham, G.L., Frazier, V.S., 1995. Compositions comprising 4,5-dichloro-2-*n*-octyl-3-isothiazolone and certain commercial biocides. EP Patent 680 695, assigned to Rohm & Haas Co., November 8, 1995.

Eagar, R.G., Leder, J., Stanley, J.P., Theis, A.B., 1988. The use of glutaraldehyde for microbiological control in waterflood systems, Mater. Perf. 27 (8), 40–45.

Elboujdaini, M., Sastri, V.S., 1995. Field studies of microbiological corrosion in water injection plant. In: Proceedings Volume, 50th Annual NACE International Corrosion Conference (Corrosion 95), Orlando, FL, March 26–31, 1995.

Enzien, M.V., Pope, D.H., Wu, M.M., Frank, J., 1996. Nonbiocidal control of microbiologically influenced corrosion using organic film-forming inhibitors. In: Proceedings Volume, 51st Annual NACE International Corrosion Conference (Corrosion 96), Denver, CO, March 24–29, 1996.

Farmer, D.A., Jr., Katz, L.E., 1983. Process for producing sodium and zinc pyrithione. US Patent 4 396 766, assigned to Olin Corporation (New Haven, CT), August 2, 1983.

Farquhar, G.B., 1990. A review of trends in MIC (microbiologically influenced corrosion). Mater. Perf. 32 (1), 53–55.

Gironda, K.F., Redlich, G.H., Petigara, R.B., 1995. Bromate stabilization of nitrate-free 3-isothiazolones at ph 4-5.1. US Patent 5 478 797, assigned to Rohm & Haas Co., December 26, 1995.

Gregg, M., Dickinson, A., Oates, S., Walsh, G.G., Mulak, K.J., 2006. A novel approach to managing a seawater injection biocide program reduces risk, improves biological control, and reduces capital and opex costs on an offshore platform. In: Corrosion 2006, NACE International, San Diego, CA.

Hamilton, W.A., 1983. Sulphate-reducing bacteria and the offshore oil industry. Trends Biotechnol. 1 (2), 36–40.

Hamilton, W.A., 1986. Mechanisms of microbial corrosion. In: Proceedings Volume, Inst. Petrol. Microbiol Comm Microbial Problems in the Offshore Oil Ind. International Conference, Aberdeen, Scotland, April 15–17, 1986, pp. 1–11.

Hegarty, B.M., Levy, R., 1996. Control of oilfield biofouling. EP Patent 706 759, April 17, 1996.

Hill, E.C., Hill, G.C., Robbins, D.A., 1989. An informative and practical strategy for preventing spoilage and improving preservation using a simple assay for biocides and preservatives. Int. Biodeterior. 25 (1–3), 245–252.

Hitzman, D.O., Dennis, D.M., 1997. Sulfide removal and prevention in gas wells. In: Proceedings Volume, SPE Prod. Oper. Symposium, Oklahoma City, March 9–11, 1997, pp. 433–438.

Horstmann, D.G., Jones, D.S., 1990. Synergistic biocides of certain nitroimidazoles and aldehydes. US Patent 4 920 141, assigned to Petrolite Corp., April 24, 1990.

Hsu, J.C., 1994. Synergistic microbicidal combinations containing 3-isothiazolone and commercial biocides. US Patent 5 278 178, January 11, 1994.

Hsu, J.C., 1995. Biocidal compositions. EP Patent 685 159, December 6, 1995.

Jakubowski, J.A., 1986. Admixtures of 2-bromo-2-bromomethylglutaronitrile and 2,2-dibromo-3-nitrilopropionamide. US Patent 4 604 405, assigned to Calgon Corp., August 5, 1986.

Jones, C.R., Diaz, R., Hernandez, K., Talbot, R.E., Fidoe, S.D., Downward, B.L., 2006. Keeping pace with the need for advanced, high performance biocide formulations of oil production applications. In: Corrosion 2006, NACE International, San Diego, CA.

Karaseva, E.V., Dedyukhina, S.N., Dedyukhin, A.A., 1995. Treatment of water-based drilling solution to prevent microbial attack – by addition of dimethyl-tetrahydro-thiadiazine-thione bactericide. RU Patent 2 036 216, May 27, 1995.

Khanlarova, A.G., Musaev, M.R., Samedov, A.M., Kandinskaya, L.I., Gasanov, A.G., Alieva, L.I., et al., 1993. Inhibiting growth of sulphate-reducing bacteria-involves introducing diammonium salts of tetrahydrophthalic acid or methyl-tetrahydrophthalic acid into bacteria-containing circulating water. SU Patent 1 828 917, July 23, 1993.

Kramer, J.F., 2006. A new high performance quaternary phosphonium biocide for biofouling control in industrial water systems. In: Corrosion 2006, NACE International, San Diego, CA.

Kramer, J.F., 2007. Efficacy of bromochlorodimethylhydantoin against legionella pneumophila in industrial cooling water systems. In: Corrosion 2007, NACE International, Nashville, TN.

Kriel, B.G., Crews, A.B., Burger, E.D., Vanderwende, E., Hitzman, D.O., 1993. The efficacy of formaldehyde for the control of biogenic sulfide production in porous media. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, New Orleans, LA, March 2–5, 1993, pp. 441–448.

Lamarre, T.M., Martin, C.H., 1990. Synergistic biocide of tributyl tetradecyl phosphonium chloride and 1.5-pentanedial. CA Patent 1 269 300, May 22, 1990.

Leder, J., 1990. Antimicrobial composition and method of use. EP Patent 364 789, April 25, 1990.

Leder, J., 1991. Antimicrobial composition and method of use in oil well flooding. US Patent 5 055 493, October 8, 1991.

Lein Jr., G.M., 1989. Preparation of isothiazolones. EP Patent 318 194, May 31, 1989.

Littmann, E.S., McLean, T.L., 1987. Chemical control of biogenic H_2S in producing formations. In: Proceedings Volume, SPE Prod. Oper. Symposium, Oklahoma City, March 8–10, 1987, pp. 339–342.

Lloyd, G.R., Neail, P.W., 1993. Biocides for minimum environmental impact. In: Proceedings Volume, no. 2 III-7, 2nd Shell Co. Australia et al Australian International Oil, Gas & Petrochem Conference (Offshore Australia 93), Melbourne, Australia, November 23–26, 1993.

Macleod, N., Bryan, E., Buckley, A.J., Talbot, R.E., Veale, M.A., 1995. Control of reservoir souring by a novel biocide. In: Proceedings Volume, 50th Annual NACE International Corrosion Conference (Corrosion 95), Orlando, FL, March 26–31, 1995.

Mansfeld, F., Little, B., 1990. The application of electrochemical techniques for the study of MIC (microbiologically influenced corrosion) – a critical review. In: Proceedings Volume, NACE International Corrosion Forum (Corrosion 90), Las Vegas, NV, April 23–27, 1990.

Mason, J.A., 1990. Use of chlorous acid in oil recovery. US Patent 4 892 148, January 9, 1990.

Mattox, J.R., 1989. Stabilized isothiazolone compositions. EP Patent 315 464, May 10, 1989.

Maxwell, S., 1986. Improved monitoring of bacterially mediated corrosion risks in offshore systems. Inst. Petrol. Quart. J. Tech. Paper 1–25.

Maxwell, S., McLean, K.M., Kearns, J., 1986. Biocide application and monitoring in a waterflood system. In: Proceedings Volume, Inst. Petrol. Microbiol Comm Microbial Problems in the Offshore Oil Ind. International Conference, Aberdeen, Scotland, April 15–17, 1986, pp. 209–218.

McCabe, M.A., Wilson, J.M., Weaver, J.D., Venditto, J.J., 1991. Biocidal well treatment method. US Patent 5 016 714, assigned to Halliburton Co., May 21, 1991.

McLennan, J.M., Brunt, K.D., Guthrie, W.G., 1987. Solid antibacterial compositions. GB Patent 2 183 477, June 10, 1987.

Miranda-Tello, E., Fardeau, M.-L., Fernández, L., Ramírez, F., Cayol, J.-L., Thomas, P., et al., 2003. Desulfovibrio capillatus sp. nov., a novel sulfate-reducing bacterium isolated from an oil field separator located in the gulf of mexico. Anaerobe 9 (2), 97–103.

Moody, S.S., Montgomerie, H.T.R., 1996. Control of oilfield biofouling. EP Patent 706 974, April 17, 1996.

Morpeth, F.F., Greenhalgh, M., 1990. Composition and use. EP Patent 390 394, assigned to Imperial Chemical Inds Pl, October 3, 1990.

Morris III, E.A., Dziewulski, D.M., Pope, D.H., Paakkonen, S.T., 1994. Field and laboratory studies into the detection and treatment of microbiologically influenced souring (MIS) in natural gas storage facilities. In: Proceedings Volume, 49th Annual NACE International Corrosion Conference (Corrosion 94), Baltimore, MD, February 27–March 4, 1994.

Morris III, E.A., Pope, D.H., 1994. Field and laboratory investigations into the persistence of glutaraldehyde and acrolein in natural gas storage operations. In: Proceedings Volume, 49th Annual NACE International Corrosion Conference (Corrosion 94), Baltimore, MD, February 27–March 4, 1994.

Muganlinskij, F.F., Lyushin, M.M., Samedov, A.M.O., Akosta, V.K.U. Suppressing activity of sulphate-reducing bacteria on petroleum extraction – by treating flooding water with di-(tri-*n*-butyl)-(1,4-benzodioxan-6,7-dimethyl) diammonium dichloride. RU Patent 2 033 393, April 20, 1995.

Munn, S.J., Allanou, R., Aschberger, K., Berthault, F., Cosgrove, O., de Bruijn, J., et al., 2004. Edetic acid (EDTA). European Union Risk Assessment Report 49, Institute for Health and Consumer Protection, European Chemicals Bureau, Luxembourg, http://ecb.jrc.ec.europa.eu/documents/Existing-Chemicals/RISK_ASSESSMENT/REPORT/edtareport061.pdf.

Nalepa, C.J., Azomia, F.D., 2006. Development of a high activity liquid biocide for industrial water treatment. In: Corrosion 2006, NACE International, San Diego, CA.

Nigam, S.C., Stiffler, C., 2003. Method for preparing 1,2-dibromo-2,4-dicyanobutane. US Patent 6 548 692, assigned to ISP Investments Inc. (Wilmington, DE), April 15, 2003.

Novikov, I.A., Gurov, B.N., Shtuchnaya, G.V., Fomchenkov, V.M., Kholodenko, V.P., 2001. Rapid assay for assessment of the potential of chemical biocides against microbial destructors of industrial materials. Appl. Biochem. Microbiol. 37 (1), 110–114.

Oblinger, J.L., Koburger, J.A., 1975. Understanding and teaching the most probable number technique. J. Milk Food Technol. 38 (9), 540–545.

Oppong, D., Hollis, C.G., 1995. Synergistic antimicrobial compositions containing (thiocyanomethylthio) benzothiazole and an organic acid. WO Patent 9 508 267, assigned to Buckman Labs International Inc., March 30, 1995.

Oppong, D., King, V.M., 1995. Synergistic antimicrobial compositions containing a halogenated acetophenone and an organic acid. WO Patent 9 520 319, assigned to Buckman Labs International Inc., August 3, 1995.

Penkala, J., Law, M.D., Horaska, D.D., Dickinson, A.L., 2004. Acrolein 2-propenal: a versatile microbiocide for control of bacteria in oilfield systems. In: Corrosion 2004, NACE International, New Orleans, LA.

Piddock, L.J.V., 1990. Techniques used for the determination of antimicrobial resistance and sensitivity in bacteria. J. Appl. Microbiol. 68 (4), 307–318.

Pope, D.H., 1997. Concern over MIC (microbiologically-influenced corrosion) expanding among corrosion engineers. Pipe Line Gas Ind. 80 (2), 23–25.

Pope, D.H., Dziewulski, D., Frank, J.R., 1990. Microbiologically influenced corrosion in the gas industry. Pipeline 62 (5), 8–9.

Pope, D.H., Dziewulski, D.M., Lockwood, S.F., Werner, D.P., Frank, J.R., 1992. Microbiological corrosion concerns for pipelines and tanks. In: Proceedings Volume, API Pipeline Conference, Houston, TX, April 7–8, 1992, pp. 290–321.

Postgate, J.R., 1979. The Sulphate-Reducing Bacteria. Cambridge University Press, Cambridge.

Prasad, R., 1988. Pros and Cons of ATP (adenosine triphosphate) measurement in oil field waters. In: Proceedings Volume, NACE Corrosion 88, St Louis, MO, March 21–25, 1988.

Raad, I., Sherertz, R., 2001. Chelators in combination with biocides: treatment of microbially induced biofilm and corrosion. US Patent 6 267 979, assigned to Wake Forest University (Winston-Salem, NC) Board of Regents, The University of Texas System (Austin, TX), July 31, 2001.

Rajasekar, A., Anandkumar, B., Maruthamuthu, S., Ting, Y.-P., Rahman, P., 2010. Characterization of corrosive bacterial consortia isolated from petroleum-product-transporting pipelines. Appl. Microbiol. Biotechnol. 85 (4), 1175–1188.

Rayudu, S.R., Pera, J.D., 1989. A method of inhibiting the growth of microorganisms in aqueous liquids. EP Patent 313 272, April 26, 1989.

Recommended practice for biological analysis of water-flood injection, 1975. API Standard API RP 38-3, American Petroleum Institute, Washington, DC, WITHDRAWN No Replacement.

Rodin, V.B., Zhigletsova, S.K., Kobelev, V.S., Akimova, N.A., Kholodenko, V.P., 2005. Efficacy of individual biocides and synergistic combinations. Int. Biodeterior. Biodegrad. 55 (4), 253–259.

Salanitro, J.P., Williams, M.P., Langston, G.C., 1993. Growth and control of sulfidogenic bacteria in a laboratory model seawater flood thermal gradient. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, New Orleans, LA, March 2–5, 1993, pp. 457–467.

Sandbeck, K.A., Hitzman, D.O., 1995. Biocompetitive exclusion technology: a field system to control reservoir souring and increase production. In: US DOE Rep, no. CONF-9509173, 5th US DOE et al Microbial Enhanced Oil Recovery & Relat Biotechnol. for Solving Environ. Probl International Conference, Dallas, TX, September 11–14, 1995, pp. 311–319.

Sarioglu, F., Javaherdashti, R., Aksöz, N., 1997. Corrosion of a drilling pipe steel in an environment containing sulphate-reducing bacteria. Int. J. Pres. Ves. Pip. 73 (2), 127–131.

Schowanek, D., Feijtel, T.C.J., Perkins, C.M., Hartman, F.A., Federle, T.W., Larson, R.J., 1997. Biodegradation of [S,S], [R,R] and mixed stereoisomers of ethylene diamine disuccinic acid (EDDS), a transition metal chelator. Chemosphere 34 (11), 2375–2391.

Sears, J.T., Mueller, R., Reinsel, M.A., 1996. Inhibition of sulfate-reducing bacteria via nitrite production. WO Patent 9 612 867, assigned to Montana State Univ., May 2, 1996.

Simpson, G.D., Miller, R.F., Laxton, G.D., Clements, W.R., 1993. A focus on chlorine dioxide: the “ideal” biocide. In: Proceedings Volume, Annual NACE Corrosion Conference (Corrosion 93), New Orleans, LA, March 7–12, 1993.

Smith, K., Persinski, L.J., Wanner, M., 2008. Effervescent biocide compositions for oilfield applications. US Patent Application 20080004189, assigned to Weatherford/Lamb Inc., Houston, TX, January 3, 2008.

Starkey, R.J., Monteith, G.A., Aften, C.W., 2008. Biocide for well stimulation and treatment fluids. US Patent Application 20080032903, February 7, 2008.

Sunde, E., Thorstenson, T., Torsvik, T., 1990. Growth of bacteria on water injection additives. In: Proceedings Volume, 65th Annual SPE Technical Conference, New Orleans, LA, September 23–26, 1990, pp. 727–733.

Sunde, E., Thorstenson, T., Torsvik, T., Vaag, J.E., Espedal, M.S., 1993. Field-related mathematical model to predict and reduce reservoir souring. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, New Orleans, LA, March 2–5, 1993, pp. 449–456.

Sweeny, P.G., 1996. Hydantoin-enhanced halogen efficacy in pulp and paper applications. WO Patent 9 611 882, April 25, 1996.

Theis, A.B., Leder, J., 1992. Method for the control of biofouling. US Patent 5 128 051, July 7, 1992.

Trushevskaya, A.M., Sklyarskaya, L.B., Zhurakivskij, I.M., 1992. Suppressing growth of sulphate(s)-reducing bacteria in stratal injection water by addition of zinc slurry solutions obtained as waste from filtration stage in production of naphthol-di:sulphonic acid. SU Patent 1 730 502, April 30, 1992.

Veale, M.A., Bryan, E., Talbot, R.E., 1990. A new biocide with respect to industrial water treatment and oilfield applications. In: Proceedings Volume, Norwegian Soc. Chartered Eng. Oil Field Chem. Conference, Geilo, Norway, March 19–21, 1990.

Videla, H.A., Guiamet, P.S., Pardini, O.R., Echarte, E., Trujillo, D., Freitas, M.M.S., 1991. Monitoring biofilms and MIC (microbially induced corrosion) in an oilfield water injection system. In: Proceedings Volume, Annual NACE Corrosion Conference (Corrosion 91), Cincinnati, OH, March 11–15, 1991.

von Rège, H., Sand, W., 1998. Evaluation of biocide efficacy by microcalorimetric determination of microbial activity in biofilms. J. Microbiol. Methods 33 (3), 227–235.

Ward, E.C., Glaser, D.E., 2007. A new look at azoles. In: Corrosion 2007, NACE International, Nashville, TN.

Weimer, P.J., Odom, J.M., Cooling, F.B.I., Anderson, A.G., 1995. Anthraquinones as inhibitors of sulfide production from sulfate-reducing bacteria. US Patent 5 385 842, January 31, 1995.

Wen, J., Zhao, K., Gu, T., Raad, I.I., 2009. A green biocide enhancer for the treatment of sulfatereducing bacteria (srb) biofilms on carbon steel surfaces using glutaraldehyde. Int. Biodeterior. Biodegrad. 63 (8), 1102–1106.

Wheat, P.F., 2001. History and development of antimicrobial susceptibility testing methodology. J. Antimicrob. Chemother. 48 (Suppl.), 1–4.

Williams, T.M., 2006. The mechanism of action of isothiazolone biocide. In: Corrosion 2006, NACE International, San Diego, CA.

Williams, T.M., 2007a. Efficacy of chloromethyl-methylisothiazolone (CMIT/MIT) biocide versus legionella and protozoa. In: Corrosion 2007, NACE International, Nashville, TN.

Williams, T.M., 2007b. Methylisothiazolone: a new biocide product for closed loop systems. In: Corrosion 2007, NACE International, Nashville, TN.

Wrench, E., 1990. Anti-microbial agent. WO Patent 9 006 054, June 14, 1990.

Wrench, E., 1991. Anti-microbial agent. GB Patent 2 244 216, November 27, 1991.

Youssef, N., Elshahed, M.S., McInerney, M.J., 2009. Microbial processes in oil fields: culprits, problems, and opportunities. In: Laskin, A.I., Sariaslani, S., Gadd, G.M. (Eds.), Advances in Applied Microbiology, vol. 66. Academic Press, New York, ch. 6, pp. 141–251.

Zhou, X., King, V.M., 1995. A rapid bactometer method for screening of biocides against sulfate-reducing bacteria. Appl. Microbiol. Biotechnol. 43 (2), 336–340.

Zhou, Y., 1990. Bactericide for drilling fluid. Drill. Fluid Completion Fluid 7 (3), 2A, 10–12.

TRADENAMES

TABLE 5.7 Tradenames in References

Tradename Description	Supplier
Disotate® EDTA compound (Raad and Sherertz, 2001)	Forest Pharmaceuticals
Endtrate® EDTA compound (Raad and Sherertz, 2001)	Abbott
Etidronate™ Etidronic acid salt, 1-hydroxyethane 1,1-diphosphonic acid salt (Raad and Sherertz, 2001)	Various manufacturers

Chapter 6

Corrosion Inhibitors

The history of corrosion inhibitors and neutralizers and their invention, development, and application in the petroleum industry has been reviewed by Fisher (1993). Early corrosion inhibitor applications in each of the various segments of the industry, including oil wells, natural gas plants, refineries, and product pipelines, are included.

Corrosion and scale deposition are the two most costly problems in oil industries. Corrodible surfaces are found throughout production, transport, and refining equipment. The *Corrosion and Scale Handbook* gives an overview of the problems and methods of prevention (Becker, 1998).

In many oil field operations, the contact of fluids with air is inevitable. A striking example is recovery stimulation by in situ combustion. Reducing agents can be used to remove oxygen. The conditions must be controlled so that oxygen removal is complete, yet little unreacted excess scavenger remains in the system. In addition, mechanical scavenging can be accomplished by vacuum deaeration or counter-current scrubbing with an oxygen free gas. For economical reasons there are many systems where a one step corrosion inhibitor would be preferred.

Even when oxygen is not present in the corrosion system, oil field corrosion is associated with deposition conditions. Iron sulfide or other solid particles can deposit on the steel surface and prevent access by corrosion inhibitors. In some cases, these deposits can act as harbors for anaerobic bacteria, which can also become involved in the corrosion process. Sulfate-reducing bacteria can even produce their own environment beneath a biofilm that is safe from turbulence and flow velocities. As the biofilm grows, it forms an exoskeleton, which provides a site for the growth of sessile bacteria (Martin et al., 2005). Hydrogen sulfide is produced by these bacteria and is released to the protected environment where it reacts with the dissolved iron from the corrosion process to form iron sulfide.

The biofilm is formed from polysaccharides and other related molecules forming a semi-permeable matrix. Within the pores of this biofilm, the sulfate-reducing bacteria grow and produce locally high concentrations of H_2S, which

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accelerates the corrosion process and causes severe pitting. Electrochemical polarization curves had been used to show the particular conditions responsible for ferrous metal corrosion when oxygen contacts both sour H_2S and sweet CO_2 production fluids (Martin et al., 2005).

Carbon dioxide sweet corrosion is a well-known problem in gas production. Carbon dioxide dissolves in brine to form carbonic acid, which ionizes to yield a low pH value. This acidic solution strongly enhances corrosion in carbon steel pipes and facilities. The presence of carbon dioxide would lead to corrosion rates of several mm/year if no proper corrosion protection methods were undertaken (Oberndorfer et al., 2007).

CLASSIFICATION OF CORROSION INHIBITORS

Corrosion inhibitors have been divided into many groups, such as (Dietsche et al., 2007):

- Cathodic and anodic inhibitors,
- Inorganic and organic corrosion inhibitors, or
- Filming and non-filming inhibitors.

Low molecular weight corrosion inhibitors often change the surface tension of water. Actually these groups act as surfactants, since they form a protective layer on the metal surfaces (Dietsche et al., 2007). Polymeric corrosion inhibitors act in the same way as ordinary low molecular weight inhibitors.

Polymeric film-forming corrosion inhibitors differ from polymer coatings as they exhibit a specific interaction with the surface before the dry film is formed. Polymeric corrosion inhibitors may not form a barrier layer against oxygen and water, but instead they change the corrosion potential of the metal (Dietsche et al., 2007).

From the chemists's point of view, corrosion inhibitors can be classified into the following broad groupings:

- Amides and imidazolines,
- Salts of nitrogenous molecules with carboxylic acids, i.e., fatty acids and naphthenic acids),
- Nitrogen quaternaries,
- Polyoxylated amines, amides, imidazolines, and
- Nitrogen heterocyclics.

FIELDS OF APPLICATION

Corrosion problems may occur in numerous systems within the petroleum industry. These include:

- Acid stimulation jobs,
- Cooling systems,

- Drilling muds,
- Oil production units,
- Oil storage tanks,
- Protection of pipelines,
- Refinery units,
- Scale removal treatments using acids,
- Steam generators, and
- Technological vessels.

Many anticorrosion compositions involve environmentally dangerous products, such as chromates, fatty amines of high molecular weights, imidazolines, etc. The use of some of the alternatives, for instance, polyphosphate or polyphosphonate, is limited because they precipitate in the presence of the salts of alkaline earth metals, or because of their high costs.

Acidization

Acidization is an oil reservoir stimulation technique for increasing well productivity. Stainless steels have been used successfully to combat hydrogen sulfide (H_2S) and carbon dioxide (CO_2) corrosion, but these materials are susceptible to hydrochloric acid (HCl). HCl is used in oil and gas production to stimulate the formation.

The downhole temperature may be in excess of 200°C in deep wells, and acid treatment occurs through steel tubes, hence this process requires a high degree of corrosion inhibition. Electrochemical measurements are nonpredictive in inhibited concentrated HCl at high temperatures (Hausler, 1986).

Oil Storage Tanks

Storage tank bottoms are protected from corrosion through the use of cathodic protection. In general, this method is successful, but problems arise when there is not complete contact with the soil. This occurs when the bottom buckles slightly, leaving air spaces, after the filling or emptying of the tank. Or, over time, a portion of the base may erode away. In either case, the electrical continuity is lost. Other methods of protection, such as protective coatings, are not suitable.

When the bottom plates are welded together, the coating is partially destroyed. Research and field work showed that protection can be achieved using volatile corrosion inhibitors under the tank (Gelner, 1996). This works alone or in combination with cathodic protection.

Double tank bottoms for leakage monitoring are often specified for new tanks, but the same problem of coating destruction occurs. Volatile corrosion inhibitors are an excellent solution from both a technical and an economic standpoint. This type of corrosion inhibitor has a long history of corrosion protection under the conditions of wet, corrosive environments in void spaces.

Pipelines

The normal industrial practice for controlling the internal corrosion of petroleum pipelines is to use coatings, nonmetallic pipeline materials, or corrosion inhibitors. Corrosion inhibitors, which are used for the protection of oil pipelines, are often complex mixtures.

The consequences of pipeline failure can include inventory loss, production shutdown, environmental damage, safety risks, and excessive repair and replacement costs (Kennard and McNulty, 1993). Chemical treatment can delay or inhibit the internal corrosion of a pipeline so that the line can fulfill its operating requirements over its design life.

Using pigs for corrosion inhibitor applications is particularly useful in gas and gas-condensate transmission pipelines, especially in multiphase flow service. Selecting a pig for inhibitor batching is based on its ability to create a good seal between the pig cups and the pipe wall. The thickness of the film deposited during inhibition must be known to correctly size the slug inhibitor. Epoxide resins with aromatic amines are used as coatings for pipelines (Camberlin et al., 1999a,b,c).

Production Wells

Unalloyed or low-alloyed steels of various strength are generally used in the production of oil and gas. Inhibitors must be injected into the borehole to increase the life of well casing, flow lines, and equipment of unalloyed and low-alloyed steels in corrosive media. If the inhibitor is improperly chosen, considerable corrosion damage may result, such as damage without hydrogen influence and hydrogen-induced damage in the presence of H_2S.

Agitator autoclave tests can be used as screening tests despite the more intensive localized corrosion attack and the generally greater erosion rates in field tests. This test method elucidates the influences of certain test parameters including temperature, H_2S/CO_2 ratio, and flow rate (Faessler, 1990).

Scale Removal Treatments Using Acids

Acids injected downhole for scale removal treatments are extremely corrosive to the production tubing and casing liners. Inhibitors are added to the stimulation fluids to minimize this corrosion. The effectiveness of inhibitors can be estimated with laboratory screening methods (Burger and Chesnut, 1992).

APPLICATION TECHNIQUES

Application techniques include batch and continuous application.

Batch Versus Continuous Application

Batch treatment of pipelines with liquid or gel slugs of inhibitor, with continuous injection as a backup (or vice versa), are accepted methods of corrosion prevention (Kennard and McNulty, 1992). Batching liquid or gel inhibitors using pigs is more likely to attain complete coverage of the internal surface of the pipe wall than is continuous injection.

The film laid down is quite resilient and long casting. Important factors to optimize the application include determining film thickness and selecting an appropriate pigging system and program. Cleaning of the pipeline before inhibitor pigging is recommended.

Emulsions

Corrosion inhibitors are often emulsions that are able to form an organic film on the parts to be protected.

Application in Solid Form

The preparation of a corrosion inhibitor in solid form allows the development of a new technique of continuous intensive anticorrosive protection for gas and oil pipelines, as well as for acidizing operations of oil wells (Guimaraes et al., 1994). The controlled dissolution of the solid inhibitor creates a thin protective layer on the metallic surface, which prevents or at least minimizes undesirable corrosion reactions.

CHARACTERIZATION

The common method of treating rod-pumped wells is to periodically batch the inhibitor into them. The treatment period for a given well is selected using empirical rules based on well production volumes. To be successful and economic, the corrosion inhibition program must carefully control the inhibitor concentration in the well fluids.

Environmental aspects and efficacious inhibitor usage necessitate the measurement of very low corrosion inhibitor concentrations. Inhibitor concentrations as low as one part per million are significant, thus requiring an analytical technique that has a detection limit of a fraction of a part per million.

Accurate monitoring of the residual concentrations of the inhibitors is most important in systems in which the volume of water is unknown, or is highly variable. Frequent monitoring of the inhibitor concentration in the water exiting the pipeline is the simplest, and sometimes the only method that can be used to ensure that the line in fact is being protected.

Dye Transfer Method

The classic method for the determination of corrosion inhibitors in oil field brines is the dye transfer method. This method is basically sensitive to amines, but has many variations that the analyst may use to determine the amount of corrosion inhibitor, in either water or crude oil. Unfortunately these methods detect all amines present as corrosion inhibitors (Matherly et al., 1995).

Liquid Chromatography

Improved high-pressure liquid chromatography and high-performance liquid chromatography (HPLC) methods have been developed for the analysis of quaternary salt type corrosion inhibitors in brine waters (Cossar and Carlile, 1993), but they are not suitable for imidazolines and amido amines. A method based on fluorescence detection has been described for the quantitative analysis of the imidazoline-type and amido amine type corrosion inhibitors in both oil field water and crude oil samples by HPLC (Matherly et al., 1995).

Another analytic procedure based on HPLC has been developed for the quantitative determination of nitrogen-containing corrosion inhibitors (McKerrell and Lynes, 1988). The method was primarily developed for the analysis of certain oil pipeline condensate samples.

A fully automated instrumental procedure has been developed for analyzing residual corrosion inhibitors in production waters in the field, using ultraviolet and fluorescence spectrophotometric techniques.

Laboratory evaluations have shown that fluorescence is more suitable for field application because it minimizes errors from high salinity, contamination, and matrix effects. Comparison of the automated fluorescence technique with the classic extraction-dye transfer technique showed the former to be easier, faster, and to have greater to accuracy, and precision (Son and Chakravarty, 1996).

Thin Layer Chromatography

Attempts have been made using thin layer chromatography, to analyze amounts of residual inhibitors down to less than one part per million (Buck et al., 1993).

Ultraviolet Spectroscopy

Ultraviolet spectroscopy can be used to detect low levels of organic corrosion inhibitors in produced water. An analytic method has been developed using a diode array ultraviolet spectrophotometer (Fortenberry et al., 1993).

Corrosion Tests

Immersion tests, weathering, electrochemical measurements, and microscopy are all used to monitor the effect of different classes of organic inhibitors and their synergy with other additives (Dietsche et al., 2007).

Standard procedures have been developed to remove corrosion products without significant removal of the base metal layer. This allows an accurate determination of the mass loss of the metal or alloy that has occurred during exposure to a corrosive environment (ASTM Standard, 2010b).

Electrochemical measurements of the corrosion rate often provide results in terms of an electrical current or electrical resistance. Although the conversion of these current values into mass loss rates or penetration rates is based on the law of Faraday, calculations can be complex for alloys and metals with elements having multiple valence values. Guidance in calculating mass loss and penetration rates for such alloys has been provided, and some typical values of equivalent weights for a variety of metals and alloys have been compiled (ASTM Standard, 2010a).

There is a standard that specifies the mechanisms of corrosion and parameters for the selection of materials for pipes, tubes, and equipment for the transport and processing of hydrocarbons. Guidelines are given for International Organization for Standardization (2010):

1. Corrosion assessments,
2. Choice of materials for specific applications and systems,
3. Performance of specific materials, and
4. Corrosion tests.

Standards concerning materials for use in H_2S-containing environments in oil and gas production have also been provided (International Organization for Standardization, 2009a,b,c).

SIDE EFFECTS

Stabilizer for Emulsions

Some corrosion inhibitors have a side effect of stabilizing emulsions. This is sometimes undesirable.

Antisynergism with Alcohols

In stimulation fluid that contains concentrated HCl, the partial substitution of water by alcohols such as methanol, ethanol, and glycerol increases the corrosivity of the acid fluids; and so reduces the efficiency of the corrosion inhibitors (Mainier et al., 1990). This effect is especially important for fatty amine based inhibitors. For products containing acetylenic-type inhibitors the detrimental effect is less important and weight losses may be maintained within acceptable limits by using slightly higher, but still reasonable, levels of inhibitor.

Synergism with Surfactants

Certain surfactants greatly improve the performance of *trans*-cinnamaldehyde as a corrosion inhibitor for steel in HCl (Growcock, 1987; Shah et al., 1994, 1992), by enhancing the adsorption at the surface of the steel. Increased solubility or dispersibility of the inhibitor is an incidental effect. *N*-dodecylpyridinium bromide is effective in this aspect far below its critical micelle concentration, probably as a result of electrostatic adsorption that leads to the formation of a hydrophobic monolayer, which attracts the inhibitor. On the other hand, an ethoxylated, nonyl phenol acts by incorporating the inhibitor into micelles, which themselves adsorb on the steel surface and facilitate the adsorption of *trans*-cinnamaldehyde.

Interactions with Kinetic Gas Hydrate Inhibitors

Gas hydrate inhibitors are often added together with corrosion inhibitors, but the two may be incompatible in the formulation.

It has been discovered that quaternary alkylaminoalkyl alkoxy esters and amides, respectively, both exhibit an excellent performance as corrosion inhibitors and gas hydrate inhibitors, as well as an improved film persistence and good biodegradability (Dahlmann and Feustel, 2008).

The general method for the preparation of alkylaminoalkyl alkoxy monoesters from dicarboxylic anhydrides has been described in detail (Dahlmann and Feustel, 2008; Leinweber and Feustel, 2009). The anhydride is heated in nitrogen atmosphere with an alkoxylated alkylenediamine. The products are then quaternized with dimethyl sulfate. For example, *N*,*N*-dibutylamino-*N*-tri(ethoxy)ethyl dodecenyl-tetradecenylsuccinate is obtained from dodecenyl-tetradecenylsuccinic anhydride and ethoxylated dibutylamine. The method is also suitable for polymer analog synthesis.

As a consequence of their ester and amide structure, these compounds have better biodegradability and can be used at a lower dosage (Dahlmann and Feustel, 2008). A series of compounds has been synthesized and tested both as gas hydrate inhibitors and corrosion inhibitors.

Interactions take place between kinetic gas hydrate inhibitors and corrosion inhibitors. Two theories concerning these interactions have been developed and tested. The first theory involves competition between them, which at the surface interface can be elucidated by measurements of the surface tension. The second theory postulates absorption of the corrosion inhibitor onto a polymeric kinetic gas hydrate inhibitor.

One commercially available kinetic gas hydrate inhibitor, poly(vinylcaprolactam) and three commercial available corrosion inhibitors, cocodimethyl benzyl ammonium chloride, aminoethyl fatty imidazoline, and an ethyoxylated phosphate ester were used to test these ideas (Moore et al., 2009).

The corrosion inhibitors had a varying negative impact on the kinetic gas hydrate inhibitor. However, the results from the corrosion testing indicate only a minimal interference of the performances. The efficiency of all corrosion inhibitors tested have been found to be dependent on the structure of the polymer (Moore et al., 2009), indicating that the second theory (absorption) is more sound.

Effect of Flow on Inhibitor Film Life

Experiments using low- and high-velocity conditions were performed in standard laboratory tests (Eaton and Sutton, 1994). It was found that corrosion is governed by the flow of reactants and products to and from the corroding surface. Corrosion in oxygenated fluids increases with the velocity of the fluid because a greater amount of oxygen is made available to the surface.

Corrosion of steel in fluids containing CO_2 produces a protective iron carbonate film that initially results in decreased corrosion. However, at high velocities the protective layers are broken off, thus exposing the bare metal to the aggressive medium and increasing the corrosion rate. Inhibitor films are protective because they reduce the transfer rate of the corrosants, but they can become ineffective because of aging, removal, and dilution. In all of the previous examples the velocity is an important variable, governing the ability of the inhibitor to control the corrosion rate.

INHIBITOR CHEMICALS

Amides and Imidazolines

Amides

An amide-type corrosion inhibitor is prepared as follows: methyl methacrylate is converted with tallow triamine or tallow tetramine at 80–90°C into the corresponding amides. After completion of this reaction, the temperature is raised to initiate polymerization (Niu et al., 1988), which is performed at temperatures up to 200°C. The polymer controls the corrosion of metal surfaces in contact with a corrosive hydrocarbon-containing medium.

Ammonium salts of alkenyl succinic half-amides have been described as corrosion inhibitors to combat corrosion in media containing CO_2, H_2S, and elemental sulfur (Oppenlaender et al., 1993). The inhibitor composition may contain a dispersing agent, such as a low molecular weight or polymeric anionic surfactant, such as an alkylsulfonic acid or an alkyl-aryl sulfonic acid.

Ethoxylated and propoxylated alkyl phenol amines, converted into the amides with a fatty acid or similar long chain diacids, are effective in controlling sour and sweet corrosion (Valone, 1987a,b, 1989a,b,c). Properties of fatty acids are shown in Table 6.1 and the structure of some acids are shown in Figure 6.1.

Tall oil is a waste product from the paper making industry. Tall oil derivates have been proposed as alterative biofuel materials (AltIparmak et al., 2007). Tall oil fatty acids consist of resinic acids and of a mixture of linolic acid, conjugated C_{18} fatty acids, oleic acid, 5,9,12-octadecatrienic acid, and saturated fatty acids. Resin acids are abietinic acid, dehydroabietic acid, and others. The overall composition of tall oil fatty acids is shown in Table 6.2.

Polyimido amines

Corrosion inhibiting compositions for metals that are subjected to highly acidic environments may be produced by reacting a styrene/maleic anhydride (MA) copolymer with a poly(amine) in a condensation reaction to produce a polyimido amine inhibitor (Schilling, 1995). Such inhibitors exhibit film

TABLE 6.1 Fatty Acids

Name	Formula	Melting Point/[°C]
Lauric acid	$CH_3-(CH_2)_{10}-COOH$	44
Myristic acid	$CH_3-(CH_2)_{12}-COOH$	59
Palmitic acid	$CH_3-(CH_2)_{14}-COOH$	63
Stearic acid	$CH_3-(CH_2)_{16}-COOH$	70
Oleic acid	$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$	16
Linoleic acid	$CH_3(CH_2)_4-(CH=CH-CH_2)_2-(CH_2)_6-COOH$	−5
Linolenic acid	$CH_3-CH_2-(CH=CH-CH_2)_3-(CH_2)_6-COOH$	−11

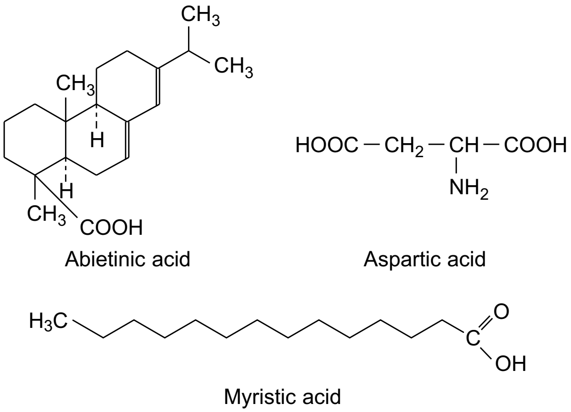


FIGURE 6.1 Acids for inhibitors.

forming characteristics. Some relevant poly(amine)s are listed in Table 6.3. Diamines are shown in Figure 6.2.

Polypeptides

Polypeptides have been under consideration as corrosion inhibitors because of their environmental acceptability (Obeyesekere et al., 2001). Polyaspartate is the most efficient corrosion inhibitor known among the polypeptides (McMahon and Harrop, 1995). Its molecular weight (1–22 kDalton) does not affect its efficiency, but both high calcium ion concentration and high pH enhance the effectiveness. The performance was particularly good in batch treatment tests.

TABLE 6.2 Composition of Tall Oil Fatty Acids (Nogueira, 1996)

Component	Amount/[%]
Resinic acids	40–50
Fatty acids	30–40
Unsaponifiable material	10

TABLE 6.3 Poly(amine)s

Name	Formula	Melting Point/[°C]
Tetraethylene-pentamine	$H_2N{-}(CH_2{-}CH_2{-}NH)_4H$	−30
Ethylene diamine	$H_2N{-}CH_2{-}CH_2{-}NH_2$	9
1,2-Propylenediamine	$H_2N{-}CH_2{-}CH({-}NH_2){-}CH_3$	−37
Trimethylene diamine	$H_2N{-}CH_2{-}CH_2{-}CH_2{-}NH_2$	−12
1,4-Butanediamine	$H_2N{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}NH_2$	27

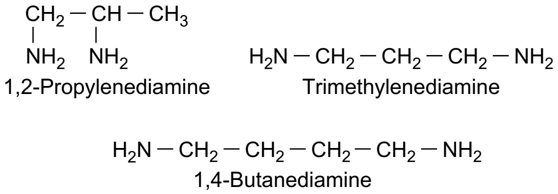


FIGURE 6.2 Diamines.

In another study, polyaspartic acid was examined as a corrosion inhibitor for steel over a range of pHs and temperatures (Silverman et al., 1995). At low to neutral pH values, it increases the corrosion rate of steel, but at pH values above 10, polyaspartic acid is a reasonably robust corrosion inhibitor.

Ampholytes

Corrosion inhibitors used in offshore oil production are highly cationic, but they are becoming less acceptable for environmental reasons. Cationic inhibitors are attracted to metal surfaces, thereby controlling the acid type corrosion. When these cationic corrosion inhibitors enter sea water, they are attracted to diatoms, which are type of algae. These algae are part of the food chain for mussels.

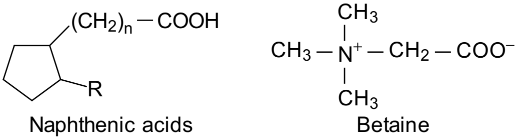


FIGURE 6.3 Naphthenic acids, betaine.

Betaines, shown in Figure 6.3, and ampholytes (Larsen, 1991) can be used instead of cationic inhibitors or can be neutralized with acids such as acetic acid, adipic acid, sebacic acid, naphthenic acids, paraffinic acids, tall oil acids, and free sulfur dioxide. They are claimed to prevent CO_2 corrosion.

Slow-release Formulation

An amido amine obtained from the reaction of tetraethylenepentamine with stearic acid is modified with propylene oxide. The product is dispersed in a polymer matrix such as an acrylic or methacrylic polymer. This inhibitor is slowly released into the surrounding environment, such as in an oil or gas well, to prevent corrosion of metal equipment in the well.

Salts of Nitrogenous Bases

A corrosion inhibitor with excellent film forming and persistency characteristics is produced by first reacting C_{18} unsaturated fatty acids with MA or fumaric acid to produce the fatty acid Diels-Alder adduct or the fatty acid-ene reaction product (Alford et al., 1994). This reaction product is further reacted in a condensation or hydrolyzation reaction with a polyalcohol to form an acid anhydride ester corrosion inhibitor. The ester may be further reacted with amines, metal hydroxides, metal oxides, ammonia, and combinations thereof to neutralize the ester.

Surfactants may be added to tailor the inhibitor formulation in order to meet the specific needs of the user, for instance the corrosion inhibitor may be formulated to produce an oil-soluble, highly water-dispersible corrosion inhibitor or an oil-dispersible, water-soluble corrosion inhibitor. Suitable carrier solvents may be used as needed to disperse the corrosion inhibitor formulation.

Similarly, a salt of an ethoxylated amine and a reaction product of an alcohol and a fatty acid MA adduct produced by a reaction between MA and an unsaturated fatty acid has been described (Dougherty et al., 1996).

Nitrogen Quaternaries

Quaternary ammonium iodides were tested, alone and in combination with propargyl alcohol, with several steels in 15% HCl. The quaternary ammonium iodides showed a better inhibitor performance to that of propargyl alcohol (propargyl: $-CH_2-C \equiv CH$) at identical dosage levels. Mixtures of propargyl alcohol and quaternary ammonium iodide showed a synergistic effect (Neemla et al., 1992), as did formic acid (Brezinski and Desai, 1998) and thiols (Vorderbruggen and Williams, 2000).

It has been shown that the corrosion rates of various steels can be reduced to less than $1\,\mathrm{mg\,cm^{-2}hr^{-1}}$ by using ternary inhibitor mixtures containing quaternary ammonium salts, *trans*-cinnamaldehyde, and potassium iodide in amounts of 0.2% of each component (Trabanelli et al., 1988).

Thio-Substituted Salts

A thio-substituted, quaternary ammonium salt can be synthesized by the Michael addition of an alkyl thiol to acrylamide (AAm) in the presence of benzyl trimethyl ammonium hydroxide as a catalyst (Haslegrave and Sullivan, 1987). The reaction leads to the crystallization of the adducts in essentially quantitative yield.

Reduction of the amides by lithium aluminum hydride in tetrahydrofuran solution produces the desired amines, which are converted to desired halide by reaction of the methyl iodide with the amines. The inhibitor is useful in controlling corrosion such as that caused by CO_2 and H_2S.

Synergism of Thiosulfate

Laboratory observations have revealed that a combination of thiosulfate with cationic nitrogenous inhibitors has a significant effect on improving their performance (Phillips et al., 1996).

Polyoxylated Amines, Amides, and Imidazolines

A mixture of alkyl-ethylene diamine and di-alkyl-diethylene triamine, with an alkyl side chain of 8–26 carbon atoms is suitable (Young, 1993) as a corrosion inhibitor. This product can be further reacted with an alkylating agent or an alkylene oxide (Ho, 1993, 1994).

The inorganic nitrite used as a corrosion inhibitor in aqueous alkylene glycol or polyalkylene glycol solutions can be replaced with polyoxyalkylene amines (Morris-Sherwood and Brink, 1987, 1990). Such polyoxyalkylene amines impart corrosion inhibition to the liquid in contact with the metal and the metal in contact with the vapors of the aqueous composition. Aqueous compositions containing the glycol and the polyoxyalkylene amine also exhibit a low foaming tendency.

Mercaptan Modified Products

In highly acidic environments, a reaction product of an isobutyraldehyde and an alkylene amine compound with an alkylsulfopropionic amide group is recommended (Zetlmeisl and French, 1992a,b). The alkylene amine compound can be the product of a reaction of equimolar amounts of *N*-dodecylmercaptan, methyl methacrylate, and diethylene triamine.

Polyamine Derivatives

Fatty Amine Adducts

Dimerized fatty acid thioesters (with a dithiol), in combination with fatty amines, are sulfur-containing corrosion inhibitors Incorvia (1988b), which are best used in a hydrocarbon solvent.

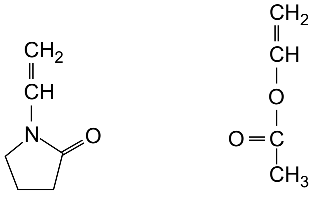
Adducts of a fatty amine adduct to unsaturated acid in which the product contains only secondary or tertiary amine groups have a lower toxicity to the environment (Clewlow et al., 1992).

Adducts to Polymers

Polymeric polyolefins, such as polybutadiene, secondary amines, and synthesis gas, are reacted in the presence of a catalyst system comprising a ruthenium-containing compound, a rhodium-containing compound, a sterically hindered phosphine, and a solvent (McEntire and Knifton, 1987).

Preferred polybutadiene feedstocks are those with a predominance of straight chain, rather than pendant olefin groups and in particular, those polymers containing both the 1,2-polybutadiene and 1,4-polybutadiene units. These polymers of high amine content are useful as downhole corrosion inhibitors.

A low molecular weight, polyfunctional polymer can be formed by polymerizing a vinyl monomer in the presence of a mercaptan chain transfer agent (Wu and Gray, 1992). The vinyl monomer may be an unsaturated acid, acrylonitrile, vinylester, a variety of AAms, or *N*-vinyl-2-pyrrolidone. The molar ratio of the vinyl monomer to the mercaptan is preferably in the range of 2–40 mol of the vinyl monomer to 1 mole of the mercaptan. The composition and methods are useful for inhibiting corrosion of downhole metal surfaces present in oil and gas wells. Relevant vinyl monomers are shown in Figure 6.4.



1-Vinyl-2-pyrrolidinone Vinylacetate

FIGURE 6.4 Vinyl monomers.

Formaldehyde Condensates with Amines

Corrosion inhibitor compositions useful for oil and gas well applications are prepared by reacting 2,5-dimethylpyridine or 2,4,6-collidine with formaldehyde or acetone and an amine such as 1-dodecanamine (Treybig and Martinez, 1988, 1989). A hydrocarbon-soluble corrosion inhibitor is obtained by the acid-catalyzed oligomerization of an alkylaniline and formaldehyde (Bacskai and Schroeder, 1988b).

These oligomers exhibit good initial inhibition of metal corrosion in aqueous environments, and this effect is more persistent than that observed for the corresponding monoamine starting material. Moreover, in an acidic environment, the products show superior persistence in inhibiting corrosion when compared with known monoamine corrosion inhibitors, such as tallow amine.

The oligomers can be formulated to be both hydrocarbon-soluble and water-dispersible. The water dispersibility can be controlled by varying the type and amount of the additional aromatic compound, such as ethoxylated alkyl phenol, that is included in the oligomerization reaction mixture (Bacskai and Schroeder, 1988a).

A corrosion inhibitor that is the adduct of a carbonyl compound, an amine, and a thiocyanate has been described (Petersen et al., 1990). The product provides protection against ferrous corrosion in severe environments at concentrations of 500 ppm. The inhibitor is employed in wells that produce both oil as well as water in high-temperature environments around 120°C.

Lignin Amines

Lignin amines with high nitrogen content are water-soluble at both alkaline and acidic pH values, and have various useful properties. For instance, they are active as flocculants, filtration aids, scale inhibitors, fluid loss additives, oil well cement additives, and corrosion inhibitors among other potential uses. The nitrogen is introduced into the lignins by the Mannich reaction (Schilling and Brown, 1988).

Amido Amine Salts

Amido amine salts have been found to be effective corrosion inhibitors, and are essentially environmentally friendly. They are used in formate solutions, as long as the high pH environment does not hydrolyze the amido group.

The compounds can be prepared by the reaction of amines with a fatty acid. For example, soya fatty acid can be reacted with *N*-ethyl ethylene diamine by heating to 150°C for a period of 4 h. The reaction product is then solubilized by forming the salts with acetic acid (Miksic et al., 2004).

Tenax 2010 (Westvaco) is a commercially available inhibitor, which is obtained from the Diels Alder reaction of MA and a fatty acid and subsequently with amines. The amido diacid is solubilized with 2-amino-2-methyl-1-propanol or ethanolamine. The reaction is shown schematically in Figure 6.5.

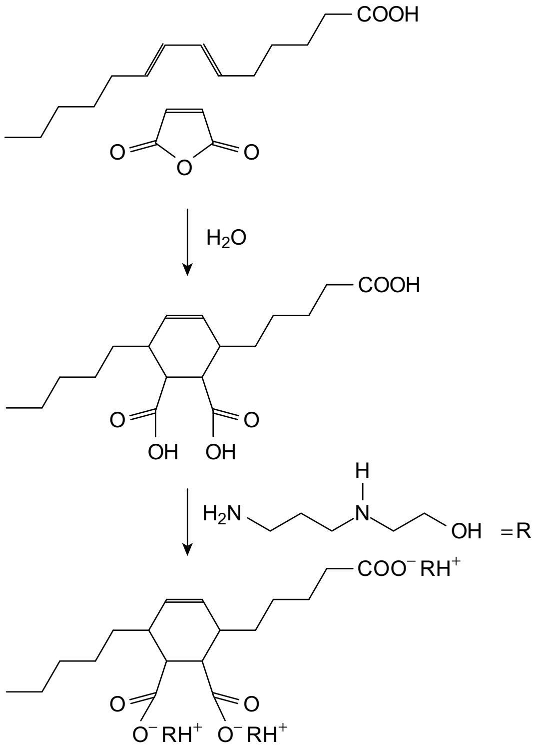
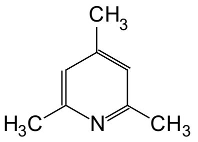


FIGURE 6.5 Diels Alder reaction of a conjugated unsaturated fatty acid (Fischer and Boyd, 1998).



Collidine

$H-C\equiv C-CH_2-OH$

Propargyl alcohol

FIGURE 6.6 Collidine, propargyl alcohol.

Fatty Acid Amides

Propargyl alcohol has been found to be active in corrosion control, and a variety of formulations containing it have been proposed. Propargyl alcohol is shown in Figure 6.6.

A condensate of a polyamine, such as diethylene triamine, triethylenetetramine, or aminoethylethanol amine, with C_{21} or C_{22} carbon fatty acids or tall oil fatty acids, can be used as corrosion inhibitor base (Schilling and Braddon, 1986). Propargyl alcohol has been found to enhance the anticorrosive effects of this composition.

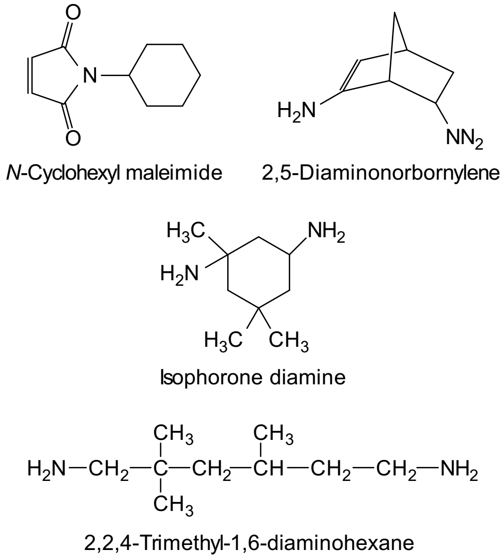


FIGURE 6.7 Amides and amines.

Most simply, a mixture of mainly 80–90% propargyl alcohol and cellosolve, with minor amounts of polyglycol, amine derivatives, a phenol-formaldehyde resin, and tar bases, has been described (Briggs, 1987, 1990).

Instead of propargyl alcohol, propargyl ether has been proposed as a corrosion inhibitor. Propargyl alcohol is added to olefins to form the corresponding ether (Karaev et al., 1996).

Fatty acid amides of isophorone diamine, 2,5-diaminonorbornylene, and 2,2,4-trimethyl-1,6-diaminohexane are particularly suitable for high-temperature and high-pressure applications (Kissel, 1999). The respective compounds are shown in Figure 6.7.

Nitrogen Heterocyclics

Hexamethylenetramine

Acetylenic alcohols such as propargyl alcohol, 1-hexyn-3-ol, and 5-decyne-4,7-diol have been used as corrosion inhibitors in HCl for the protection of ferrous metals. However, acetylenic alcohols are expensive and their use at temperatures in the range of 80–180°C (180–350°F) has been limited by the high concentrations that are needed to achieve the desired corrosion protection (Funkhouser et al., 2001).

The presence of a small amount of hexamethylenetetramine dramatically improves the performance of the acetylenic alcohols in reducing corrosion and enables their use at lower concentrations or higher temperatures than when used alone. Hexamethylenetetramine also acts as a sulfide scavenger, whereby the formation of free sulfur or the formation of ferrous sulfide precipitate is prevented.

The metal corrosion inhibiting compositions can also include solvents. The formation of ferric hydroxide precipitate, free sulfur, and other precipitates can be prevented.

Imidazolines

Quaternized imidazolines with an amido moiety are suitable corrosion inhibiting formulations for general oil and gas field applications. The synthesis of such compounds is detailed in the literature (Meyer, 2001). For aqueous systems that contain sulfide compounds, a mixture has been described that consists of an aqueous solution of an alcohol, such as diethylene glycol monobutyl ether, butyl cellosolve, additional orthophosphoric acid, a tall oil fatty acid, a substituted imidazoline, an ethoxylated fatty diamine, and a molybdate compound (Brown et al., 1996).

A modification of the previous formulation uses amine products preferably containing only tertiary amino groups (Williams et al., 1994). These amines have favorable ecotoxicity levels in marine or fresh water environments. The ecotoxicity decreases with increasing substitutions on the nitrogen atoms present. It appears that tertiary groups are less toxic than secondary groups, which are in turn less toxic than primary groups. Combinations of imidazoles with wetting agents also have been described (Braga et al., 2000).

Water-soluble corrosion inhibitors are necessary to prevent corrosion of pipe walls, joints, pumps, and collection stations. An ampholytic, substituted imidazoline has been described for inhibiting corrosion in such systems (Byrne and Johnson, 1994). This type of corrosion inhibitor is intended for continuous treatment.

Pourable emulsions comprising up to 50% of a kerosene-containing corrosion inhibiting compound have been claimed to allow longer treatment intervals (French et al., 1991a,b). A formulation that is resistant to sludge formation and does not tend to stabilize oil–water emulsions has been described in the literature. An imidazoline derivate, prepared from a long chain fatty acid and a polyamine, is dissolved in an aromatic solvent and dispersed with glycolic acid and hexylene glycol (McCullough, 1991).

In water systems, sulfate-reducing bacteria and sulfides are present. To prevent their growth, chlorine dioxide (ClO_2) is added, but this is highly corrosive to the metallic components used in oil field equipment. Chromates are successful ClO_2 corrosion inhibitors, but they are also undesirable because of their high toxicity. A mixture of an alcohol, an acid, a fatty imidazoline, an ethoxylated fatty diamine, and water can be used (Ohlsen et al., 1995) as an alternative. Such a composition has proved to be more effective than chromates inhibiting the corrosion caused by ClO_2, without the serious toxicologic effects.

It has been reported that the corrosion rate of steel in the presence of H_2S is greatly decreased by adding imidazoline compounds or quaternary ammonium salts into the drilling fluids (Jiashen and Jingmao, 1993). A concentration of $2\,\mathrm{g\,l^{-1}}$ gives an inhibition efficiency of 70–90%. If it is used together with the H_2S scavenger–alkaline zinc carbonate, the inhibition becomes even more effective.

A synergistic effect is found between imidazoline inhibitors and calcium oxide. They also inhibit dioxide corrosion to some extent in H_2S-free drilling muds. Moreover, imidazoline can improve the rheologic properties of a drilling mud.

Polyesters may be used (Alford et al., 1992, 1993a,b,c; Boyd et al., 1993) instead of a fatty acid modifier for imidazoline. In this way, a corrosion inhibitor that forms persistent films can be produced by first reacting a polybasic acid with a polyalcohol to form a partial ester. The partial ester is reacted with imidazoline or fatty diamines to result in a salt of the ester.

Pyridinium Compounds

Aliphatic pyridinium salts or aliphatic quinolinium salts in the presence of a sulfur-containing compound have been claimed to be active as corrosion inhibitors (Kennedy, 1987). *N*-(*p*-Dodecylphenyl)-2,4,6-trimethylpyridinium sulfoacetate is suitable as an inhibitor in aqueous media (Fisk and Tucker, 1991). Such pyridinium compounds exhibit greater thermal stability than *N*-aralkyl pyridinium compounds or *N*-alkyl pyridinium compounds, and the desired properties are retained both during and after exposure to elevated temperatures.

An α,β-ethylenically unsaturated aldehyde, together with organic amines, will form intermediate products, which are further reacted with a carboxylic acid, an organic halide, or an epoxide-containing compound (Treybig and Glass, 1988). The final products are suitable corrosion inhibitors for preventing corrosion of steel in contact with corrosive brine and oil and gas well fluids.

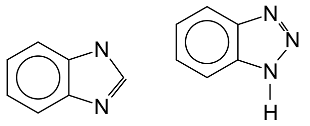
Still bottom residues, as produced in the distillation of quinoline from coal tar, can be oxidized and are then suitable as a metal corrosion inhibitor for use in aqueous acid solutions (Brezinski, 1998).

Azoles

The effectiveness of various chemicals, such as 1H-benzotriazole, 2-methylbenzotriazole, and 2-phenylbenzimidazole as a corrosion inhibitor for mild steel in 15% HCl was investigated, using weight loss and electrochemical techniques (Samant et al., 1989). 2-Phenylbenzimidazole showed the best performance of the azoles. A synergism of iodide and 2-phenylbenzimidazole was observed. Azoles are shown in Figure 6.8.

Aminopyrazine with Epoxide Compound

A condeasate of condensate aminopyrazine and an epoxide compound, such as the glycidyl ether of a mixture of C_{12} to C_{14} alkanols (Fischer, 1990) acts as an inhibitor during drilling and servicing of oil and gas wells.



Benzimidazol 1H-Benzotriazol

FIGURE 6.8 Azoles.

Carbonyl Compounds

Aldehydes with Surfactants

Mixtures of aldehydes such as *trans*-cinnamaldehyde with surfactants are active in preventing corrosion, in particular in the presence of mineral or organic acids (Frenier and Growcock, 1988b). The surfactant used was *N*-dodecylpyridinium bromide or the reaction product of trimethyl-1-heptanol with ethylene oxide (Frenier and Growcock, 1988a). Such aldehyde and surfactant mixtures provide greater and more reliable corrosion inhibition than the respective compositions containing aldehydes alone.

Aldose Group Antioxidants

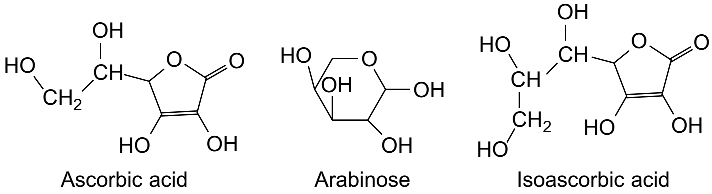
Sodium, ammonium, or calcium thiocyanate alone, or in combination with specific aldose group antioxidants can be used as corrosion inhibitors with calcium-free drilling, completion, and workover fluids in carbonate-containing or sulfate-containing wells (Dadgar, 1988a,b,c). Aldose group antioxidants include arabinose, ascorbic acid, isoascorbic acid, gluconic acid, and their corresponding salts. In addition, ammonium thioglycolate may be incorporated as another corrosion inhibitor. Thio groups and aldose group antioxidants exhibit synergistic properties (Shin, 1988). Aldose derivates are shown in Figure 6.9.

Similarly, a high-density brine, useful as a drilling fluid for deep wells, is made corrosion resistant by adding an aliphatic or aromatic aldehyde and thiocyanates (Henson and Doty, 1990). The aldehyde can be reacted with a primary amine before use.

Phosphate Esters

Phosphate ester-type inhibitors are produced by the reaction of ethoxylated, propoxylated, or butoxylated alcohols or phenols with phosphating agents (Naraghi, 1997; Naraghi and Grahmann, 1997; Walker et al., 2001). Inhibitors for both general corrosion and cracking-type corrosion are obtained by the reaction of a nitrogen base and a phosphate ester (Martin, 1988, 1993).

Although the nitrogen bases and phosphate esters have good general corrosion inhibition properties, neither provide suitable inhibition for cracking-type corrosion, but the neutralization product of the two provides inhibition of both general and cracking-type corrosion. This inhibitor type is safe for aquatic organisms and is biodegradable.



Ascorbic acid Arabinose Isoascorbic acid

FIGURE 6.9 Aldose derivates.

Silicate-based Inhibitors

Silicates (Mainier et al., 1992) offer advantages with respect to low costs, low toxicity, and low environmental impact.

Thioacetals

Many corrosion inhibitors are useful only at selected temperature levels or pH ranges for the various heavy brines. Temperature changes, or any change that affects the pH of the brine often results in loss of the corrosion inhibition. Particular problems arise in the selection of corrosion inhibitors for use in zinc halide-containing heavy brine solutions.

Many common corrosion inhibitors, such as organic thiophosphates, quaternized amines, polyphosphate esters, and filming amines, form precipitates or are ineffective when admixed with zinc halide-containing heavy brine solutions (Welton and Cassidy, 2007). Thioacetals can be synthesized by the reaction of an aldehyde with a thiol.

Preparation 6–1: Thioacetal corrosion inhibitors are formed by the reaction of cinnamaldehyde with thioethanol in glacial acetic acid. *p*-Toluene sulfonic acid is added as catalyst (Welton and Cassidy, 2007). ■

The reaction is shown in Figure 6.10. In the same way, other thioacetal compounds have been synthesized and tested for corrosion. The various thioacetals are summarized in Table 6.4.

To test their activity, a weighed coupon was suspended from a Teflon® holder inside a cell constructed of glass. The cell was then placed in an autoclave, 100 ml of 15% HCl was poured into the cell, and then enough kerosene was added such that the coupon was sufficiently submerged. Finally, the contents of the test cells were infused either with traditional corrosion inhibitors, no inhibitor, or an above-described thioacetal inhibitor at a concentration of 0.00378 mol. The autoclave was then pressurized to 68 atm (1000 psig) under a nitrogen atmosphere, and heated to 107°C for a total contact time of 3 h. The results are summarized in Table 6.5.

The dithioacetal based on cinnamaldehyde and 1,2-thioethanol was very effective in preventing corrosion (Welton and Cassidy, 2007), but thioglycolic acid was found to enhance the rate of corrosion.

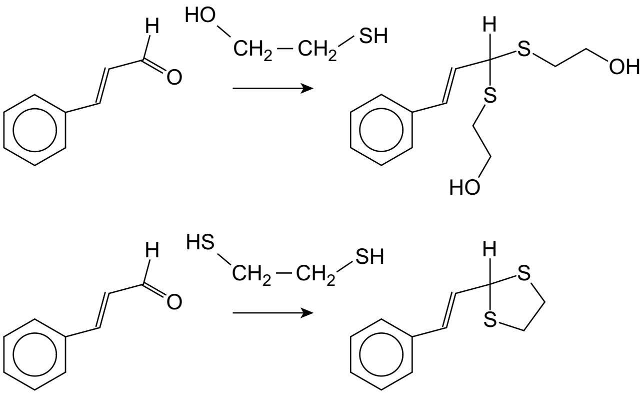


FIGURE 6.10 Formation of thioacetals (Welton and Cassidy, 2007).

TABLE 6.4 Thioacetal Compounds (Welton and Cassidy, 2007)

Number	Name
1	Cinnamaldehyde 1,2-thioethanol dithioacetal
2	Cinnamaldehyde 1,2-dimercapto ethane dithioacetal
3	Cinnamaldehyde thioacetic acid dithioacetal
4	Crotonaldehyde 1,2-thioethanol dithioacetal
5	Crotonaldehyde 1,2-dithiolane dithioacetal

TABLE 6.5 Efficacy of Thioacetal Compounds (Welton and Cassidy, 2007)

Inhibitor	Corrosion Loss/[kg m^{-2}]
None	2.13
Cinnamaldehyde	0.81
Thioglycolic acid	4.11
1 in Table 6.4	0.07
2 in Table 6.4	0.10
3 in Table 6.4	0.18
4 in Table 6.4	0.13
5 in Table 6.4	0.38

MISCELLANEOUS INHIBITORS

Antimony Halides

Antimony tribromide and other group VA halides minimize the corrosion rate effectively (Verma and Sandor, 2001). Unfortunately, antimony tribromide is toxic.

Aldol-amine Adducts

The corrosion of metal surfaces and the precipitation of a metal sulfide by an aqueous acid solution can be prevented by an aldol-amine adduct. Aldol (from acetaldehyde) $CH_3-CH(OH)CH_2CHO$ has been utilized as a H_2S scavenger that prevents the precipitation of metal sulfides from aqueous acid solutions. However, when the aldol or an aqueous solution of the aldol is stored, the solution separates quickly into two layers, with all of the aldol concentrated in the bottom layer. The bottom layer is not redispersible in the top layer or in water or acid. This bottom layer has very little activity as a sulfide scavenger, so the use of aldol as a H_2S scavenger in aqueous acid solutions can give unsatisfactory results (Brezinski, 2001a,b).

The aldol can be reacted with an amine, such as monoethanoleamine (= aminoethanol), to form an aldol-amine adduct to overcome these difficulties. The amine must be a primary amine, however. The aldol-amine adduct preferentially reacts with sulfide ions when they are dissolved in the acid compositions, thereby preventing the dissolved sulfide ions from reacting with dissolved metal ions and precipitating.

Some formulations that cannot be readily classified into any of the previous sections are summarized in Table 6.6. Some of these compounds are shown in Figure 6.11.

TABLE 6.6 Corrosion Inhibitors

Compound	References
Acetylinic alcohol[a]	Teeters (1992)
Tall oil fatty acid anhydrides	Fischer and Parker (1997)
3-Phenyl-2-propyn-1-ol[b]	Growcock and Lopp (1988)
Dicyclopentadiene dicarboxylic acid salts[c]	Darden and McEntire (1986, 1990)
Hydroxamic acid	Fong and Shambatta (1993)
Cyclohexylammonium benzoate	Johnson and Ippolito (1994, 1995)
Acyl derivatives of tris-hydroxy-ethyl-perhydro-1,3,5-triazine	Au (1986) & Au and Hussey (1989)

TABLE 6.6 Corrosion Inhibitors–Cont'd

Compound	References
2,4-Diamino-6-mercapto pyrimidine sulfate combined with oxysalts of vanadium, niobium, tantalum or titanium, zirconium, hafnium	Ramanarayanan and Vedage (1994)
Aqueous alkanol amine solution[d]	Schutt (1990) & Veldman and Trahan (1999)
Quaternized fatty esters of alkoxylated alkyl-alkylene diamines	Wirtz et al. (1989)
Mercaptoalcohols	Ahn and Jovancicevic (2001)
Polysulfide[e]	Gay et al. (1993)
Polyphosphonohydroxybenzene sulfonic acid compounds[f]	Kreh (1991)
1-Hydroxyethylidene-1,1-diphosphonic acid[g]	Sekine et al. (1991)
2-Hydroxyphosphono-acetic acid[h]	Zefferi and May (1994a,b)
Water-soluble 1,2-dithiol-3-thiones[i]	Alink (1991) & Oude Alink (1993)
Sulfonated alkyl phenol[j]	Babaian-Kibala (1993)
Polythioether	Incorvia (1988a)
Thiazolidines	Alink and Outlaw (2001)
Substituted thiacrown ethers pendent on vinyl polymers	Minevski and Gaboury (1999)
Benzylsulfinylacetic acid or benzylsulfonylacetic acid	Lindstrom and Mark (1987)
Halohydroxyalkylthio-substituted and dihydroxyalkylthio-substituted polycarboxylic acids[k]	Lindstrom and Louthan (1987)
Alkyl-substituted thiourea	Tang et al. (1995)
2,5-Bis(*N*-pyridyl)-1,3,4-oxadiazoles	Bentiss et al. (2000)

a) *In combination with* ClO_2 *treatment for bacteria control.*
b) *Aqueous* HCl
c) *0.1–6% with antifreezers such as glycols*
d) *Gas stream containing* H_2S *or* CO_2
e) *Forms a film of iron disulfide*
f) *Relatively non-toxic, substitution of chromate-based corrosion inhibitors, conventional phosphate, and organophosphonate inhibitors and the zinc-based inhibitors*
g) CO_2 *environment*
h) *Calcium chloride brine*
i) *10–500 ppm*
j) *5–200 ppm to inhibit naphthenic acid corrosion*
k) *In drilling equipment*

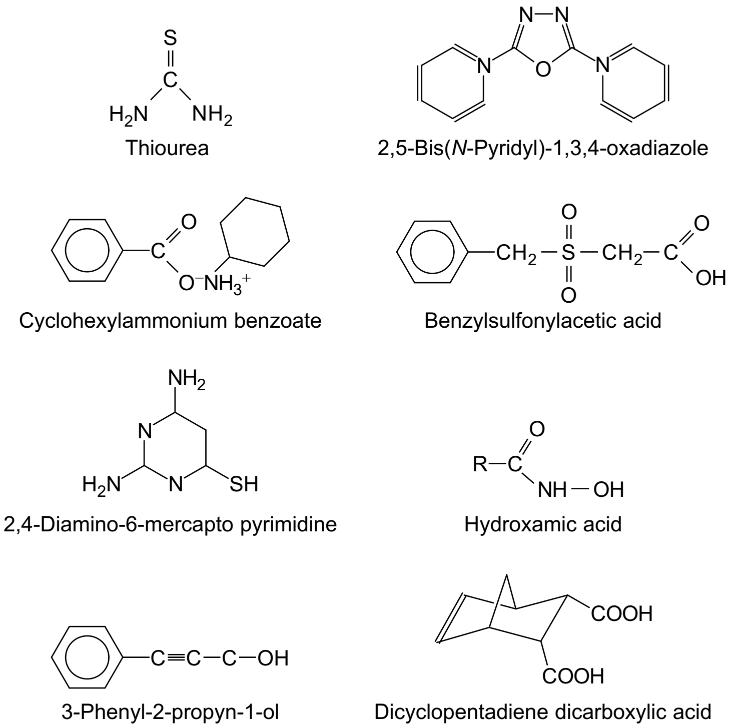


FIGURE 6.11 Miscellaneous compounds.

Encapsulated Types

Conventionally, corrosion inhibitors are applied by two basic modes: batch treatment and continuous chemical injection. Encapsulated time-release corrosion inhibitor has been shown to be highly effective against CO_2 corrosion in a field trial, and combines the advantages of both methods.

Here, the corrosion inhibitor is released in a time-controlled manner from the water-hydrocarbon interfacial region in the annulus of the well. The product is delivered like a continuous corrosion inhibitor treatment while using a conventional batch application, and exhibits a significant increase in efficiency (Weghorn et al., 2007).

Anti-biofoulant Corrosion inhibitors

Formulations containing didecyl dimethyl ammonium chloride, poly(oxy-1,2-ethandiyl) tridecyl hydroxy phosphate, and potassium dimethyl dithiocarbamate were found to be very effective inhibitors. The thiocarbonyl compound provides additional inhibition (Martin et al., 2005).

These corrosion inhibitor compositions provide a tenacious, smooth, protective film that resists the adhesion of iron sulfide, sessile bacteria, and other solids, hence they are also referred to as antibiofoulant corrosion inhibitors.

The reduced corrosion rates observed were 4–5 $\mathrm{mils\,y^{-1}}$ ($4 \times 10^{-12}\ \mathrm{m\,s^{-1}}$) in contrast to 15–35 $\mathrm{mils\,y^{-1}}$ ($2.8 \times 10^{-11}\ \mathrm{m\,s^{-1}}$) for uninhibited systems (Martin et al., 2005).

Formic Acid Free Formulation

Acid corrosion inhibitors used for oil field applications normally contain formic acid components, or compounds that produce formic acid when exposed to well conditions. Although used successfully in well stimulation operations, they have been associated with the corrosion of pipelines and other equipment (Ali et al., 2010).

Unsaturated aldehydes and ketones have been found to be suitable replacements. Some examples are given in Table 6.7. The treatment fluid is substantially free of any formic acid or its precursor.

These types of inhibitors are used for viscoelastic diverting acids, formulated by mixing a viscoelastic surfactant (VES) with the acid prior to injection into the formation. The VES is a surfactant that under certain conditions can impart viscoelasticity to a fluid (Ali et al., 2010).

Intensifiers

Corrosion inhibitor intensifiers have been used to extend the performance range of a selected acid corrosion inhibitor. The term *corrosion inhibitor intensifier* refers to compounds that are capable of enhancing the performance of a selected acid corrosion inhibitor (Malwitz, 2008).

Most intensifiers do not perform universally with all corrosion inhibitors and many have temperature, time, and environmental drawbacks. For instance, formic acid, which is sometimes used as a corrosion inhibitor intensifier, is limited to a temperature range of 120–160°C in 15% HCl (Cassidy et al., 2009). Formic acid reduces the surface tension of a 15% HCl solution (Nasr-El-Din et al., 2004).

Antimony-based intensifiers can be used with 15% HCl, but not with stronger acids such as 28% HCl (Cassidy et al., 2009). In order to extend the effectiveness of acid corrosion inhibitors, metal salts of iodide and chloride have been suggested, sometimes even salts of mercury (Cizek, 1991). Cuprous iodide is effective up to about 160°C, but has limited solubility in acid solutions. Copper is a banned substance in some areas due to environmental considerations (Cassidy et al., 2009).

Besides environmental, these salts problems are not compatible with organic corrosion inhibitor formulations (Malwitz, 2008) and so they must be formulated separately and used in combination with organic-based corrosion

TABLE 6.7 Formic acid Free Formulations (Ali et al., 2010)

Compound	Amount/[%]
Inhibitor 1	
Isopropanol	25
Cinnamaldehyde	35
Benzyl quinolinium chloride	15
Ethoxylated C_{11} alcohols	15
Inhibitor 2	
Mixture of methanol and isopropanol	10
Water	8
Naphthyl methyl quinolinium chloride	25
Ethoxylated tridecyl alcohol	10
3-Methoxy-2-benzoyl-1-propene	8
Others	1–3
Inhibitor 3	
Methanol	35
Propargyl alcohol	5
Others	60

inhibitors. Thus, the use of external intensifiers results in increased costs incurred in on-site formulation, handling, transport, and application (Malwitz, 2008). Compositions in which the intensifier is formulated directly into the composition have been developed, thereby eliminating or reducing the need for external intensifiers.

Various organic ammonium iodides, including phenyltrimethylammonium iodide, ethyl triphenylphosphonium iodide, and others have been tested as internal intensifiers. A variety of these iodide salts may be suitably formulated into corrosion inhibitor compositions (Malwitz, 2008).

The results suggest that tetramethylammonium iodide works well with formic acid as an external intensifier at a variety of temperatures and with several different metals (Malwitz, 2008).

Alternative corrosion inhibitor intensifiers have been used, based on 2-chloro-2,2-diphenylacetic acid and 2-bromo-isobutyric acid. The inhibitor in the formulation is a propargyl alcohol-based corrosion inhibitor and cinnamaldehyde (Cassidy et al., 2009). Formulations using 2-chloro-2,2-diphenylacetic acid reduced the rate of corrosion by a factor of 10 in certain systems.

In commercial corrosion inhibitors, e.g., a blend of quaternary salts, alcohols, formamide, and ethoxylated nonyl phenol, it has been shown that terpene compounds act as corrosion inhibitor intensifiers (Penna et al., 2006). Such compounds include carotene, limonene, pinene, farnesene, camphor, and menthol. They have the advantage of being naturally occurring and biodegradable.

REFERENCES

Ahn, Y.S., Jovancicevic, V., 2001. Mercaptoalcohol corrosion inhibitors. WO Patent 0 112 878, assigned to Baker Hughes Inc., February 22, 2001.

Alford, J.A., Boyd, P.G., Fischer, E.R., 1992. Polybasic acid esters as oil field corrosion inhibitors. US Patent 5 174 913, December 29, 1992.

Alford, J.A., Boyd, P.G., Fischer, E.R., 1993a. Acid-anhydride esters as oil field corrosion inhibitors (ester acide anhidride comme inhibiteur de corrosion dans le domaine des huiles). FR Patent 2 692 283, December 17, 1993.

Alford, J.A., Boyd, P.G., Fischer, E.R., 1993b. Polybasic acid esters as oil field corrosion inhibitors. CA Patent 2 075 660, March 21, 1993.

Alford, J.A., Boyd, P.G., Fischer, E.R., 1993c. Polybasic acid esters as oil field corrosion inhibitors (esters d'acides polybasiques utilises comme inhibiteurs de corrosion dans les champs petroliferes). FR Patent 2 681 597, March 26, 1993.

Alford, J.A., Boyd, P.G., Fischer, E.R., 1994. Acid-anhydride esters as oil field corrosion inhibitors. GB Patent 2 268 487, January 12, 1994.

Ali, S., Reyes, J.S., Samuel, M.M., Auzerais, F.M., 2010. Self-diverting acid treatment with formicacid-free corrosion inhibitor. US Patent Application 20100056405, March 4, 2010.

Alink, B.A.M.O., Outlaw, B.T., 2001. Thiazolidines and use thereof for corrosion inhibition. WO Patent 0 140 205, assigned to Baker Hughes Inc., June 07, 2001.

Alink, B.A.O., 1991. Water soluble 1,2-dithio-3-thiones. EP Patent 415 556, assigned to Petrolite Corp., March 06, 1991.

AltIparmak, D., Keskin, A., Koca, A., Gürü, M., 2007. Alternative fuel properties of tall oil fatty acid methyl ester-diesel fuel blends. Bioresour. Technol. 98 (2), 241–246.

ASTM Standard, 2010a. Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements, ASTM Standard, Book of Standards, vol. 03.02 ASTM G102, ASTM International, West Conshohocken, PA.

ASTM Standard, 2010b. Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens, ASTM Standard, Book of Standards, vol. 03.02 ASTM G1-03, ASTM International, West Conshohocken, PA.

Au, A.T., 1986. Acyl derivatives of tris-hydroxy-ethyl-perhydro-1,3,5-triazine. US Patent 4 605 737, August 12, 1986.

Au, A.T., Hussey, H.F., 1989. Method of inhibiting corrosion using perhydro-s-triazine derivatives. US Patent 4 830 827, May 16, 1989.

Babaian-Kibala, E., 1993. Naphthenic acid corrosion inhibitor. US Patent 5 252 254, October 12, 1993.

Bacskai, R., Schroeder, A.H., 1988a. Alkylaniline/formaldehyde co-oligomers as corrosion inhibitors. US Patent 4 778 654, October 18, 1988.

Bacskai, R., Schroeder, A.H., 1988b. Alkylaniline/formaldehyde oligomers as corrosion inhibitors. US Patent 4 780 278, October 25, 1988.

Becker, J.R., 1998. Corrosion and Scale Handbook, Pennwell Publishing Co, Tulsa.

Bentiss, F., Lagrenee, M., Traisnel, M., 2000. 2,5-bis(N-pyridyl)-1,3,4-oxadiazoles as corrosion inhibitors for mild steel in acidic media. Corrosion 56 (7), 733–742.

Boyd, P.G., Fischer, E.R., Alford, J.A., 1993. Polybasic acid esters as oil field corrosion inhibitors. GB Patent 2 259 702, March 24, 1993.

Braga, T.G., Martin, R.L., McMahon, J.A., Oude Alink, B.A., Outlaw, B.T., 2000. Combinations of imidazolines and wetting agents as environmentally acceptable corrosion inhibitors. WO Patent 0 049 204, assigned to Baker Hughes Inc., August 24, 2000.

Brezinski, M.M., 1998. Metal corrosion inhibitor for use in aqueous acid solutions. US Patent 5 792 420, assigned to Halliburton Energy Serv., August 11, 1998.

Brezinski, M.M., 2001a. Methods and acidizing compositions for reducing metal surface corrosion and sulfide precipitation. US Patent 6 315 045, assigned to Halliburton Energy Serv. Inc., November 13, 2001.

Brezinski, M.M., 2001b. Well acidizing compositions. EP Patent 1 132 570, assigned to Halliburton Energy Serv., September 12, 2001.

Brezinski, M.M., Desai, B., 1998. Method and composition for acidizing subterranean formations utilizing corrosion inhibitor intensifiers. EP Patent 869 258, assigned to Halliburton Energy Serv., October 07, 1998.

Briggs, G.L., 1987. Corrosion inhibitor for well acidizing treatments. US Patent 4 698 168, October 06, 1987.

Briggs, G.L., 1990. Corrosion inhibitor for well acidizing treatments. CA Patent 1 274 379, September 25, 1990.

Brown, J.M., Ohlsen, J.R., McBride, R.D., 1996. Corrosion inhibitor composition and method of use. US Patent 5 512 212, April 30, 1996.

Buck, E., Allen, M.C., Sudbury, B., Skjellerudsveen, B., 1993. Corrosion inhibitor detection by thin layer chromatography: Development of the technique. In: Gundry, R.D. (Ed.), Proceedings Volume, Annual NACE Corrosion Conference (Corrosion 93), New Orleans, March 7–12, 1993. NACE International, Houston, TX.

Burger, E.D., Chesnut, G.R., 1992. Screening corrosion inhibitors used in acids for downhole scale removal, Mater. Perf. 31 (7), 40–44.

Byrne, N.E., Johnson, J.D., 1994. Water soluble corrosion inhibitors. US Patent 5 322 640, assigned to Nalco Chemical Co., June 21, 1994.

Camberlin, Y., Grenier, J., Poncet, S., Bonnet, A., Pascault, J.P., Sautereau, H., 1999a. Utilization of polymer compositions for the coating of surfaces, and surface coating containing such compositions (utilisation de compositions de polymeres pour le revetement de surfaces et revetement de surfaces comprenant ces compositions). EP Patent 931 819, assigned to Inst. Francais Du Petrole, July 28 1999.

Camberlin, Y., Grenier, J., Vallet, J., Bonnet, A., Pascault, J.P., Taha, M., 1999b. Polymer compositions, their preparation and their use (compositions de polymeres, leurs preparations et leurs utilisations). FR Patent 2 773 809, assigned to Inst. Francais Du Petrole, July 23 1999.

Camberlin, Y., Grenier, J., Vallet, J., Bonnet, A., Pascault, J.P., Taha, M., 1999c. Polymer compositions, their preparation and uses (compositions de polymeres, leurs preparations et leurs utilisations). EP Patent 931 803, assigned to Inst. Francais Du Petrole, July 28 1999.

Cassidy, J.M., Kiser, C.E., Wilson, J.M., 2009. Corrosion inhibitor intensifier compositions and associated methods. US Patent Application 20090156432, assigned to Halliburton Energy Services, Inc., June 18, 2009.

Cizek, A., 1991. Corrosion inhibition using mercury intensifiers. US Patent 4 997 040, assigned to Baker Hughes Incorporated, Houston, TX, March 5, 1991.

Clewlow, P.J., Haslegrave, A.J., Carruthers, N., Hedges, W.M., Bourland, B.I., Sullivan, D.S., Montgomerie, H.T.R., 1992. Amine adducts as corrosion inhibitors. EP Patent 520 761, December 30, 1992.

Cossar, J., Carlile, J., 1993. A new method for oilfield corrosion inhibitor measurement. In: Gundry, R.D. (Ed.), Proceedings Volume, Annual NACE Corrosion Conference (Corrosion 93), New Orleans, March 7–12, 1993. NACE International, Houston, TX.

Dadgar, A., 1988a. Corrosion inhibitors for clear, calcium-free high density fluids. US Patent 4 784 779, November 15, 1988.

Dadgar, A., 1988b. Corrosion inhibitors for clear, calcium-free high density fluids. EP Patent 290 486, November 17, 1988.

Dadgar, A., 1988c. Corrosion inhibitors for clear, calcium-free high density fluids. WO Patent 8 802 433, April 07, 1988.

Dahlmann, U., Feustel, M., 2008. Corrosion and gas hydrate inhibitors having improved water solubility and increased biodegradability. US Patent 7 341 617, assigned to Clariant Produkte (Deutschland) GmbH Sulzbach, DE, March 11, 2008.

Darden, J.W., McEntire, E.E., 1986. Dicyclopentadiene dicarboxylic acid salts as corrosion inhibitors. EP Patent 200 850, assigned to Texaco Development Corp., November 12, 1986.

Darden, J.W., McEntire, E.E., 1990. Dicyclopentadiene dicarboxylic acid salts as corrosion inhibitors. CA Patent 1 264 541, January 23, 1990.

Dietsche, F., Essig, M., Friedrich, R., Kutschera, M., Schrepp, W., Witteler, H., Anchor, M.J., Friedrich, K., 2007. Organic corrosion inhibitors for interim corrosion protection. In: CORROSION 2007. NACE International, Nashville, Tennessee, p. 12. NACE Paper 07358.

Dougherty, J.A., Outlaw, B.T., Alink, B.A.O., 1996. Corrosion inhibition by ethoxylated fatty amine salts of maleated unsaturated acids. US Patent 5 582 792, December 10, 1996.

Eaton, P., Sutton, G., 1994. The effect of flow on inhibitor film life. In: Morris, C.P., Naraghi, A., Nick, G. (Eds.), Proceedings Volume, 49th Annual NACE International Corrosion Conference (Corrosion 94), Baltimore, February 27, 94–3, 4, 1994. NACE International, Houston, TX.

Faessler, K., 1990. Testing of corrosion inhibitors under pressure conditions in the presence of H_2S and CO_2 (Prüfung von Korrosionsinhibitoren Unter Druckbedingungen in Gegenwart von H_2S und CO_2). In: Proceedings Volume, BASF et al., Chem. Prod. in Petrol. Prod. Mtg. H_2S – A Hazardous Gas in Crude Oil Recovery Discuss, Clausthal-Zellerfeld, Ger, September 12–13, 1990.

Fischer, E.R., Boyd, P.G., 1998. Water soluble corrosion inhibitors. US Patent 5 759 485, assigned to Westvaco Corporation New York, June 2, 1998.

Fischer, E.R., Parker, III., J.E., 1997. Tall oil fatty acid anhydrides as corrosion inhibitor intermediates. Corrosion 53 (1), 62–64.

Fischer, G.C., 1990. Corrosion inhibitor compositions containing inhibitor prepared from amino substituted pyrazines and epoxy compounds. US Patent 4 895 702, January 23, 1990.

Fisher, L.E., 1993. Corrosion inhibitors and neutralizers: Past, present and future. In: Gundry, R.D. (Ed.), Proceedings Volume, Annual NACE Corrosion Conference (Corrosion 93), New Orleans, March 7–12, 1993. NACE International, Houston, TX.

Fisk, T.E., Tucker, C.J., 1991. *N*-(hydrophobe aromatic) pyridinium compounds. US Patent 5 000 873, March 19, 1991.

Fong, D.W., Shambatta, B.S., 1993. Hydroxamic acid containing polymers used as corrosion inhibitors. CA Patent 2 074 535, assigned to Nalco Chemical Co., January 25, 1993.

Fortenberry, Jr., C.L., Grahmann, N.J., Miller, C.D., Son, A.J., 1993. Analysis of residual corrosion inhibitors in oilfield brines. In: Proceedings Volume, 68th Annual SPE Tech. Conference, Houston, October 3–6, 1993. Society of Petroleum Engineers, Richardson, TX, pp. 965–979.

French, E.C., Fahey, W.F., Harte, J.G. 1991a. Method of oil well corrosion inhibition via emulsions and emulsions therefor. US Patent 5 027 901, July 02, 1991.

French, E.C., Fahey, W.F., Harte, J.G., 1991b. Method of oil well corrosion inhibition via emulsions and emulsions therefor. CA Patent 2 019 516, March 06, 1991.

Frenier, W.W., Growcock, F.B., 1988a. Mixtures of a,b-unsaturated aldehydes and surface active agents used as corrosion inhibitors in aqueous fluids. US Patent 4 734 259, March 29, 1988.

Frenier, W.W., Growcock, F.B., 1988b. Process and composition for inhibiting iron and steel corrosion. EP Patent 289 665, November 09, 1988.

Funkhouser, G.P., Cassidy, J.M., Lane, J.L., Frost, K., Gardner, T.R., King, K.L., 2001. Metal corrosion inhibitors, inhibited acid compositions and methods. US Patent 6 192 987, assigned to Halliburton Energy Serv., February 27, 2001.

Gay, R.J., Gay, C.C., Matthews, V.M., Gay, F.E.M., Chase, V., 1993. Dynamic polysulfide corrosion inhibitor method and system for oil field piping. US Patent 5 188 179, February 23, 1993.

Gelner, L., 1996. Protection of storage tank bottoms using volatile corrosion inhibitors (VCI). In: Proceedings Volume, vol. 1, 7th NACE International et al Middle East Corrosion Conference, Manama, Bahrain, February 26–28, 1996. NACE International, Houston, TX, pp. 102–109.

Growcock, F.B., 1987. Surfactants can affect corrosion inhibition of oil-field steel. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, San Antonio, February 4–6, 1987. Society of Petroleum Engineers, Richardson, TX, Paper No. 16 625, pp. 1–7

Growcock, F.B., Lopp, V.R., 1988. The inhibition of steel corrosion in hydrochloric acid with 3-phenyl-2-propyn-1-ol. Corros. Sci. 28 (4), 397–410.

Guimaraes, P.I.C., Monteiro, A.P., Mainier, F.B., 1994. New corrosion inhibitors in solid form to protect carbon steel pipes in acidizing operations. In: Proceedings Volume, vol. 2, no. TT-104, 5th Brazil Petrol. Congr. (Conexpo Arpel 94), Rio De Janeiro, Brazil, October 16–20, 1994. Instituto Brasileiro de Petroleo, Rio de Janeiro.

Haslegrave, J.A., Sullivan, D.S., 1987. N, S containing corrosion inhibitors. US Patent 4 673 436, June 16, 1987.

Hausler, R.H., 1986. On the use of linear polarization measurements for the evaluation of corrosion inhibitors in concentrated HCl at 200°F (93°C). Corrosion 42 (12), 729–739.

Henson, E.R., Doty, P.A., 1990. Corrosion inhibitors for aqueous brines. US Patent 4 980 074, assigned to Dow Chemical Co., December 25, 1990.

Ho, A.W., 1993. Derivatives of polyalkylenepolyamines as corrosion inhibitors. WO Patent 9 307 307, April 15, 1993.

Ho, A.W., 1994. Derivatives of polyalkylenepolyamines as corrosion inhibitors. US Patent 5 275 744, January 04, 1994.

Incorvia, M.J., 1988a. Polythioether corrosion inhibition system. US Patent 4 759 908, July 26, 1988.

Incorvia, M.J., 1988b. Thiol ester corrosion inhibition system. US Patent 4 744 948, May 17, 1988.

International Organization for Standardization, 2009a. Petroleum and natural gas industries – materials for use in H_2S-containing environments in oil and gas production – Part 1: General principles for selection of cracking-resistant materials, ISO Standard ISO 15156-2, International Organization for Standardization, Geneva, Switzerland.

International Organization for Standardization, 2009b. Petroleum and natural gas industries – Materials for use in H_2S-containing environments in oil and gas production – Part 2: Cracking-resistant carbon and low-alloy steels, and the use of cast irons, ISO Standard ISO 15156-2, International Organization for Standardization, Geneva, Switzerland.

International Organization for Standardization, 2009c. Petroleum and natural gas industries – materials for use in H_2S-containing environments in oil and gas production – Part 3: Cracking-resistant CRAs (corrosion-resistant alloys) and other alloys, ISO Standard ISO 15156-3, International Organization for Standardization, Geneva, Switzerland.

International Organization for Standardization, 2010. Petroleum, Petrochemical and Natural Gas Industries – Materials Selection and Corrosion Control for Oil and Gas Production Systems, ISO Standard ISO 21457, International Organization for Standardization, Geneva, Switzerland.

Jiashen, Z., Jingmao, Z., 1993. Control of corrosion by inhibitors in drilling muds containing high concentration of H_2S. Corrosion 49 (2), 170–174.

Johnson, D.M., Ippolito, J.S., 1994. Corrosion inhibitor and sealable thread protector end cap for tubular goods. US Patent 5 352 383, October 04, 1994.

Johnson, D.M., Ippolito, J.S., 1995. Corrosion inhibitor and sealable thread protector end cap for tubular goods. US Patent 5 452 749, September 26, 1995.

Karaev, S.F.O., Gusejnov, S.O.O., Garaeva, S.V.K., Talybov, G.M.O., 1996. Producing propargyl ether for use as metal corrosion inhibitors-by condensing propargyl alcohol with olefin in presence of phospho-tungstic acid. RU Patent 2 056 401, March 20, 1996.

Kennard, M.A., McNulty, G., 1993. Depositing corrosion inhibitors effectively, Pipeline Gas J. 220 (4), 66–71.

Kennard, M.A., McNulty, J.G., 1992. Conventional pipeline-pigging technology: Pt.2: Corrosioninhibitor deposition using pigs, Pipes Pipelines Int. 37 (4), 14–20.

Kennedy, Jr., W.C., 1987. Corrosion inhibitors for cleaning solutions. US Patent 4 637 899, January 20, 1987.

Kissel, C.L., 1999. Process and composition for inhibiting corrosion (verfahren und zusammensetzung zur inhibierung von korrosion). EP Patent 906 969, assigned to Degussa AG, April 07, 1999.

Kreh, R.P., 1991. Method of inhibiting corrosion and scale formation in aqueous systems. US Patent 5 073 339, December 17, 1991.

Larsen, A.L., 1991. Process for inhibiting corrosion in oil production fluids. EP Patent 446 616, assigned to Norol Hoechst Oil Chem. Assoc., September 18, 1991.

Leinweber, D., Feustel, M., 2009. Corrosion and gas hydrate inhibitors with an increased biological degradability and a reduced toxicity. US Patent 7 615 102, assigned to Clariant Produkte (Deutschland) GmbH Frankfurt, DE, November 10, 2009.

Lindstrom, M.R., Louthan, R.P., 1987. Inhibiting corrosion. US Patent 4 670 163, assigned to Phillips Petroleum Co., June 02, 1987.

Lindstrom, M.R., Mark, H.W., 1987. Inhibiting corrosion: Benzylsulfinylacetic acid or benzylsulfonylacetic acid. US Patent 4 637 833, January 20, 1987.

Mainier, F., Saliba, C.A., Gonzalez, G., 1990. Effectiveness of acid corrosion inhibitors in the presence of alcohols, SPE Unsolicited Pap SPE-20404, Petrobras Research Center, Rio de Janeiro, Brazil.

Mainier, F.B., Lazaro, W., Do, R.F.F., 1992. Silicate-based corrosion-inhibitor in drilling fluids: An environmentally-friendly option (inibidor de corrosao a base de silicato em fluidos de perfuracao: Uma opcao nao agressiva ao meio ambiente). In: Proceedings Volume, vol. 1, 8th Petrobras et al Latin Amer. Drilling Congr., Rio De Janeiro, Brazil, October 14–16, 1992, pp. 467–475.

Malwitz, M.A., 2008. Corrosion inhibitor composition comprising a built-in intensifier. US Patent Application 20080146464, June 19, 2008.

Martin, R.L., 1988. Multifunctional corrosion inhibitors. US Patent 4 722 805, February 02, 1988.

Martin, R.L., 1993. The reaction product of nitrogen bases and phosphate esters as corrosion inhibitors. EP Patent 567 212, October 27, 1993.

Martin, R.L., Brock, G.F., Dobbs, J.B., 2005. Corrosion inhibitors and methods of use. US Patent 6 866 797, assigned to BJ Services Company, March 15 2005.

Matherly, R.M., Jiao, J., Ryman, J.S., Blumer, D.J., 1995. Determination of imidazoline and amidoamine type corrosion inhibitors in both crude oil and produced brine from oilfield production. In: Proceedings Volume, 50th Annual NACE International Corrosion Conference (Corrosion 95), Orlando, FL, March 26–31, 1995. NACE International, Houston, TX.

McCullough, T.M., 1991. Emulsion minimizing corrosion inhibitor for naphtha/water systems. US Patent 5 062 992, assigned to Betz Laboratories Inc., November 05, 1991.

McEntire, E.E., Knifton, J.F., 1987. Process for formation of dialkylaminomethylated internal olefin polymers. US Patent 4 657 984, April 14, 1987.

McKerrell, E.H., Lynes, A., 1988. Development of an HPLC (high performance liquid chromatography) method for the determination of nitrogen containing corrosion inhibitors in a mixed hydrocarbon/glycol matrix. In: Proceedings Volume, no. 67, 3rd Royal Soc. Chem. Ind. Chem. in the Oil Ind. International Symposium, Manchester, England, April 19–20, 1988, pp. 212–222.

McMahon, A.J., Harrop, D., 1995. Green corrosion inhibitors: An oil company perspective. In: Proceedings Volume, 50th Annual NACE International Corrosion Conference (Corrosion 95), Orlando, FL, March 26–31, 1995. NACE International, Houston, TX.

Meyer, G.R., 2001. Corrosion inhibiting compositions. GB Patent 2 353 793, assigned to Nalco Exxon Energy Chem. L, March 07, 2001.

Miksic, B.A., Furman, A., Kharshan, M., Braaten, J., Leth-Olsen, H., 2004. Corrosion resistant system for performance drilling fluids utilizing formate brine. US Patent 6 695 897, assigned to Cortec Corporation St. Paul, MN, February 24, 2004.

Minevski, L.V., Gaboury, J.A., 1999. Thiacrown ether compound corrosion inhibitors for alkanolamine units. EP Patent 962 551, assigned to Betzdearborn Europe Inc., December 08, 1999.

Moore, J., Vers, L.V., Conrad, P., 2009. SS: Flow assurance: Understanding kinetic hydrate inhibitor and corrosion inhibitor interactions. In: Offshore Technology Conference, no. OTC 19869, Houston, TX, Paper Number 19869-MS, pp. 1-21. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=OTC-19869-MS&societyCode=OTC.

Morris-Sherwood, B.J., Brink, Jr., E.C., 1987. Corrosion inhibiting composition. EP Patent 221 212, May 13, 1987.

Morris-Sherwood, B.J., Brink, Jr., E.C., 1990. Corrosion inhibiting composition and method. CA Patent 1 264 539, January 23, 1990.

Naraghi, A., 1997. Corrosion inhibitor containing phosphate groups. US Patent 5 611 991, March 18, 1997.

Naraghi, A., Grahmann, N., 1997. Corrosion inhibitor blends with phosphate esters. US Patent 5 611 992, March 18, 1997.

Nasr-El-Din, H.A., Al-Othman, A.M., Taylor, K.C., Al-Ghamdi, A.H., 2004. Surface tension of HCl-based stimulation fluids at high temperatures. J. Pet. Sci. Eng. 43 (1–2), 57–73.

Neemla, K.D., Saxena, R.C., Jayaraman, A., 1992. Corrosion inhibition of oil-well equipment during acidization. Corrosion Prev. Contr. 39 (3), 69–73.

Niu, J.H.Y., Edmondson, J.G., Lehrer, S.E., 1988. Method of inhibiting corrosion of metal surfaces in contact with a corrosive hydrocarbon containing medium. EP Patent 256 802, February 24, 1988.

Nogueira, J.M.F., 1996. Refining and separation of crude tall-oil components. Sep. Sci. Technol. 31 (17), 2307–2316.

Oberndorfer, M., Thayer, K., Havlik, W., 2007. Corrosion control in the oil and gas production – 5 successful case histories. In: CORROSION 2007, NACE International, Nashville, Tennessee, NACE paper No. 07317, pp. 17.

Obeyesekere, N., Naraghi, A., McMurray, J.S., 2001. Synthesis and evaluation of biopolymers as low toxicity corrosion inhibitors for north sea oil fields. In: Proceedings Volume, NACE International Corrosion Conference [Corrosion 2001], Houston, TX, March 11–16, 2001. NACE International, Houston, TX, Paper Number 01049, pp. 1–14.

Ohlsen, J.R., Brown, J.M., Brock, G.F., Mandlay, V.K., 1995. Corrosion inhibitor composition and method of use. US Patent 5 459 125, October 17, 1995.

Oppenlaender, K., Wegner, B., Slotman, W., 1993. Ammonium salt of an alkenylsuccinic half-amide and the use thereof as corrosion inhibitor in oil and/or gas production technology. US Patent 5 250 225, assigned to BASF AG, October 05, 1993.

Oude Alink, B.A., 1993. Water soluble 1,2-dithio-3-thiones. US Patent 5 252 289, assigned to Petrolite Corp., October 12, 1993.

Penna, A., Arias, G.F.D.L., Rae, P.J., 2006. Corrosion inhibitor intensifier and method of using the same. US Patent Application 20060264335, assigned to BJ Services Company Houston, TX, November 23, 2006.

Petersen, P.R., Coker, L.G., Sullivan, D.S., 1990. Method of inhibiting corrosion using n-s containing compounds. GB Patent 2 221 458, February 07, 1990.

Phillips, N.J., Renwick, J.P., Palmer, J.W., Swift, A.J., 1996. The synergistic effect of sodium thiosulphate on corrosion inhibition. In: Proceedings Volume, vol. 1, 7th NACE International et al Middle East Corrosion Conference, Manama, Bahrain, February 26–28, 1996. NACE International, Houston, TX, pp. 110–137.

Ramanarayanan, T.A., Vedage, H.L., 1994. Inorganic/organic inhibitor for corrosion of iron containing materials in sulfur environment. US Patent 5 279 651, January 18, 1994.

Samant, A.K., Koshel, K.C., Virmani, S.S., 1989. Azoles as corrosion inhibitors for mild steel in a hydrochloric acid medium, SPE Unsolicited Pap SPE-19022, KDM Inst. of Petroleum Exploration, February 1989.

Schilling, P., 1995. Polyamine condensates of styrene-maleic anhydride copolymers as corrosion inhibitors. US Patent 5 391 636, February 21, 1995.

Schilling, P., Braddon, D.V., 1986. Corrosion inhibitors. US Patent 4 614 600, assigned to Westvaco Corp., September 30, 1986.

Schilling, P., Brown, P.E., 1988. Cationic and anionic lignin amines corrosion inhibitors. US Patent 4 789 523, assigned to Westvaco Corp., December 06, 1988.

Schutt, H.U., 1990. Reducing stress corrosion cracking in treating gases with alkanol amines. US Patent 4 959 177, September 25, 1990.

Sekine, I., Yuasa, M., Shimode, T., Takaoka, K., 1991. Inhibition of corrosion. GB Patent 2 234 501, February 06, 1991.

Shah, S.S., Fahey, W.F., Alink, B.A.O., 1994. Corrosion inhibition in highly acidic environments by use of pyridine salts in combination with certain cationic surfactants. US Patent 5 336 441, August 09, 1994.

Shah, S.S., Fahey, W.F., Oude Alink, B.A., 1992. Corrosion inhibition in highly acidic environments by use of pyridine salts in combination with certain cationic surfactants. CA Patent 2 066 797, November 30, 1992.

Shin, C.C., 1988. Corrosion inhibiting composition for zinc halide-based clear, high density fluids. WO Patent 8 802 432, April 07, 1988.

Silverman, D.C., Kalota, D.J., Stover, F.S., 1995. Effect of pH on corrosion inhibition of steel by polyaspartic acid. In: Proceedings Volume, 50th Annual NACE International Corrosion Conference (Corrosion 95), Orlando, FL, March 26–31, 1995. NACE International, Houston, TX, Paper Number 95110818, pp. 1–8.

Son, A.J., Chakravarty, J., 1996. Analysis of residual corrosion inhibitors by fluorescence and ultraviolet spectrophotometry. In: Proceedings Volume, 51st Annual NACE International Corrosion Conference (Corrosion 96), Denver, March 24–29, 1996. NACE International, Houston, TX, pp. 344/1–344/23.

Tang, Y., Han, Z., Wang, H., Chen, H., 1995. Sp-2 acid corrosion inhibitor. J. Univ. Pet., China 19 (1), 98–101.

Teeters, S.M., 1992. Corrosion inhibitor. US Patent 5 084 210, assigned to Chemlink Inc., January 28, 1992.

Trabanelli, G., Zucchi, F., Brunoro, G., 1988. Inhibition of corrosion resistant alloys in hot hydrochloric acid solutions. Werkst. Korros. 39 (12), 589–594.

Treybig, D.S., Glass, T.W., 1988. Corrosion inhibitors. US Patent 4 784 796, November 15, 1988.

Treybig, D.S., Martinez, R.G., 1988. Process for preventing corrosion of a metal in contact with a well fluid. US Patent 4 740 320, April 26, 1988.

Treybig, D.S., Martinez, R.G., 1989. Compositions prepared from hydrocarbyl substituted nitrogen-containing aromatic heterocyclic compounds, an aldehyde and/or ketone and an amine. US Patent 4 871 848, October 03, 1989.

Valone, F.W., 1987a. Corrosion inhibiting system containing alkoxylated amines. EP Patent 207 713, January 07, 1987.

Valone, F.W., 1987b. Corrosion inhibiting system containing alkoxylated amines. US Patent 4 636 256, January 13 1987.

Valone, F.W., 1989a. Corrosion inhibiting system containing alkoxylated alkylphenol amines. US Patent 4 867 888, September 19, 1989.

Valone, F.W., 1989b. Corrosion inhibiting system containing alkoxylated amines. CA Patent 1 259 185, September 12, 1989.

Valone, F.W., 1989c. Corrosion inhibiting system containing alkoxylated dialkylphenol amines. US Patent 4 846 980, July 11, 1989.

Veldman, R.R., Trahan, D.O., 1999. Gas treating solution corrosion inhibitor. WO Patent 9 919 539, assigned to Coastal Fluid Technol. Llc., April 22, 1999.

Verma, S.K., Sandor, G.R., 2001. Corrosion inhibitors for use in oil and gas wells and similar applications. WO Patent 0 146 552, assigned to Fmc Corp., June 28, 2001.

Vorderbruggen, M.A., Williams, D.A. 2000. Acid corrosion inhibitor. US Patent 6 117 364, assigned to Nalco Exxon Energy Chem. Lp., September 12, 2000.

Walker, M.L., Martin, R.L., Poelker, D.J., 2001. High performance phosphorus-containing corrosion inhibitors for inhibiting corrosion by drilling system fluids. EP Patent 1 076 113, assigned to Baker Hughes Inc., February 14, 2001.

Weghorn, S.J., Reese, C.W., Oliver, B., 2007. Field evaluation of an encapsulated time-release corrosion inhibitor. In: CORROSION 2007. NACE International, Nashville, Tennessee, Paper

Number 07321, pp. 1–10. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=NACE-07321&societyCode=NACE.

Welton, T.D., Cassidy, J.M., 2007. Thiol/aldehyde corrosion inhibitors. US Patent 7 216 710, assigned to Halliburton Energy Services, Inc. Duncan, OK, May 15, 2007.

Williams, D.A., Looney, J.R., Sullivan, D.S., Bourland, B.I., Haslegrave, J.A., Clewlow, P.J., Carruthers, N., O'Brien, T.M., 1994. Amine derivatives as corrosion inhibitors. US Patent 5 322 630, assigned to Exxon Chemical Patents In, June 21, 1994.

Wirtz, H., Hoffmann, H., Ritschel, W., Hofinger, M., Mitzlaff, M., Wolter, D., 1989. Optionally quaternized fatty esters of alkoxylated alkyl-alkylene diamines (gegebenenfalls quaternierte fettsaeureester von oxyalkylierten alkyl-alkylendiaminen). EP Patent 320 769, June 21, 1989.

Wu, Y., Gray, R.A., 1992. Compositions and methods for inhibiting corrosion. US Patent 5 118 536, assigned to Phillips Petroleum Co., June 02, 1992.

Young, L.A., 1993. Low melting polyalkylenepolyamine corrosion inhibitors. WO Patent 9 319 226, September 30, 1993.

Zefferi, S.M., May, R.C., 1994a. Corrosion inhibition of calcium chloride brine. US Patent 5 292 455, assigned to Betz Laboratories Inc., March 08, 1994.

Zefferi, S.M., May, R.C., 1994b. Corrosion inhibition of calcium chloride brine. CA Patent 2 092 207, August 26, 1994.

Zetlmeisl, M.J., French, E.C., 1992a. Corrosion inhibition in highly acidic environments. US Patent 5 169 598, December 08, 1992.

Zetlmeisl, M.J., French, E.C., 1992b. Corrosion inhibition in highly acidic environments. CA Patent 2 067 313, November 30, 1992.

TRADENAMES

TABLE 6.8 Tradenames in References

Tradename Description	Supplier
Rhodafac® RS-410 Poly(oxy-1,2-ethandiyl) tridecyl hydroxy phosphate (Martin et al., 2005)	Rhodia

Chapter 7

Scale Inhibitors

In certain operations in petroleum industries, such as production, stimulation, and transport, there is a risk of scale deposition. This can occur when a solution becomes supersaturated, which occurs mostly if the temperature changes in the course of injection operations.

Scale is also formed, if two chemicals that will form a precipitate are brought together, e.g., if a hydrogen fluoride solution meets calcium ions. From a thermodynamic perspective, there is a stable region, a metastable region, and an unstable region, separated by the binodal curve and the spinodale curve, respectively.

Scales may consist of calcium carbonate, barium sulfate, gypsum, strontium sulfate, iron carbonate, iron oxides, iron sulfides, and magnesium salts (Keatch, 1998). There are relevant monographs, e.g., *the Corrosion and Scale Handbook* (Becker, 1998), as well as reviews (Crabtree et al., 1999) available in the literature. Case studies have been presented for North Sea carbonate reservoirs (Jordan et al., 2003, 2005) and the Gulf of Mexico (Jordan et al., 2002). A more recent publication focuses on green systems (Frenier and Hill, 2004).

CLASSIFICATION AND MECHANISM

The problem is basically similar to preventing scale in washing machines and similar chemicals are used. Inhibition can be achieved, either by adding substances that react with potential scale-forming substances so that thermodynamically, a table region is reached, or by adding substances that suppress crystal growth.

Conventional scale inhibitors are hydrophilic, i.e., they dissolve in water. In the case of downhole squeezing, the scale inhibitor should be adsorbed on to the rock to prevent it washing out before it can act as desired, but this may change the surface tension and the wettability of the system. To overcome these disadvantages, oil-soluble and coated scale inhibitors have been developed.

Petroleum Engineer's Guide to Oil Field Chemicals and Fluids. DOI: 10.1016/B978-0-12-383844-5.00007-6

Frequently, scale inhibitors are applied in combination with corrosion inhibitors (Martin et al., 2005). Scale inhibitors can be classified into two main groups:

- Thermodynamic inhibitors and
- Kinetic inhibitors.

Thermodynamic inhibitors are complexing and chelating agents, suitable for specific scales. The action of kinetic inhibitors may be understood in terms of stereospecific and nonspecific mechanisms.

Scale prevention is important to ensure continuous production from existing reserves that produce brine. Wells can be abandoned prematurely because of poor management of scale and corrosion (Kan and Tomson, 2010). The scale inhibitor operates in two ways (Viloria et al., 2010):

1. Adsorption effects and
2. Morphologic changes of the growing sites.

The adsorption effects are caused by the inhibitor molecules occupying nucleation sites that are preferred by the scale-forming molecules. Crystals cannot find active places at which to adhere to the surface, therefore crystal nucleation is prevented.

Another absorption-based inhibitor mechanism is based on morphological changes that can prevent the formation of crystals in the presence of the inhibitor. Depending on the inhibitor characteristics, and the nature of the substrate, it is possible for it to be adsorbed over the crystalline net, forming complex surfaces or nets, which have difficulty remaining and growing in active places.

Sea water often reacts with the formation water in offshore fields to produce barium, calcium, and strontium sulfate deposits, which hinder oil production. In some fields, $CaCO_3$ is a major problem.

In some regions, the formation water chemistry varies considerably (Duccini et al., 1997). For example, in the Central North Sea Province, levels of barium ions vary from a few $mg\,l^{-1}$ to $g\,l^{-1}$, and the pH varies from 4.4 to 7.5; a pH as high as 11.7 has been measured. In the southern region of the North Sea, the waters have a high salinity and are rich in sulfate and acidic compounds. The ideal scale inhibitor should have the following properties (Duccini et al., 1997):

- Effective scale control at low inhibitor concentration,
- Compatibility with sea and formation water,
- Balanced adsorption-desorption properties, allowing the chemicals to be slowly and homogeneously released into the production water,
- High thermal stability,
- Low toxicity and high biodegradability, and
- Low cost.

TABLE 7.1 Types of Scale Inhibitors (Viloria et al., 2010)

Inhibitor Type	Limitations
Inorganic polyphosphates	Suffer hydrolysis and can precipitate as calcium phosphates because of temperature, pH, solution quality, concentration, phosphate type, and the presence of some enzymes.
Organic polyphosphates	Suffer hydrolysis with temperature. Not effective at high calcium concentrations. Must be applied in high doses.
Polymers based on carboxylic acids	Limited calcium tolerance (2000 ppm) although some can work at concentrations higher than 5000 ppm. Larger concentrations are needed.
Ethylene diamine tetraacetic acid	Expensive

Scale inhibitors are broadly classified as organic or inorganic (Viloria et al., 2010). Inorganic types include condensed phosphate, such as polymetaphosphates or phosphate salts. Suitable organic scale inhibitors are polyacrylic acid (PAA), phosphinocarboxylic acid, sulfonated polymers, and phosphonates (Duccini et al., 1997).

Phosphonates are maximally effective at high temperatures, whereas sulfonated polymers are better at low temperatures (Talbot et al., 2009). Copolymers that contain both phosphonate and sulfonate moieties can operate well over a range of temperatures. A phosphonate end-capped vinyl sulfonic acid/acrylic acid copolymer has been shown to be particularly useful in the scale inhibition of barium sulfate scale in water-based systems. (Talbot et al., 2009). The basic limitations of scale inhibitors are given in Table 7.1.

Thermodynamic Inhibitors

Thermodynamic inhibitors are complexing and chelating agents, suitable for specific scales. For example, common chemicals for the inhibition of barium sulfate are ethylene diamine tetraacetic acid (EDTA) and nitrilo triacetic acid. The solubility of calcium carbonate can be influenced by varying the pH or the partial pressure of carbon dioxide (CO_2). The solubility increases with decreasing pH and increasing partial pressure of CO_2, and it decreases with temperature.

However, usually solubility increases with higher temperature. The temperature coefficient of solubility is dependent on the enthalpy of dissolution. An exothermic enthalpy of dissolution causes a decrease in solubility with increased temperature, and vice versa.

Kinetic Inhibitors

Kinetic inhibitors for hydrate formation may also be effective for preventing scale deposition (Sikes and Wierzbicki, 1996). This mode of operation may be understood in terms of stereospecific and nonspecific mechanisms of scale inhibition.

Adherence Inhibitors

Another mechanism of scale inhibition is based on adherence inhibitors, in which surface active chemicals simply suppress the adherence of crystals to the metal surfaces.

MATHEMATICAL MODELS

Mathematical models have been developed (Mackay and Sorbie, 1998, 1999; Mackay et al., 1998; Shuler and Jenkins, 1989), including simulation scale formation of iron carbonate and iron monosulfide by thermodynamic and electrochemical means (Anderko, 2000; Mackay and Sorbie, 1998; Malandrino et al., 1998; Zhang et al., 2000). An accurate model to predict pH, scale indices, density, and inhibitor needs has been discussed, experimental data to validate the model have been examined, and an estimation of the error in analysis has been presented (Kan and Tomson, 2010).

The scaling tendency of sulfates, barite, celestite, and halites are not a strong function of the pH of the brine. In contrast, carbonates, such as calcite, dolomite, and siderite, and sulfide scales are acid-soluble, hence their scaling tendencies are strongly dependent on the pH of the brine. Scale prediction is more complicated in these cases (Kan and Tomson, 2010).

Optimal Dose

A method to estimate the optimal dose of a scale inhibitor has been described (Mikhailov et al., 1987). The method starts by measuring the chemical composition and temperature of the water and using these parameters to calculate a stability index predicting the optimal dose of a scale inhibitor.

Precipitation Squeeze Method

In the precipitation squeeze method, the scale inhibitor reacts to form an insoluble salt, which precipitates in the pores of the formation rock. For example, a phosphonate scale inhibitor and a calcium chelate are employed as a precipitation squeeze treatment, as has phosphinic polycarboxylate and polyepoxysuccinic acid (Brown and Brock, 1995).

An anionic scale inhibitor and a multivalent cation salt are dissolved in an alkaline aqueous liquid to provide a solution, which contains both scale-inhibiting anions and multivalent cations that are mutually soluble under alkaline conditions. However, at lower pH the inhibitor is not soluble. One compound that reacts at a relatively slow rate to reduce the pH of the alkaline solution is dissolved in the solution. The rate at which the pH of the solution is reduced can be adjusted by the formulation (Collins, 2000).

Near-well squeeze treatment models assume that the flow pattern around the well is radial. It has been investigated whether strictly non-radial flow patterns around the well have a major effect on the squeeze treatment. It has been found that fractured wells have longer squeeze lifetimes than non-fractured wells.

Further, the calculations reveal that for fractured wells, inhibitor adsorption on the face of the fracture itself has no impact on the treatment lifetime. In a fractured well, the inhibitor is more retarded by contact with rock over a greater distance in comparison to a matrix with radial treatment (Rakhimov et al., 2010).

INHIBITOR CHEMICALS

Chemically, inhibitors can be broadly subdivided into acids and complexing agents. Scale inhibitors described in the recent literature are summarized in Table 7.2.

TABLE 7.2 Scale Inhibitors

Compound	References
1-Hydroxyethylidene-1,1-diphosphonic acid	He et al. (1999)
Carbonic dihydrazide, $H_2N-NH-CO-NH-NH_2$	Mouche and Smyk (1995)
Polyaminealkylphosphonic acid and carboxymethyl cellulose or polyacrylamide	Kochnev et al. (1993)
Polyacrylic acid and chromium	Yan (1993)
Polyacrylates[a]	Watkins et al. (1993)
Amine methylene phosphonate[b]	Graham et al. (2000)
Phosphonomethylated polyamine	Singleton et al. (2000)
Sulfonated polyacrylate copolymer	Chilcott et al. (2000)
Bis[tetrakishydroxymethylphosphonium] sulfate	Larsen et al. (2000)
Phosphonates	Holzner et al. (2000), Jordan et al. (1997)

TABLE 7.2 Scale Inhibitors—Cont'd

Compound	References
Carboxymethyl inulin	Kuzee and Raaijmakers (1999)
Polycarboxylic acid salts	Dobbs and Brown (1999)
Phosphoric acid esters of rice bran extract	Zeng and Fu (1998)
Polyphosphino maleic anhydride	Yang and Song (1998)
N,*N*-Diallyl-*N*-alkyl-*N*-sulfoalkyl ammonium betaine copolymer (with *N*-vinylpyrrolidone or acrylamide (AAm)), diallylmethyltaurine hydrochloride ($CH_2=CH-CH_2Cl \times CH_3-NH-CH_2-CH_2-SO_3^- Na^+$)	Fong et al. (2001)
Aminotrimethylenephosphonic acid	Kowalski and Pike (2001), Tantayakom et al. (2005, 2004)
Polyaspartates	Fan et al. (1998)
Polyacrolein	Siegmeier et al. (1998)
Naphthylamine polycarboxylic acids	Carter et al. (1998)
Phosphonic acid and hydrofluoric acid	Dean et al. (1998)
Tertiary amines[c]	Reizer et al. (2002)
Diethylentrilopentrakismethylenephosphonic acid	Tantayakom et al. (2005)
Tetrakis hydroxyorgano phosphonium salts	Jones and Grech (2004), Jones and Taylor (2004), Talbot and Grech (2005)
Phosphino-polycarboxylic acid	Andrei and Gagliardi (2004), Andrei and Malandrino (2003)
Diethylentriaminepentaacetic acid	Mendoza et al. (2002)
Ethylene diamine tetraacetic acid	Mendoza et al. (2002)
Vinylsulfonate copolymer	Jordan et al. (2005)
Phosphinated maleic copolymer	Gupta and Kirk (2009)

a) In borate crosslinked fracturing fluids
b) High temperature applications
c) Oil-soluble

Water-soluble Inhibitors

Acids

Both inorganic acids, such as hydrochloric acid and hydrofluoric acid, and organic acids, such as formic acid, can be used to increase the pH. They are used in combination with surfactants.

Acids, when used as scale inhibitors, are extremely corrosive as has been evaluated in the laboratory. Parameters included acid type, metallurgy, temperature, inhibitor type and concentration, duration of acid-metal contact, and the effect of other chemical additives (Burger and Chesnut, 1992). Lead and zinc sulfide scale deposits can be removed by an acid treatment (Jordan et al., 2000).

Hydrofluoric Acid

It is known that permeability impairment may be improved by injecting acid formulations containing HF into the formation. Such methods are known to improve production from both subterranean calcareous and siliceous formations.

Most sandstone formations are composed of over 70% sand quartz, i.e. silica, bonded together by various amount of cementing material including carbonate, dolomite, and silicates. Suitable silicates include clays and feldspars. A common method of treating sandstone formations involves the introduction of hydrofluoric acid into the wellbore and allowing it to react with the surrounding formation.

Hydrofluoric acid exhibits high reactivity toward siliceous minerals, such as clays and quartz fines, and reacts very quickly with authigenic clays, such as smectite, kaolinite, illite, and chlorite, especially at temperatures above 65°C. It is therefore capable of attacking and dissolving siliceous minerals, but undesirable precipitation reactions occur if hydrofluoric acid contacts metallic ions present in the formation, such as sodium, potassium, calcium, and magnesium.

Sandstone or siliceous formations and calcareous formations may be treated with an aqueous well treatment composition containing a hydrofluoric acid source in combination with a boron containing compound and a phosphonate acid, ester, or salt in order to increase the permeability of the formation being treated by inhibiting or preventing the formation of undesirable inorganic scales, such as calcium fluoride, magnesium fluoride, potassium fluorosilicate, sodium fluorosilicate, fluoroaluminate, etc. (Ke and Qu, 2010)

Encapsulated Scale Inhibitors

This type of scale inhibitor allows chemical release over an extended period of time (Hsu et al., 2000; Powell et al., 1995). Microencapsulated formulations may have a gelatin coating with a multipurpose cocktail, such as (Kowalski and Pike, 1999, 2001):

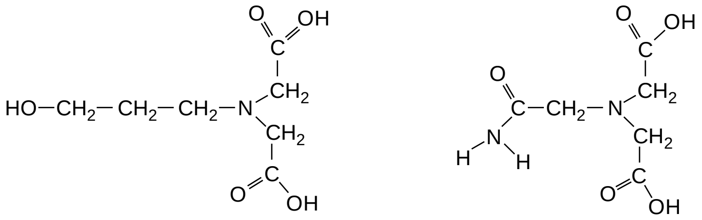
- Scale inhibitor,
- Corrosion inhibitor,
- Biocide,
- Hydrogen sulfide scavengers,
- Demulsifier, and
- Clay stabilizer.

Chelating Agents

Trace amounts of chelating agents, such as EDTA, citric acid, or gluconic acid may lower the efficiency of scale inhibitors (Barthorpe, 1993). The concentration of calcium ions and magnesium ions affects the inhibition of barium sulfate (Boak et al., 1999). Pentaphosphonate, hexaphosphonate, phosphinopolycarboxylic acid (PPCA) salts, and polyvinyl sulfonate (PVS) scale inhibitors were studied. String chelating agents, given in Table 7.3, also stabilize the coating of encapsulated formulations (Kowalski and Pike, 1999). Some chelating agents based on imino acids are shown in Figure 7.1.

TABLE 7.3 Chelating Agents for the Stabilization of Coatings (Kowalski and Pike, 1999)

Chelating agent	Acronym
N-3-Hydroxypropylimino-*N*,*N*-diacetic acid	3-HPIDA
N-2-Hydroxypropylimino-*N*,*N*-diacetic acid	2-HPIDA
N-Glycerylimino-*N*,*N*-diacetic acid	GLIDA
Dihydroxyisopropylimino-*N*,*N*-diacetic acid	DHPIDA
Methylimino-*N*,*N*-diacetic acid	MIDA
2-Methoxyethylimino-*N*,*N*-diacetic acid	MEIDA
Amidoiminodiacetic acid = sodium amidonitrilo triacetic acid	SAND
Acetamidoiminodiacetic acid	AIDA
3-Methoxypropylimino-*N*,*N*-diacetic acid	MEPIDA
Trishydroxymethylmethylimino-*N*,*N*-diacetic acid	TRIDA



N-(3-Hydroxypropyl)imino-*N*-*N*-diacetic acid

Amidoiminodiacetic acid

FIGURE 7.1 Chelating agents.

EDTA

A conventional scale dissolver for barite consists of a concentrated solution of potassium carbonate, potassium hydroxide, and the potassium salt of EDTA. Carbonate scales, on the other hand, may be dissolved using simple mineral acids, such as HCl (Jones et al., 2008). In addition, surfactants, e.g., *N*-erucyl-*N*,*N*-bis-2-hydroxyethyl-*N*-methyl ammonium chloride are advantageous for controlling the viscosity of the fluids (Jones et al., 2008).

These surfactants can form worm-like micelles when mixed with brines. These structures contribute significantly to the viscoelasticity of the fluid. This is lost rapidly when the fluid contacts hydrocarbons, since they cause the micelles to change structure or disband.

The difference in viscosity of the fluid when in contact with hydrocarbons and water allows a selective placement of the scale treatment. As a result, scale may be preferentially removed from hydrocarbon-bearing zones. This can lead to a stimulation of hydrocarbon production without a substantial increase in the water cut of produced fluids (Jones et al., 2008).

The EDTA can also be regenerated. Eq. 7.1 illustrates in simplified form the dissolution and subsequent isolation of a barium sulfate scale and the regeneration of EDTA (Keatch, 2008).

$$\begin{aligned} &\mathrm{EDTA{-}K_4 + K_2CO_3 + BaSO_4} &&\rightarrow \mathrm{EDTA{-}K_2Ba + K_2CO_3 + K_2SO_4} \\ &\mathrm{K_2CO_3 + 2HCl} &&\rightarrow \mathrm{2KCl + H_2O + CO_2} \\ &\mathrm{EDTA{-}K_2Ba + K_2SO_4} &&\rightarrow \mathrm{EDTA{-}K_4 + BaSO_4\downarrow} \end{aligned} \tag{7.1}$$

Phosphonates

Previous studies have strongly indicated that amine methylene phosphonic acid-based inhibitor species, such as pentaphosphonate and hexaphosphonate, are considerably less thermally stable than polymeric species, such as PVS and the S-Co species, so the phosphonate-based species were reported to be less applicable for deployment in high-temperature reservoir systems. However, species based on different amine methylene phosphonic acid revealed that certain species are thermally stable at temperatures exceeding 160°C (Graham et al., 2002).

In studies, a series of phosphonate-based scale inhibitors were thermally aged at 160°C, and it was reported that the scale inhibitors were still able to prevent carbonate scale in dynamic test after aging. However, thermal aging did reduce the performances of some of the phosphonate compounds against sulfate scale (Dyer et al., 2004).

Esterified phosphono or phosphino acids with a long chain alcohol are effective as oil-soluble scale inhibitors, and as wax or asphaltene inhibitors or dispersants in oil production. The esters can be prepared by azeotropic condensation of the phosphino acids with the alcohol or by telomerizing an ester of an unsaturated carboxylic acid with a phosphite or hypophosphite telogen (Woodward et al., 2004).

In contrast, laboratory studies demonstrate that changing from a phosphonate to a vinylsulfonate copolymer-based scale inhibitor could significantly extend the lifetime of a treatment (Jordan et al., 2005).

Alkaline Earth Sulfates

In dissolution studies of barite, using EDTA-based and diethylentriaminepentaacetic acid-based chelating agents, it has been verified that the presence of dicarboxylic acid additives, such as oxalate ion, improve the performance of the chelating agents. However, other related additives such as malonate and succinate reduce the effectiveness.

Oxalate ions catalyze the surface complexation reaction between the chelant and the barite surface by the formation of a two-ligand surface complex. The adverse effect observed for the other dicarboxylic acids is believed to arise because of steric effects, which prevent the formation of such a complex.

In extended studies with other barite related scales, such as celestite ($SrSO_4$), gypsum ($CaSO_4 \times 2H_2O$), and anhydrite ($CaSO_4$), it was observed that scale dissolvers, which are optimized for their effectiveness against one type of scale, such as barite, may not be the most effective against other scales (Mendoza et al., 2002).

Biodegradable Scale Inhibitors

Many oil companies are requesting environmentally friendly fracturing fluids. Fracturing fluids are composed from a variety of compounds, each having a special function and usually, contain scale inhibitors. Fracturing fluids are explained in Chapter 17. Biodegradable chelants can be selected from a variety of compounds (Crews, 2006).

Sodium Iminodisuccinate

This compound is a maleic acid derivative used as a chelant for divalent and trivalent ions. It complexes ions that can cause emulsions, form scale, can denature enzyme breakers, and cause crosslinked gel instability, and thus it can prevent these ions from having these undesirable effects.

Disodium Hydroxyethyleneiminodiacetic Acid

This is one of the few amino carboxylic acid chelants that is readily biodegradable. It is useful for the chelation of divalent and trivalent ions that cause scale, can denature enzymes, and create crosslinked gel instability.

Sodium Gluconate and Sodium Glucoheptonate

These polyols are commonly used for chelation of mineral vitamins such as calcium, magnesium, iron, manganese, and copper. They have been also found to be useful to complex titanate, zirconate, and borate ions for crosslink delay purposes. They are also excellent iron complexors for enzyme breaker stability and crosslinked gel stability.

Sodium Polyaspartate

This compound is also known as polymerized aspartic amino acid. It chelates with multiple types of divalent and trivalent ions, and is useful in breaking emulsions and scale prevention.

Polyaspartic acid-based chemicals are environmentally friendly and biodegradable oil field chemicals. They can be used both as corrosion inhibitors and scale inhibitors in brine-injection petroleum recovery. They exhibit a good calcium compatibility. At pH 5, polyaspartates are resistant to calcium ion concentrations of 8500–7500 ppm, in comparison with 5000 ppm for phosphonate and maleic acid polymer products.

Calcium compatibility is superior to that of phosphonate and maleic acid polymer products at concentrations of 5%. Polyaspartates also do not interfere with the oil-water separation process (Fan et al., 2001).

These chemicals are used as scale inhibitors and also as preconditioning solutions for other scale inhibitors. It has been claimed that a polyaspartate preconditioning solution at low pH enhances the adsorption of a phosphonate scale inhibitor to a rock material (Montgomerie et al., 2004).

Bioreactors near the site of the borehole have been suggested for the synthesis well treatment chemicals could even well treatment be achieved by introducing downhole thermophilic *Archea* or other thermophilic bacteria or organisms which are capable of generating well treatment chemicals (Kotlar and Haugan, 2005).

Oil-soluble Scale Inhibitors

Phosphonic acids, such as diethylene triamine tetramethylene phosphonic acid, or bis-hexamethylene triamine pentakismethylene phosphonic acid or acrylic copolymers, PAA, PPCA, or phosphate esters are suitable oil-soluble scale inhibitors. These basic compounds are blended with amine compounds to form an oil-soluble mix (Reizer et al., 2002). *tert*-Alkyl primary amines with 12–16 carbon atoms are oil soluble and effect the oil solubility of the scale inhibitor.

Aloe-based Scale Inhibitor

An aloe gel dissolved in water has been used as a scale inhibitor. It comprises polysaccharides, solubilized in water between 60°C–90°C. Carboxyl and alcohol functional groups are present in the chains that interact with divalent ions such as Ca^{2+} and Mg^{2+}.

Unlike chemically synthesized inhibitors, the active ingredients in the aloe plant gel are naturally occurring compounds. The scale inhibitor can be applied at low and high calcium concentrations and will not precipitate because of hydrolysis. Hydrolysis, in fact, favors the interaction with ions in the solution and thus its efficiency as a scale inhibitor may even increase (Viloria et al., 2010).

Reaction with calcium to form calcium-encapsulating gels is believed to occur via an egg-box model, as shown in Figure 7.2. In general, gels can be formed by the interaction of multivalent ions with polymers. This phenomenon is also known as physical crosslinking.

The chains of the gel interact via Ca^{2+}, hence conferring stability towards systemic forces or other conditions.

The model assumes that calcium ions serve as an ionic bridge between carboxyl groups from two different chains in close contact. According to this polysaccharide model, the chains interact via Ca^{2+} allowing a structure coordinated packaging.

Inhibitors for Special Tasks

Iron Sulfide

Ferrous sulfide deposits are a major source of economic loss in the oil industry. The deposits are mainly the result of a reaction between hydrogen sulfide, formed by sulfate-reducing bacteria, and ferrous metal oil field equipment or an iron compound in the formation. They obstruct the flow of oil through wells and in the adjacent strata, and also in pipelines and in processing and refinery plants. Ferrous sulfide particles also tend to stabilize oil water emulsions that often form, especially during secondary oil recovery, and present major problems to oil producers.

The simplest way to dissolve such deposits is by contact with a strong acid. Unfortunately this method generates large volumes of highly toxic hydrogen sulfide gas, which in the past has been responsible for fatalities.

An alternative method of treating the deposits is with powerful oxidizing agents, which avoids the toxicity hazards but produces oxidation products, including elemental sulfur, which is so corrosive to pipework that it has not generally been practiced.

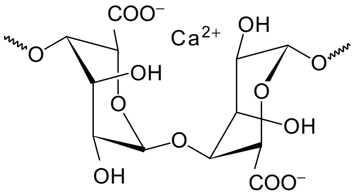


FIGURE 7.2 Egg-box model (Viloria et al., 2010).

It has been found that trishydroxymethylphosphine (THP) is capable of solubilizing iron sulfide by forming a bright red, water-soluble complex. THP is believed to be formed in oil wells, which are treated with tetrakishydroxmethylphosphonium salts.

Such salts, especially the sulfate salts, are commonly added to oil wells as biocides. They are highly effective for killing the sulfate-reducing bacteria, whose activity was largely responsible for the original formation of the iron sulfide deposits. However, the effectiveness of THP as a solubilizing agent for iron sulfides varies considerably from well to well because complexation with iron sulfide requires the presence of ammonium ions. Although normally present in oil field water, their concentration is frequently less than the optimum for iron sulfide removal. The pH is critical to the formation of the complex.

Water-soluble condensates of THP with co-condensable organic nitrogen compounds such as urea and thiourea are also capable of solubilizing iron sulfide. These condensates provide more consistent performance than THP ammonia mixtures, but they may also cause deposition of polymers if used in high concentration.

THP and amino carboxylic acids or amino phosphonic acids act synergistically to dissolve iron sulfide deposits, even in the absence of ammonia. Moreover, THP is stable in the presence of amino phophonates even when the two are formulated together, and stored for extended periods prior to use (Fidoe et al., 2005).

Lead Sulfide

Scales from lead sulfide are much more difficult to inhibit than those of calcium carbonate or barium sulfate. Test methods have been developed in order to test the performance of the inhibition of lead sulfide (Chen et al., 2010).

Scale inhibitors, including phosphonate-based scale inhibitors, PPCA, polymaleic acid, PAA, polyaspartate, PVS, and acrylic copolymers have been tested. Their performance with respect to the inhibition of lead sulfide can be classified as follows (Chen et al., 2010):

1. Dispersion inhibitors,
2. Nucleation inhibitors, and
3. Poor performance inhibitors.

Dispersion inhibitors exhibit a dispersion effect on the formation of lead sulfide. Nucleation and growth scale inhibitors inhibit the nucleation and the growth of lead sulfide.

Zinc Sulfide

Generally, a zinc bromide ($ZnBr_2$) brine will be used when the brine is required to have a density of about 1.7 $kg\,l^{-1}$ (14.0 ppg) or above. If a reservoir contains hydrogen sulfide, then zinc sulfide (ZnS) scales can form (Wang et al., 2008).

Usually an acid treatment is performed to remove such scales, but there are significant risks associated with acid treatments in high-temperature, high-pressure gas wells. The acid treatment may restore production to its previous level, but new zinc sulfide deposits can be formed in the well in a short period of time, and a re-treatment is required.

Phosphonate and phosphonic acid type scale inhibitors control the ZnS scale at relatively low concentrations. Polymeric scale inhibitors, such as a copolymer of the sodium salt 2-acrylamido-2-methyl-1-propane sulfonic acid and acrylic acid (AA) are also effective in fresh water and low density brines, but not high-density brines. For these brines, copolymers from AAm and diallyidimethylammonium salts are more effective (Wang et al., 2008). The incorporation of a nitrogen heterocyclic compound in the copolymer improves its thermal stability. Such heterocyclic compounds include *N*-vinylpyrrolidone, *N*-vinylcaprolactam, *N*-vinylimidazole, and *N*-vinylpyridine.

The cationic nature of the copolymer greatly improves its compatibility for use as a scale inhibitor with high-density brines.

Naturally Occurring Radioactive Materials

In oil and gas fields, uranium, as ^{238}U and ^{235}U, and thorium, as ^{232}Th, are present in immobile chemical forms, whereas radium and its isotopes, and their γ-emitting daughter nuclides, can easily be transported with chloride-rich formation waters. Once radium isotopes are leached from their lithological origin, they are no longer supported by their ancestors, and thus they decay.

Radium and its isotopes tend to co-precipitate alongside sparingly soluble alkaline cations mainly as the sulfate, or carbonate, or silicate. Formation and produced waters can therefore become radioactive due to the transportation of radium isotopes. External (near any processing equipment) and internal (during maintenance or workovers) radioactive hazards could exist due to naturally occurring radioactive materials that adhere to scale during processing (Bader, 2006). For these reasons, it is highly desirable to establish an effective scale control.

High Reservoir Temperatures

Conventional polymer and phosphonate scale inhibitors may not be appropriate for the application in high-pressure and high-temperature reservoirs. Only a limited range of commercially available oil field scale inhibitor chemicals are sufficiently thermally stable at temperatures above 150°C. They include homopolymers of vinylsulfonate and copolymers of AA and vinylsulfonate. Other polymers, such as polymaleic acid, polyitaconic acid, and maleic acid/AA copolymers, may offer similar thermal stability (Collins, 1995). Thermal stability tests, influence on pH, ionic strength, and oxygen on conventional polymer and phosphonate scale inhibitors, for example, on phosphinopolycarboxylate, PVS, pentaphosphonate, and hexaphosphonate, have been presented (Dyer et al., 1999; Graham et al., 1998a,b, 1997).

As pointed out above, it was originally believed that phosphonate scale inhibitors would not work in high-temperature inhibition applications, but it has been more recently shown that phosphonate inhibitors are somewhat effective at 200°C under strictly anoxic conditions and in NaCl brines (Fan et al., 2010). In contrast, phosphonate inhibitors may precipitate with Ca^{2+} ions in a brine at high temperatures.

CHARACTERIZATION

Spectroscopic Methods

Field desorption mass spectrometry (Shen and Al-Saeed, 1990), ^{13}C nuclear magnetic resonance, and Fourier transform infrared spectroscopy (Newton, 1988) have all been used to characterize oil field chemicals, including scale inhibitors. Ion chromatography is suitable for the simultaneous determination of hydroxyethylsulfonate, sodium vinylsulfonate, chloride, and sulfate reaction byproducts (Atwood, 1992; Weber, 1987).

Turbidimetry

Phase diagrams of a polyacrylate-phosphonate system with temperature and calcium ion concentration can be established by turbidimetric measurements (Weber, 1987). Conductometric titrations also are suitable to characterize the phase behavior of scale inhibitors (Drela et al., 1998).

Static Bottle Test

Using alkaline surfactant polymer floods in sandstone reservoirs may cause silicate scaling. Silicate scaling has been a significant problem in alkaline surfactant polymer flooded fields in China (e.g., Daqing field) and Canada.

Methods for static and dynamic testing under specific field conditions using alkaline surfactant polymer floods have been reviewed. The tests serve to screen chemical inhibitors for the prevention of magnesium silicate scaling (Arensdorf et al., 2010).

In a static bottle test, water samples that serve for connate cationic and connate anionic waters are mixed together and afterwards mixed with an alkaline surfactant polymer solution. The compositions of these solutions are shown in Table 7.4.

The mixtures are initially clear, but slowly develop turbidity over the course of several hours, which is monitored with a photometer. At elevated temperatures, the scale formation is sometimes very fast. Typically, in a static test, silicate slowly forms from the beginning of the test and calcium carbonate forms after two hours.

It is interesting to note that none of the chemicals tested acted as a threshold inhibitor and prevented scaling at low doses. Rather, the inhibitors tended to delay the scaling process (Arensdorf et al., 2010).

TABLE 7.4 Compositions of Test Solutions (Arensdorf et al., 2010)

Compound	ASP	Anionic $g\,l^{-1}$	Cationic
NaCl	2.5	2.4	3.5
KCl	0.08		016
$NaHCO_3$	2,8	5.6	
Na_2SO_4	0.3	0.6	
$Na_2SiO_3 \times 5\,H_2O$	14.2		
$MgCl_2 \times 6\,H_2O$		2	
$CaCl_2 \times 2\,H_2O$		0.6	
$BaCl_2 \times 2\,H_2O$		0.06	
pH	10.7	7.0	

It turned out that the static and dynamic tests correlate well for the individual inhibitors. The dynamic tests reveal that calcium carbonate is formed slowly, while a silicate scale is formed more quickly in other studies (Arensdorf et al., 2010).

In other studies dramatic differences have been observed for dynamic and static test conditions, indicating that the structures, which cause adherence and blocking of the pipework during flow may be different to those that dominate under bulk conditions (Senthilmurugan et al., 2010).

REFERENCES

Anderko, A., 2000. Simulation of $FeCO_3$/FeS scale formation using thermodynamic and electrochemical models. In: Proceedings Volume, NACE International Corrosion Conference, Corrosion 2000, Orlando, FL, March 26–31, 2000.

Andrei, M., Gagliardi, F., 2004. Redissolution studies in bulk and in coreflood for PPCA scales inhibitor. J. Pet. Sci. Eng. 43, 35–55.

Andrei, M., Malandrino, A., 2003. Comparative coreflood studies for precipitation and adsorption squeeze with ppca as the scales inhibitor. Pet. Sci. Technol. 21, 1295–1315.

Arensdorf, J.J., Hoster, D., McDougall, D.B., Yuan, M., 2010. Static and dynamic testing of silicate scale inhibitors. In: International Oil and Gas Conference and Exhibition in China. Society of Petroleum Engineers, Beijing, China, Paper Number 132212-MS, pp. 1–7. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-132212-MS&societyCode=SPE.

Atwood, S.E., 1992. Identification of sulfonation by-products by ion chromatography. US Patent 5 133 868, assigned to Marathon Oil Co., July 28, 1992.

Bader, M.S., 2006. Methods to solve alkaline-sulfate scales and related-gases problems. US Patent 7 093 663, August 22, 2006.

Barthorpe, R.T., 1993. The impairment of scale inhibitor function by commonly used organic anions. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, New Orleans, LA, March 2–5, 1993, pp. 69–76.

Becker, J.R., 1998. Corrosion and Scale Handbook. Pennwell Publishing Co, Tulsa.

Boak, L.S., Graham, G.M., Sorbie, K.S., 1999. The influence of divalent cations on the performance of BaSO4 scale inhibitor species. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, Houston, TX, February 16–19, 1999, pp. 643–648.

Brown, J.M., Brock, G.F., 1995. Method of inhibiting reservoir scale. US Patent 5 409 062, assigned to Betz Laboratories, Inc., Trevose, PA, April 25, 1995.

Burger, E.D., Chesnut, G.R., 1992. Screening corrosion inhibitors used in acids for downhole scale removal. Mater. Perf. 31 (7), 40–44.

Carter, C.G., Kreh, R.P., Fan, L.D.G., 1998. Composition and method for inhibiting scale and corrosion using naphthylamine polycarboxylic acids. EP Patent 538 969, assigned to Betzdearborn Inc., May 27, 1998.

Chen, T., Chen, P., Montgomerie, H., Hagen, T.H., Jeffrey, C., 2010. Development of test method and inhibitors for lead sulfide. In: SPE International Conference on Oilfield Scale. Society of Petroleum Engineers, Aberdeen, UK. Paper Number 130926-MS, pp. 1–13. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-130926-MS&societyCode=SPE.

Chilcott, N.P., Phillips, D.A., Sanders, M.G., Collins, I.R., Gyani, A., 2000. The development and application of an accurate assay technique for sulphonated polyacrylate co- polymer oilfield scale inhibitors. In: Proceedings Volume, 2nd Annual SPE Oilfield Scale International Symposium, Aberdeen, Scotland, January 26–27, 2000.

Collins, I.R., 1995. Scale inhibition at high reservoir temperatures. In: Proceedings Volume, IBC Tech. Serv. Ltd Advances in Solving Oilfield Scaling International Conference, Aberdeen, Scotland, November 20–21, 1995.

Collins, I.R., 2000. Oil and gas field chemicals. US Patent 6 148 913, assigned to BP Chemicals Limited, London, GB, November 21, 2000.

Crabtree, M., Eslinger, D., Fletcher, P., Miller, M., Johnson, A., King, G., 1999. Fighting scale – removal and prevention. Oilfield Rev. 11 (3), 30–45.

Crews, J.B., 2006. Biodegradable chelant compositions for fracturing fluid. US Patent 7 078 370, assigned to Baker Hughes Incorporated, Houston, TX, July 18, 2006.

Dean, G.D., Nelson, C.A., Metcalf, S., Harris, R., Barber, T., 1998. New acid system minimizes post acid stimulation decline rate in the wilmington field, los angeles county, california. In: Proceedings Volume, 68th Annual SPE Western Regional Meeting, Bakersfield, CA, May 10–13, 1998.

Dobbs, J.B., Brown, J.M., 1999. An environmentally friendly scale inhibitor. In: Proceedings Volume, NACE International Corrosion Conference, Corrosion 99, San Antonio, April 25–30, 1999.

Drela, I., Falewicz, P., Kuczkowska, S., 1998. New rapid test for evaluation of scale inhibitors. Water Res. 32 (10), 3188–3191.

Duccini, Y., Dufour, A., Harm, W.M., Sanders, T.W., Weinstein, B., 1997. High performance oilfield scale inhibitors. In: Corrosion97. NACE International, New Orleans, LA.

Dyer, S.J., Anderson, C.E., Graham, G.M., 2004. Thermal stability of amine methyl phosphonate scale inhibitors. J. Pet. Sci. Eng. 43, 259–270.

Dyer, S.J., Graham, G.M., Sorbie, K.S., 1999. Factors affecting the thermal stability of conventional scale inhibitors for application in high pressure/high temperature reservoirs. In: Proceedings

Volume, SPE Oilfield Chem. International Symposium, Houston, TX, February 16–19, 1999, pp. 167–177.

Fan, J.C., Fan, L.D.G., Liu, Q.W., Reyes, H., 2001. Thermal polyaspartates as dual function corrosion and mineral scale inhibitors. Polym. Mater. Sci. Eng. 84, 426–427.

Fan, C., Kan, A.T., Zhang, P., Lu, H., Work, S., Yu, J., Tomson, M.B., 2010. Scale prediction and inhibition for unconventional oil and gas production. In: SPE International Conference on Oilfield Scale. Society of Petroleum Engineers, Aberdeen, UK. Paper Number 130690-MS, pp. 1–22. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-130690-MS&societyCode=SPE.

Fan, G., Koskan, L.P., Ross, R.J., 1998. Polyaspartates: An emerging green technology in oil production. In: Book of Abstr (ACS), no. ENVR 029, 215th ACS Nat. Mtg., Dallas, March 29–April 2, 1998.

Fidoe, S.D., Talbot, R.E., Jones, C.R., Gabriel, R., 2005. Treatment of iron sulphide deposits. US Patent 6 926 836, assigned to Rhodia Consumer Specialties Limited, Watford, GB, August 9, 2005.

Fong, D.W., Marth, C.F., Davis, R.V., 2001. Sulfobetaine-containing polymers and their utility as calcium carbonate scale inhibitors. US Patent 6 225 430, assigned to Nalco Chemical Co., May 1, 2001.

Frenier, W.W., Hill, D.G., 2004. Green inhibitors-development and applications for aqueous systems. In: Proceedings Volume, Vol. 3 of Reviews on Corrosion Inhibitor Science and Technology, Corrosion-2004 Symposium, New Orleans, LA, United States, March 28–April 1, 2004, pp. 6/1–6/39.

Graham, G.M., Dyer, S.J., Shone, P., 2000. Potential application of amine methylene phosphonate based inhibitor species in HP/HT (high pressure/high temperature) environments for improved carbonate scale inhibitor performance. In: Proceedings Volume, 2nd Annual SPE Oilfield Scale International Symposium, Aberdeen, Scotland, January 26–27, 2000.

Graham, G.M., Dyer, S.J., Shone, P., 2002. Potential application of amine methylene phosphonate based inhibitor species in hp/ht environments for improved carbonate scale inhibitor performance. SPE Prod. Facil. 17, 212–220.

Graham, G.M., Dyer, S.J., Sorbie, K.S., Sablerolle, W., Graham, G.C., 1998a. Practical solutions to scaling in HP/HT (high pressure/high temperature) and high salinity reservoirs. In: Proceedings Volume, 4TH IBC UK Conf. Ltd Advances in Solving Oilfield Scaling International Conference, Aberdeen, Scotland, January 28–29, 1998.

Graham, G.M., Dyer, S.J., Sorbie, K.S., Sablerolle, W.R., Shone, P., Frigo, D., 1998b. Scale inhibitor selection for continuous and downhole squeeze application in HP/HT (high pressure/high temperature) conditions. In: Proceedings Volume, Annual SPE Technical Conference, New Orleans, LA, September 27–30, 1998, pp. 645–659.

Graham, G.M., Jordan, M.M., Sorbie, K.S., Bunney, J., Graham, G.C., Sablerolle, W., Hill, P., 1997. The implication of HP/HT (high pressure/high temperature) reservoir conditions on the selection and application of conventional scale inhibitors: Thermal stability studies. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, Houston, TX, February 18–21, 1997, pp. 627–640.

Gupta, D.V.S., Kirk, J.W., 2009. Method of inhibiting or controlling formation of inorganic scales. US Patent 7 491 682, assigned to BJ Services Company, Houston, TX, February 17, 2009.

He, S., Kan, A.T., Tomson, M.B., 1999. Inhibition of calcium carbonate precipitation in NaCl brines from 25 to 90°C. Appl. Geochem. 14 (1), 17–25.

Holzner, C., Kleinstueck, R., Spaniol, A., 2000. Phosphonate-containing mixtures (phosphonathaltige mischungen). WO Patent 0 032 610, assigned to Bayer AG, June 8, 2000.

Hsu, J.F., Al-Zain, A.K., Raju, K.U., Henderson, A.P., 2000. Encapsulated scale inhibitor treatments experience in the ghawar field, saudi arabia. In: Proceedings Volume, 2nd Annual SPE Oilfield Scale International Symposium, Aberdeen, Scotland, January 26–27, 2000.

Jones, C.R., Grech, J.M., 2004. Formulation for corrosion and scale inhibition. WO Patent 2 004 083 131, assigned to Rhodia Cons Spec. Ltd., Jones Christopher Raymond, and Grech Jason Mark, September 30, 2004.

Jones, C.R., Taylor, R.S., 2004. Sludge control in crude oil. WO Patent 2 004 104 367, assigned to Rhodia Cons Spec. Ltd., Jones Christopher Raymond, and Taylor Robert S, December 2, 2004.

Jones, T.G.J., Tustin, G.J., Fletcher, P., Lee, J.C.-W., 2008. Scale dissolver fluid. US Patent 7 343 978, assigned to Schlumberger Technology Corporation, Ridgefield, CT, March 18, 2008.

Jordan, M.M., Kemp, S., Sorhaug, E., Sjursaether, K., Freer, B., 2003. Effective management of scaling from and within carbonate oil reservoirs, North Sea basin. Chem. Eng. Res. Des. 81, 359–372.

Jordan, M.M., Sjursaether, K., Bruce, R., Edgerton, M.C., 2000. Inhibition of lead and zinc sulphide scale deposits formed during production from high temperature oil and condensate reservoirs. In: Proceedings Volume, SPE Asia Pacific Oil & Gas Conference, Brisbane, Australia, October 16–18, 2000.

Jordan, M.M., Sjursaether, K., Collins, I.R., 2005. Scale control within the north sea chalk/limestone reservoirs—the challenge of understanding and optimizing chemical-placement methods and retention mechanisms: Laboratory to field. SPE Prod. Facil. 20 (4), 262–273.

Jordan, M.M., Sjuraether, K., Collins, I.R., Feasey, N.D., Emmons, D., 2002. Life cycle management of scale control within subsea fields and its impact on flow assurance Gulf of Mexico and the North Sea basin. Spec. Publ. R. Soc. Lond. 280, 223–253.

Jordan, M.M., Sorbie, K.S., Chen, P., Armitage, P., Hammond, P., Taylor, K., 1997. The design of polymer and phosphonate scale inhibitor precipitation treatments and the importance of precipitate solubility in extending squeeze lifetime. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, Houston, TX, February 18–21, 1997, pp. 641–651.

Kan, A.T., Tomson, M.B., 2010. Scale prediction for oil and gas production. In: International Oil and Gas Conference and Exhibition in China. Society of Petroleum Engineers, Beijing, China. Paper Number 132237-MS, pp. 1–29. http://www.onepetro.org/mslib/app/Preview.do?paperNumber=SPE-132237-MS&societyCode=SPE.

Ke, M., Qu, Q., 2010. Method for controlling inorganic fluoride scales. US Patent 7 781 381, assigned to BJ Services Company LLC, Houston, TX, August 24, 2010.

Keatch, R.W., 1998. Removal of sulphate scale from surface. GB Patent 2 314 865, January 14, 1998.

Keatch, R., 2008. Method for dissolving oilfield scale. US Patent 7 470 330, assigned to M-1 Production Chemicals UK Limited, Aberdeen, GB, Oilfield Mineral Solutions Limited, Edinburgh, GB, December 30, 2008.

Kochnev, E.E., Merentsova, G.I., Andreeva, T.L., Ershov, V.A., 1993. Inhibitor solution to avoid inorganic salts deposition in oil drilling operations-contains water, carboxymethylcellulose or polyacrylamide and polyaminealkyl phosphonic acid and has improved distribution uniformity. SU Patent 1 787 996, assigned to Sibe Oil Ind. Res. Inst., January 15, 1993.

Kotlar, H.K., Haugan, J.A., 2005. Genetically engineered well treatment microorganisms. GB Patent 2 413 797, assigned to Statoil Asa, November 9, 2005.

Kowalski, T.C., Pike, R.W., 1999. Microencapsulated oil field chemicals. US Patent 5 922 652, July 13, 1999.

Kowalski, T.C., Pike, R.W., 2001. Microencapsulated oil field chemicals. US Patent 6 326 335, assigned to Corsicana Technologies Inc., December 4, 2001.

Kuzee, H.C., Raaijmakers, H.W.C., 1999. Method for preventing deposits in oil extraction. WO Patent 9 964 716, assigned to Cooperatie Cosun Ua, December 16, 1999.

Larsen, J., Sanders, P.F., Talbot, R.E., 2000. Experience with the use of tetrakishydroxymethylphosphonium sulfate (thps) for the control of downhole hydrogen sulfide. In: Proceedings Volume, NACE International Corrosion Conference, Corrosion 2000, Orlando, FL, March 26–31, 2000.

Mackay, E.J., Sorbie, K.S., 1998. Modelling scale inhibitor squeeze treatments in high crossflow horizontal wells. J. Can. Pet. Technol. 39 (10), 47–51.

Mackay, E.J., Sorbie, K.S., 1999. An evaluation of simulation techniques for modelling squeeze treatments. In: Proceedings Volume, Annual SPE Technical Conference, Houston, TX, October 3–6, 1999, pp. 373–387.

Mackay, E.J., Sorbie, K.S., Jordan, M.M., Matharu, A.P., Tomlins, R., 1998. Modelling of scale inhibitor treatments in horizontal wells: Application to the alba field. In: Proceedings Volume, SPE Formation Damage Contr. Int. Symposium, Lafayette, LA, February 18–19, 1998, pp. 337–348.

Malandrino, A., Andrei, M., Gagliardi, F., Lockhart, T.P., 1998. A thermodynamic model for PPCA (phosphino-polycarboxylic acid) precipitation. In: Proceedings Volume, 4th IBC UK Conf. Ltd., Advances in Solving Oilfield Scaling International Conference, Aberdeen, Scotland, January 28–29, 1998.

Martin, R.L., Brock, G.F., Dobbs, J.B., 2005. Corrosion inhibitors and methods of use. US Patent 6 866 797, assigned to BJ Services Company, March 15, 2005.

Mendoza, A., Graham, G.M., Farquhar, M.L., Sorbie, K.S., 2002. Controlling factors of EDTA and DTPA based scale dissolvers against sulphate scale. Prog. Min. Oilfield Chem. 4, 41–58.

Mikhailov, S.A., Khmeleva, E.P., Moiseeva, E.V., Sleta, T.M., 1987. Determination of the optimal dose of salt deposition inhibitors. Neft Khoz (7), 43–45.

Montgomerie, H.T.R., Chen, P., Hagen, T., Wat, R.M.S., Selle, O.M., Kotlar, H.K., 2004. Method of controlling scale formation. WO Patent 2 004 011 772, assigned to Champion Technology Inc., Statoil Asa, Montgomerie Harry Trenouth Rus, Chen Ping, Hagen Thomas, Wat Rex Man Shing, Selle Olav Martin, and Kotlar Hans Kristian, February 5, 2004.

Mouche, R.J., Smyk, E.B., 1995. Noncorrosive scale inhibitor additive in geothermal wells. US Patent 5 403 493, assigned to Nalco Chemical Co., April 4, 1995.

Newton, J.A., 1988. Applications of spectroscopic quality control techniques for oilfield chemicals. In: Proceedings Volume, NACE Corrosion 88, St Louis, March 21–25, 1988.

Powell, R.J., Fischer, A.R., Gdanski, R.D., McCabe, M.A., Pelley, S.D., 1995. Encapsulated scale inhibitor for use in fracturing treatments. In: Proceedings Volume, Annual SPE Technical Conference, Dallas, October 22–25, 1995, pp. 557–563.

Rakhimov, A.Z., Vazquez, O., Sorbie, K.S., Mackay, E.J., 2010. Impact of fluid distribution on scale inhibitor squeeze treatments. In: SPE EUROPEC/EAGE Annual Conference and Exhibition. Society of Petroleum Engineers, Barcelona, Spain.

Reizer, J.M., Rudel, M.G., Sitz, C.D., Wat, R.M.S., Montgomerie, H., 2002. Scale inhibitors. US Patent 6 379 612, assigned to Champion Technology Inc., April 30, 2002.

Senthilmurugan, B., Ghosh, B., Graham, G.M., Kundu, S.S., 2010. The influence of maleic acid copolymers on the growth and microstructure of calcite scale. In: SPE International Conference on Oilfield Scale. Society of Petroleum Engineers, Aberdeen, UK.

Shen, J., Al-Saeed, A.S., 1990. Study of oil field chemicals by combined field desorption/collisionactivated dissociation mass spectrometry via linked scan. Anal. Chem. 62 (2), 116–120.

Shuler, P.J., Jenkins, W.H., 1989. Prevention of downhole scale deposition in the ninian field. In: Proceedings Volume, Vol. 2, SPE Offshore Europe Conference, Aberdeen, Scotland, September 5–8, 1989.

Siegmeier, R., Kirschey, M., Voges, M., 1998. Acrolein based polymers as scale inhibitors. In: Proceedings Volume, no. PAP 70, NACE International Corrosion Conference, Corrosion 98, San Diego, March 22–27, 1998.

Sikes, C.S., Wierzbicki, A., 1996. Stereospecific and nonspecific inhibition of mineral scale and ice formation. In: Proceedings Volume, 51st Annual NACE International Corrosion Conference, Corrosion 96, Denver, March 24–29, 1996.

Singleton, M.A., Collins, J.A., Poynton, N., Formston, H.J., 2000. Developments in phosphonomethylated polyamine (PMPA) scale inhibitor chemistry for severe BaSO4 scaling conditions. In: Proceedings Volume, 2nd Annual SPE Oilfield Scale International Symposium, Aberdeen, Scotland, January 26–27, 2000.

Talbot, R.E., Grech, J.M., 2005. Formulation for corrosion and scale inhibition. WO Patent 2 005 040 050, assigned to Rhodia Cons Spec. Ltd., Talbot Robert Eric, and Grech Jason Mark, May 6, 2005.

Talbot, R.E., Jones, C.R., Hills, E., 2009. Scale inhibition in water systems. US Patent 7 572 381, assigned to Rhodia UK Limited, Hertfordshire, GB, August 11, 2009.

Tantayakom, V., Fogler, H.S., Chavadej, S., 2005. Scale inhibitor precipitation kinetics. In: Proceedings Volume, 7th World Congress of Chemical Engineering, Glasgow, United Kingdom, July 10–14, 2005, pp. 85704/1–85704/8.

Tantayakom, V., Fogler, H.S., de Moraes, F.F., Bualuang, M., Chavadej, S., Malakul, P., 2004. Study of Ca-ATMP precipitation in the presence of magnesium ion. Langmuir 20 (6), 2220–2226.

Viloria, A., Castillo, L., Garcia, J.A., Biomorgi, J., 2010. Aloe derived scale inhibitor. US Patent 7 645 722, assigned to Intevep, S.A., Caracas, VE, January 12, 2010.

Wang, X., Qu, Q., Ke, M., 2008. Method for inhibiting or controlling inorganic scale formations with copolymers of acrylamide and quaternary ammonium salts. US Patent 7 398 824, assigned to BJ Services Company, Houston, TX, July 15, 2008.

Watkins, D.R., Clemens, J.J., Smith, J.C., Sharma, S.N., Edwards, H.G., 1993. Use of scale inhibitors in hydraulic fracture fluids to prevent scale build-up. US Patent 5 224 543, assigned to Union Oil Co. California, July 6, 1993.

Weber, E., (Ed.), 1987. Molecular Inclusion and Molecular Recognition – Clathrates 1, Vol. 140 of Topics in Current Chemistry. Springer Verlag, Berlin.

Woodward, G., Jones, C.R., Davis, K.P., 2004. Novel phosphonocarboxylic acid esters. WO Patent 2 004 002 994, assigned to Rhodia Consumer Specialities L, Woodward Gary, Jones Christopher Raymond, and Davis Keith Philip, January 8, 2004.

Yan, T.Y., 1993. Process for inhibiting scale formation in subterranean formations. WO Patent 9 305 270, assigned to Mobil Oil Corp., March 18, 1993.

Yang, L., Song, B., 1998. Phosphino maleic anhydride polymer as scale inhibitor for oil/gas field produced waters. Oilfield Chem. 15 (2), 137–140.

Zeng, Y.B., Fu, S.B., 1998. The inhibiting property of phosphoric acid esters of rice bran extract for barium sulfate scaling. Oilfield Chem. 15 (4), 333–335, 365.

Zhang, H., Mackay, E.J., Sorbie, K.S., Chen, P., 2000. Non-equilibrium adsorption and precipitation of scale inhibitors: Corefloods and mathematical modelling. In: Proceedings Volume, SPE Oil & Gas International Conference in China, Beijing, China, November 7–10, 2000, pp. 18.

TRADENAMES

TABLE 7.5 Tradenames in References

Tradename Description	Supplier
BRIQUEST® 543 Sodium diethylene triamine pentakismethylene phosphonate (Fidoe et al., 2005)	Rhodia Consumer Specialties Ltd.
Dequest® 2060 Diethylene triamine pentamethylene phosphonic acid (Collins, 2000)	Monsanto
Empol™ (Series) Oligomeric oleic acid (Jones et al., 2008)	Henkel
Gyptron® KT-178 Diethylene triamine tetramethylene phosphonic acid (DETA), Scale inhibitor (Reizer et al., 2002)	Champion Technologies
Primene® Primary aliphatic amines with highly branched alkyl chains (Reizer et al., 2002)	Rohm & Haas
Rhodafac® RS-410 Polyoxy-1,2-ethandiyl tridecyl hydroxy phosphate (Martin et al., 2005)	Rhodia
Scaletreat® XL14FD polymaleate (Collins, 2000)	TR Oil Services Ltd.

Chapter 8

Gelling Agents

Organic and inorganic gels are used to seal formations with high permeability. Sealing can be permanent or temporary. In this way, undesirable flows in the formation can be suppressed. Gelling agents are mainly used for water shutoff and to limit sand production. Some agents can be also used for primary plugging of surface and flow strings, as well as for eliminating lost circulation (Ryabokon and Goldshtein, 1989), but the high cost often limits wide applications.

Flow-deflecting technologies based on gel-forming agents are effective in highly water-invaded multizone reservoirs, where redistribution of the flow is achieved by equalizing the injectivity profile of the injection wells and reducing the content of produced water in the producing wells. Redistribution also reduces the consumption of electricity, demulsifiers, and fuels used for oil treating in the field.

To broaden the use of gel technologies, problems in developing and manufacturing mobile units for preparing and injecting large volumes of gels and for producing non-freezing agents for year-round stimulation treatments must be solved (Gustov et al., 1996).

PLACING GELS

A key issue in gel technology is how to place gels in thief zones without damaging oil-productive zones. Diffusion, dispersion, and viscous fingering during this placement may modify their injection profiles. In laboratory studies, the effects of diffusion and dispersion may lead to the conclusion that zone isolation is not needed in field applications, but these conclusions may be erroneous (Seright, 1991b). In practice, flow profiles can be modified by the unrestricted injection of Newtonian and non-Newtonian gelling agents. Studies have revealed that (Seright, 1991b):

- Zone isolation is more important during the placement of gels in unfractured wells than in fractured wells.
- Productive zones in unfractured wells can be seriously damaged if the zones are not isolated.

Petroleum Engineer's Guide to Oil Field Chemicals and Fluids. DOI: 10.1016/B978-0-12-383844-5.00008-8

- In non-isolated zones a minimum penetration into unfractured zones with low permeability can be achieved by using water-like gelling agents.
- The non-Newtonian rheology of polymeric gelling agents will not reduce the need for zone isolation.

Various rheological models have been used to describe the properties of non-Newtonian gelling agents. The placement of the gel has been simulated in linear and radial parallel corefloods, as well as in fractured and unfractured injection wells. These studies concluded that non-Newtonian gelling agents do not reduce the need for zone isolation during gel placement in radial flow systems (Seright, 1991a).

BASIC MECHANISMS OF GELLING AGENTS

The subdivision of sealing agents into gelling agents and plugging agents is somewhat arbitrary. Gelling may be understood as a sealing that is less perfect than plugging. Therefore this chapter summarizes gelling agents that are formed by physical crosslinking, whereas Chapter 18 deals with gels that are formed by chemical reactions, for instance, by in situ polymerization. Furthermore, if a chemical composition is exclusively used as a plugging formulation, it has been included in Chapter 18.

The formation of gels can be achieved by various chemical principles:

- Bringing polyanionic and polycationic substances together,
- Physical crosslinking of carboxyl-functional polymers with multivalent ions, and
- Using chelating agents.

Polymer–Crosslinker–Retarder Systems

Typical compositions consist of water, at least one polymer capable of being gelled when contacted with a crosslinking agent, a polyvalent metal cation crosslinking agent, and a reactivity-retarding chelating agent. The latter is selected from water-soluble dicarboxylic acids, for example, hydroxy carboxylic acids or ketocarboxylic acids (Mumallah, 1990). Examples of polymers are given in Table 8.1, and of crosslinkers in Table 8.2.

TABLE 8.1 Examples of Polymers

Polymer
Polyacrylamide
Carboxymethyl cellulose
Polyacrylonitrile, hydrolyzed

TABLE 8.2 Commonly Used Salts, Crosslinkers, and Chelating Agents

Salt
Aluminum citrate
Chromium sulfate
Ferrochrome lignosulfonate
Manganese nitrate
Potassium bichromate
Sodium bichromate
Ferric acetylacetonate
Ammonium ferric oxalate

Carboxylic Acids as Retarders

Chelating agents with multiple carboxyl groups retard the gelation of polymers because of reaction of multivalent cations with the chelating agent. Any water-soluble dicarboxylic acids, hydroxy carboxylic acids, ketocarboxylic acids, and their corresponding salts may serve as a chelating agent (Mumallah, 1990).

GELLING IN OIL-BASED SYSTEMS

Gelled oil systems are used for fracturing, for sand control applications, and for coiled tubing clean-out applications, especially in water-sensitive formations. Because of the low sand-suspension capabilities of conventional gelled oils when pumping at high rates, foaming of the fluids is often recommended (Samuel, 2009).

Gelled oils are, however, difficult to foam, and often require fluorosurfactant compounds that are not environmentally friendly. In addition, the friction loss experienced with conventional gelled oil fluids is generally higher than that experienced with water-based fluids, especially in turbulence, causing some conventional gelled oils to stick to tubing walls.

Gel-enhancing surfactants are used to improve the properties of the organic base fluids. Zwitterionic surfactants, such as erucyl amidopropyl betaine makes the gel viscoelastic, increases its stability, and decreases the sensitivity to the concentrations of the gelling agent and to the metal carboxylate. Aluminum carboxylates can be used as activators for gelling agents, but are themselves able to raise the viscosity of hydrocarbon-based fluids. Organo phosphate esters are typical gelling agents (Samuel, 2009). Viscoelastic gelled oils are used in (Samuel, 2009):

- Hydraulic fracturing,
- Frac packing,

- Gravel packing,
- Diversion,
- Fluid loss control,
- Lost circulation control,
- Sand control,
- Wellbore clean-out,
- Pipeline sweeping,
- Organic scale dissolution
- Sand removal, and
- Drilling.

Aluminum Phosphate Ester Salts

Organic liquid gels are used for temporary plugging during fracturing operations. This type of gelling agent permits on-the-fly gelling of hydrocarbons, particularly those used in hydraulic fracturing of subterranean formations to enhance oil and gas production. A gel of an organic liquid, such as diesel or crude oil, can be formed using an aluminum phosphate diester in which all of the reagents are substantially free of water and pH-affecting substances (Gross, 1987; Harris et al., 1986; Jones et al., 1999).

The diester may be prepared by the reaction of a triester with phosphorous pentoxide to produce a polyphosphate, which is then reacted with an alcohol to produce a phosphate diester. The latter is then added to the organic liquid along with a nonaqueous source of aluminum, such as aluminum isopropoxide in diesel oil, to produce the metal phosphate diester.

The conditions in the preceding two reaction steps are controlled to provide a gel with good viscosity characteristics versus temperature and time. The gel is useful in fracturing subterranean formations by entraining a solid particulate proppant in it, and pumping the resultant mixture into the rock formation at sufficient pressure to fracture it.

A similar process reacts triethyl phosphate and phosphorous pentoxide to form a polyphosphate in an organic solvent (Huddleston, 1992). More than 1.3 mol of triethyl phosphate with respect to phosphorous pentoxide is the best ratio. In the second step, a mixture of higher aliphatic alcohols (from hexanol to decanol), is added in an amount of 3 mol per 1 mol phosphorous pentoxide. Aluminum sulfate is used as a crosslinker. Hexanol results in a high-temperature viscosity of the gel, while maintaining pumpable viscosities at ambient temperatures (Huddleston, 1989).

Less Volatile Phosphoric Acid Esters

A high-viscosity gelled hydrocarbon with a proppant material such as sand can be used in fracturing processes. Rapid gelation of hydrocarbon liquids is also required when tanks or vessels containing such liquids are damaged, in order to avoid spillage and resultant damage to the environment (Delgado and Keown, 2009).

The problem with volatile phosphorus-containing compounds is that they cause fouling in separation units, such as fractionation towers in refineries. This problem can be traced to the phosphate esters present in the fluid that is used to fracture the formation. Volatile, phosphorus-containing compounds tend to condense in the towers at 250°C and below (Lukocs et al., 2007).

Long chain phosphoric acid esters are shown in Figure 8.1. These compounds are prepared from tributyl phosphate and phosphorous pentoxide to produce a polyphosphate intermediate. The polyphosphate is broken up by the reaction with long chain alcohols (Delgado and Keown, 2009; Lukocs et al., 2007), such as a blend of octanol and decanol (Epal 810), or ethylene glycol phenyl ether (Delgado and Keown, 2009). Eventually, a liquid alkyl phosphate diester is obtained. These phosphate esters are suitable as gelling agents for the liquid hydrocarbons used as fracturing fluids.

Aluminum Trichloride

Aluminum trichloride, a cheap, abundant waste product of the chemical industry, forms a gel under certain conditions with carbonates and on mixing with

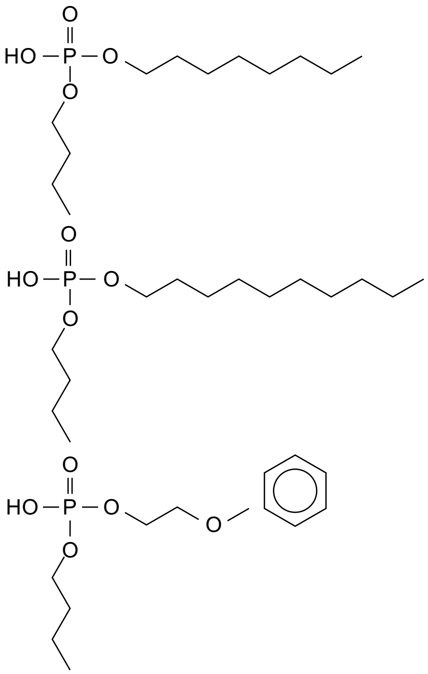


FIGURE 8.1 Long chain phosphoric acid esters (Delgado and Keown, 2009).

alkalies. Laboratory and field tests have shown that aluminum trichloride can be used as a gel-forming agent for reducing the permeability of water-conducting channels (Garifullin et al., 1996).

Biopolymers

Curdlan

A process using a microbially gelled biopolymer was developed and used in coreflood experiments to modify the permeability (Bailey et al., 1995). Curdlan is a microbial carbohydrate with β-linkages, as shown in Figure 8.2.

An alkaline-soluble curdlan biopolymer was mixed with microbial nutrients and acid-producing alkaliphilic bacteria and injected into Berea Sandstone cores.

Concurrent bottle tests with the polymer solution were incubated beside the core. In the bottle tests, the polymer formed a rigid gel in 2–5 d at 27°C. After 7 days of incubation, a pressure of 25–35 psi was required to start flow through the cores, and the permeability of the cores was decreased from 850 to 2.99 mD and from 904 to 4.86 mD, respectively, giving residual resistance factors of 334 and 186.

Poly-3-hydroxybutyrate

Alcaligenes eutrophus produces a massive amount of intracellular polyester (poly(3-hydroxybutyrate) (PHB)), which can amount to 70% of the cell weight. This bacterium was selected for plugging studies in porous media (Nanda et al., 1987).

To simulate the subsurface environment, both static drainage and pressurized pumping flow systems of *Alcaligenes eutrophus* living cells and PHB suspensions through laboratory sand packs were investigated (Li et al., 1993). A PHB water solution is a commercial product in powder form that disperses well but is not completely dissolved in water, and showed plugging effects that were solely dependent on the concentration of PHB.

These facts signify that *A. eutrophus* and its microbial product, PHB, are efficient plugging agents with potential applications in microbial-enhanced oil recovery, such as in selective plugging. This is due to their relative nonagglomerating cell size, their rod shape of 0.7 μ in diameter and 1.8–2.6 μ in length,

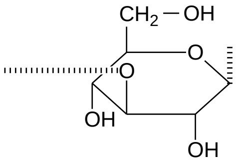


FIGURE 8.2 Curdlan.

and their lack of any exopolymer in culture solutions, especially PHB produced internally in cells.

Succinoglycan

Aqueous solutions of succinoglycan can be crosslinked by means of a polyvalent metal cation (Dasinger and McArthur, 1988). Gelation occurs after 3–24 h but can be further delayed by an appropriate chelating agent. Chelating agents are multifunctional carboxylic acids or their metal salts, especially citrate, oxalate, and malate metal salts.

The aqueous gels are useful in profile modification, or permeability reduction, of subterranean hydrocarbon-bearing formations in enhanced oil recovery. The application is simple: A gel is pumped into a formation for a period of time that is sufficient to obtain the desired in-depth penetration and decrease in permeability of the high-permeability zones of the formation. Usually, an in-depth penetration of 75–900 feet from the well is sufficient.

Organic Polysilicate Ester

The permeability of subterranean oil-bearing formations can be controlled by injection of an organic polysilicate ester (Hoskin and Rollmann, 1988). Polysilicate esters may be built up from simple, monohydroxylic alcohols such as methanol, ethanol, propanol, or butanol, or from diols such as ethylene glycol, or polyols such as glycerol or polyalkylene oxides.

The polysilicates are injected into a formation via injection wells, in an amount from 10–100% of the pore volume of the zone to be treated. In the formation, the polysilicate esters form gels that selectively decrease the permeability of the very permeable regions of the formation.

Latex

The use of polyisoprene or butadiene-styrene latex with bentonite or chalk filler and polyoxypropylene as an additive has been used as a plugging solution for oil and gas wells (Kuznetsov et al., 1992). The solution can be pumped, but coagulates within the formation at temperatures of 100°C within 2 h, so causing a reduction in permeability. The formulation is particularly useful in deep oil deposits.

Reversible Gelling System

An all-oil reversible gelling system has been made from a polymer, a crosslinking agent, a gel accelerator, and an oxidant. The crosslinking agent is activated at elevated temperatures and the system forms a gel. After use, the oxidant decomposes the gel meaning that portions of oil producing or water or gas injecting subterranean formations can be temporarily sealed (Ventresca et al., 2009).

All the components are oil-soluble, so the system does not leave residues that can cause formation damage in the more permeable zones.

The polymer is preferably a styrene-butadiene copolymer. The crosslinker is a peroxide, similar to the oxidant. The gel accelerator is benzothiazil-2-cyclohexyl sulfenamide, as known in vulcanization technology. The oxidant is a peroxide, e.g., cumyl hydroperoxide or *tert*-butyl hydroperoxide (Ventresca et al., 2009).

The initial mixture contains the non-crosslinked polymer chains. When exposed to sufficient temperatures, typically temperatures of 95–120°C, the crosslinking agent decomposes into radicals that initiate the crosslinking reactions over a comparatively short period of time, and a polymeric gel results. The gel accelerator serves to shorten the gelling time of the system.

The oxidant reverses the crosslinking of the system. The amount and the type of the oxidant can be formulated so as to provide a degradation time of between 20–36 h (Ventresca et al., 2009).

GELLING IN WATER-BASED SYSTEMS

Xanthan Gum

The in situ gelation of aqueous solutions of xanthan gum can be used to treat oil spills in soil as a first-aid method. In experiments, the gelling reaction has been carried out using both Cr^{3+} and Al^{3+} cations. Cr^{3+} takes around 1 h to gel, whereas Al^{3+} forms gels in xanthan almost instantaneously at low pH. Aqueous solutions of xanthan exhibit shear thinning behavior, which is highly desirable for these applications (Gioia and Urciuolo, 2004).

Carboxymethyl Cellulose

A mixture of lignosulfonate with modified carboxymethyl cellulose (CMC) and metal ions as crosslinkers has been suggested as a plugging agent (Ostryanskaya et al., 1992). CMC, modified with polyoxyethylene glycol ethers of higher fatty alcohols, combines the properties of a surfactant and CMC. It there re-reduces the viscosity of the composition and increases the strength of the produced gel. Sodium and potassium bichromates act as crosslinking agents. Ionic crosslinks are formed as a result of the reaction of Cr^{3+} and Ca^{2+} ions with molecules of modified CMC.

A gel-forming composition is obtained by mixing aqueous solutions of the respective components. Highly mineralized water also can be used, and the gelation time can be controlled by changing the contents of $CaCl_2$ and bichromates.

Polydimethyl Diallyl Ammonium Chloride

Polydimethyl diallyl ammonium chloride is a strongly basic, cation-active polymer. A mixture of this compound with the sodium salt of CMC, which is an anion-active polymer, is applied in an equimolar ratio (Dobroskok et al., 1992) in aqueous sodium chloride solution. The proposed plugging composition has high efficiency with a wide pH range.

Lignosulfonate and Carboxymethyl Cellulose

An aqueous solution of 3–6% lignosulfonate and 2–8% CMC, modified with polyoxyethylene glycol ethers of higher fatty alcohols, form the base of a plugging system (Ostryanskaya et al., 1992). Lignosulfonate is a waste product from the cellulose-paper industry. Sodium or potassium bichromate and calcium chloride are as crosslinking agents, added in amounts of 2–5%. The final product is obtained by mixing aqueous solutions of the components in a cement mixer.

Polydimethyl diallyl ammonium chloride, which is a strongly basic cation-active polymer, and the sodium salt of CMC, which is an anion-active polymer form a plugging solution when mixed in equimolar ratios. The aqueous solution contains 0.5–4% of each polymer. Gelling occurs because the macro ions from different molecules link together. The proposed plugging composition has high efficiency within a wide pH range (Dobroskok et al., 1992).

Polyacrylamide-based Formulations

Aqueous solutions of polyacrylamide (PAM) may be used as plugging solutions for high-permeability formations. Partially hydrolyzed polyacrylamide (PHPA) also has been used (Merrill, 1993), and completely hydrolyzed polyacrylonitrile has been proposed (Perejma and Pertseva, 1994).

The polymer solutions are pumpable, but in the presence of multivalent metal ions, gels are formed. Gel formation is caused by intermolecular crosslinking, in which the metal ion forms bonds to the polymer.

The metal ions are often added as salts of organic compounds, which form chelates, causing a delayed gelation. The components of the gelling agent are pumped down in two stages. Some metal cations cannot be used with brines, but brines are often produced in wells, and it is desirable to find uses for them to avoid disposal processes.

Delayed Gelation

Complexing Agents

Delayed gelation can be achieved by adding complexing agents to the mixture. If metal ions are initially present as complexes, all the components of the gelling composition can be injected simultaneously. It is possible to dissolve the mixture in produced brines that have high salinity, which eliminates the need for their disposal.

Examples of such compositions are a water-soluble polymer such as PAM, an iron compound such as ferric acetylacetonate or ammonium ferric oxalate, and a ketone such as 2,4-pentanedione (Moradi-Araghi, 1995). The composition forms a temporary gel that is useful for the temporary plugging of a

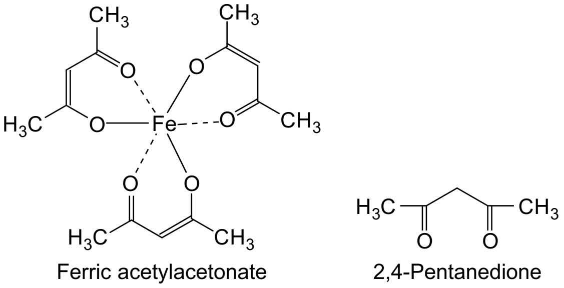


FIGURE 8.3 Complex with iron.

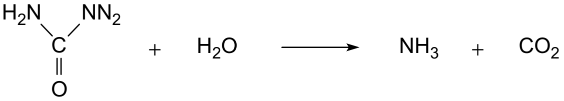


FIGURE 8.4 Hydrolysis of urea with water.

formation. These gels will disappear after 6 months. Such complexes are shown in Figure 8.3.

Adjustment of pH

Some organic reagents such as urotropin and urea hydrolyze in aqueous solution at elevated temperature and release ammonia. The hydrolysis of urea is shown in Figure 8.4.

Urotropin yields formaldehyde and ammonia by hydrolysis, so increasing the pH. The chemical reactions necessary for the formation of a gel with other components of the mixture can then take place.

Polyacrylamide and Urotropin-based Mixture

In Table 8.3 a recipe for a PAM-based mixture is shown (Lyadov, 1992a). The gel-forming properties of such a PAM and urotropin-based mixture are shown in Table 8.4.

Reinforcement by Fibers

Fibers can be added to a gelation solution (Merrill, 1994, 1995). Fibers that will not interfere with the gelation process and will provide adequate reinforcement must be chosen. In addition, they should not adversely affect the ability of the solution to be pumped and injected. Glass and cellulosic fibers are particularly useful as reinforcing fibers for plugging solutions.

Metal Ions and Salts as Crosslinking Agents

Iron Salts

Iron, cations, and some divalent cations cannot be used in a brine environment.

TABLE 8.3 Gel-Forming Composition Based on Polyacrylamide (Lyadov, 1992a)

Material	Amount/[%]
Polyacrylamide	0.05 to 3
Urotropin	0.01 to 10
Sodium bichromate	0.01 to 1
Water	100

TABLE 8.4 Gel-Forming Time at Various Temperatures (Lyadov, 1992a)

Temperature/[°C]	Time/[hr]
60	10 to 18
80	6 to 22
120	4.5 to 7

Waste Materials

Waste materials from other processes have been found to be useful, such as waste from galvanizing processes (Kosyak et al., 1993). In this case the components must be added in two stages.

Iron and chromic salts from lignosulfonate are also a source for metal ions (Kotelnikov et al., 1992). Lignosulfonates are waste products from the paper industry.

Chromium (III) Propionate

A chromium (III) propionate-polymer system is suitable for gelation treatments in oil fields, where fresh water is not available (Mumallah, 1987; Mumallah and Shioyama, 1986). It produces good, stable gels in hard brines, as well as in fresh waters. Its effectiveness is a function of gelling agent concentration (i.e., the higher the concentration of chromium propionate, the higher the residual resistance factors).

The process can be used for in-depth treatment and for near-well treatment in the same way, with aluminum citrate. Brines that contain iron and barium can be used. In comparison with aluminum citrate, the use of chromium (III) propionate gives more effective in-depth treatment at only half of the crosslinker concentration, making the chromium propionate process even more attractive for fresh water applications.

Gelation Process and Gel Breaking

Gelation of PAM with chromium ions takes place via coordination bonding with the nitrogen moiety (Nanda et al., 1987). Studies have indicated that better results can be obtained for certain concentration ranges of the reactants. Gels formed at neutral pH have been observed to be comparatively stable and to manage the reservoir temperature for 50 days. Solubility in chemicals such as HCl, mud acid, and hydrogen peroxide indicates that these chemicals can be used as breakers.

Aluminum Citrate

Aluminum citrate can be used as a crosslinker for many polymers. The gels consist of low concentrations of polymer and aluminum citrate in water. This crosslinker provides a valuable tool, in particular, for in-depth blockage of high-permeability regions of rock in heterogeneous reservoirs. The formulations can be mixed as a homogeneous solution at the surface.

PHPAs, CMC, polysaccharides, and acrylamido methylpropane sulfonate have been screened in an investigation of the performance of aluminum citrate as a chelate-type crosslinker. An overview of the performance of 18 different polymers has been presented in the literature (Smith, 1995). The performance of the colloidal dispersion gels depends strongly on the type and the quality of the polymer used.

The gels were mixed with the polymers at two concentrations, at three polymer-to-aluminum ratios, and in different concentrations of potassium chloride. The gels were quantitatively tested 1, 7, 14, and 28 days after preparation.

Interactions of Metal Salts with the Formation

Interactions of metal salts with the formation and distribution of the retained aluminum in a porous medium may significantly affect the location and strength of the resultant gels. This interaction was demonstrated with PAM–aluminum citrate gels (Rocha et al., 1989). Solutions were displaced in silica sand.

The major findings of this study were that the aluminum retention increases as the aluminum-to-citrate ratio increases. Furthermore, the amount of aluminum that is retained by silica sand increases as the displacing rate decreases. The process is reversible, but the aluminum release rate is considerably slower than the retention rate.

The amount of aluminum released is influenced by the type and the pH level of the flowing solution. The citrate ions are retained by silica sand primarily as a part of the aluminum citrate complex. Iron, cations, and some divalent cations cannot be used in the brine environment.

Bentonite Clay and Polyacrylamide

A water-expandable material based on bentonite clay and PAM is added to the circulating drilling solution (Avakov, 1992). The material expands in water to 30–40 times its initial volume within 2–3 h. During the circulation of the drilling solution, the material enters the cracks and pit spaces of the natural stratal rock. The material changes within 30–40 min into the plugging material, which is strongly fixed to the rock.

Tests showed that the additive effectively prevents the absorption of the drilling solution on the stratal rock because of the production of a strongly adhering and insulating film, which is not dislodged even after subjecting the material to an excess pressure of 3 atm for 2 h. The expansion time of the material is sufficiently slow to let it permeate into the slits and cracks of the stratal rock, yet quick enough to provide a compact insulation.

Thermal Insulation Compositions

Undesired heat loss from production tubing, and uncontrolled heat transfer to outer annuli can be detrimental to the mechanical integrity of outer annuli, because productivity losses from the well due to deposition of paraffin and asphaltene materials accelerate the formation of gas hydrates, and destabilize the permafrost in arctic regions (Wang et al., 2010).

Fluids can be added either into the annulus or riser to effectively reduce the undesired heat loss. They contain a solvent of low thermal conductivity and a viscosifying polymer or a gelling agent. Ethylene glycol, propylene glycol, glycerol, or diethylene glycol are suitable solvents. The solvent imparts low thermal conductivity to the composition and thereby provides highly desirable thermal insulation.

The gelling agent is an acrylamide copolymer. The copolymers can be slightly crosslinked, e.g., with *N*,*N*′-methylene-bis-acrylamide. Guar derivatives are suitable alternatives (Wang et al., 2010). The crosslinking agents are based on borate compounds or zirconium or titanium complexes.

Water is preferably not used in conjunction with the solvent, but may be used in small amounts in the composition, such as a portion of a crosslinking system or the buffer system.

The thermal insulating composition can be prepared on the surface and then pumped through the tubing in the wellbore or in the annulus. The composition acts in two modes (Wang et al., 2010):

1. It serves to prevent heat transfer and buildup in the outer annuli and
2. It serves to retain the heat within the produced hydrocarbons.

Polyacrylic Acid

Polymers of acrylic acid and methacrylic acid (MA) have been tested for their gel-forming ability (Parusyuk et al., 1994). They are used with gel-forming additives similar to those described for PAMs. Mixtures of latex with methacrylate–MA copolymer as an additive have also been described as plugging agents (Kuznetsov et al., 1994).

Alkali-Silicate Aminoplast Compositions

An alkaline metal silicate and an aminoplastic resin have been described as plugging compositions (Soreau and Siegel, 1986, 1990). Urea-formaldehyde, urea-glyoxal, or urea-glyoxal-formaldehyde condensation products are suitable. The composition has been suggested as useful for a reservoir rock that requires enhanced recovery methods. It can also be used for consolidation of ground and in building tunnels, dams, and other underground structures of this type.

IN SITU FORMED POLYMERS

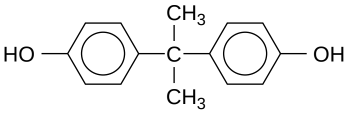
Epoxide Resins

Epoxide resins have good adhesive properties. They can be cured at low temperatures with amine hardeners and at elevated temperatures with organic anhydrides. Formulations can be adjusted to give a long pot life and a low exothermal reaction. The compositions are not miscible with well fluids and they are comparitively expensive. Standard epoxide resins are based on bisphenol-A, shown in Figure 8.5.

A method for selectively plugging wells using a low viscosity epoxide resin composition containing a single curing amine-based agent has been described (Dartez and Jones, 1994, 1995). The proposed method is applicable for plugging permeable zones in a gravel-packed well and may be used to repair leaks in well casing or production tubing, and in cementing to prevent communication between subterranean regions.

Urea-formaldehyde Resins

Urea-formaldehyde resins can be cured with isopropylbenzene production wastes containing 200–300 g l^{-1} of $AlCl_3$ as an acid hardener (Blazhevich et al., 1992). Isopropylbenzene is formed as an intermediate in the Hock process by a Friedel-Crafts reaction from propene and benzene. The mixture hardens in 45–90 min and develops an adhesion to rock and metal of 0.19–0.28 MPa for



Bisphenol-A

FIGURE 8.5 Bisphenol-A.

0.2% $AlCl_3$ and 0.01–0.07 MPa for 0.4% $AlCl_3$, respectively. The increased pot life of the formulation is particularly advantageous.

A solution of a urea-formaldehyde condensate or a phenol-formaldehyde condensate with minor amounts of lignosulfonates can be used for isolation of absorption strata during drilling of oil and gas wells (Lyadov, 1992b). The solution is prepared by mixing the resin component with lignosulfonate. Curing is achieved by thermosetting the solution at 80–120°C.

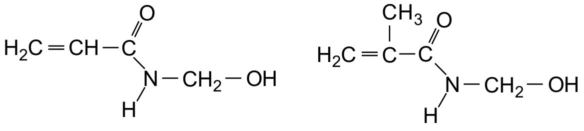
The interaction between the aldehyde and phenol groups of the lignosulfonates with methylol groups of urea-formaldehyde resins, or phenol nuclei of phenol-formaldehyde resins results in the formation of bridges within lignosulfonate macromolecules, which act as hardeners of urea-formaldehyde or phenol-formaldehyde resins. The elasticity of the created fragments results in reduced shrinkage of the hardened compound. The composition has a low toxicity, in part because of the absence of acids or alkalis. The shrinkage is only 0.1–0.6%, and a wide range of curing rates, at temperatures up to 120°C can be achieved.

Vinyl Monomers

The use of vinyl monomers for gel formation requires polymerization to take place in the formation. This technique is used to enable a solution to gel slowly even at high temperatures. An aqueous solution of a vinyl monomer is mixed with a radical-forming initiator, and if necessary, with a dispersant. The initiator decomposes at elevated temperatures and initiates the polymerization process. In this way, a gel is formed in place. The polymerization process is sensitive to molecular oxygen.

To further delay the curing reaction, polymerization inhibitors may be in small amounts added to the solution. This technique is used in the treatment of subterranean formations, especially for plugging lost circulation in drilling operations, and particularly at elevated temperatures. Acrylic acid, acrylamide, vinyl sulfonic acid, and *N*-vinylpyrrolidone may be used. The polymer so formed may be crosslinked by a multifunctional vinyl monomer such as glycerol dimethacrylate or diacrylate (Funkhouser and Frost, 1999).

Monomers like *N*-methylol acrylamide or *N*-methylol methacrylamide, shown in Figure 8.6, also have been suggested (Leblanc et al., 1990). Inhibitors can be phenol derivatives (Leblanc et al., 1988) such as *N*-nitrosophenylhydroxylamine salt (Maurer and Landry, 1990).



N-Methylol acrylamide *N*-Methylol methacrylamide

FIGURE 8.6 Unsaturated methylol amides.

REFERENCES

Avakov, V.E., 1992. Preventing absorption of drilling solution – by introduction of water-expandable material based on bentonite clay and polyacrylamide into circulating drilling solution. SU Patent 1 745 123, June 30, 1992.

Bailey, S., Bryant, R., Zhu, T., 1995. A microbial trigger for gelled polymers. In: Proceedings Volume, 5th US DOE et al Microbial Enhanced Oil Recovery & Relat Biotechnol. for Solving Environ. Probl International Conference, Dallas, TX, September 11–14, 1995, pp. 611–619.

Blazhevich, V.A., Khisaeva, D.A., Umetbaev, V.G., Legostaeva, I.V., 1992. Polymer plugging solution for oil and gas wells – contains urea-formaldehyde resin, and aluminium chloride containing waste of isopropylbenzene production as acid hardener. SU Patent 1 763 638, assigned to Bashkir Oil Ind. Res. Inst., September 23, 1992.

Dartez, T.R., Jones, R.K., 1994. Method for selectively treating wells with a low viscosity epoxy resin-forming composition. US Patent 5 314 023, May 24, 1994.

Dartez, T.R., Jones, R.K., 1995. Method for selectively treating wells with a low viscosity epoxy resin-forming composition. WO Patent 9 532 354, November 30, 1995.

Dasinger, B.L., McArthur, H.A.I., 1988. Aqueous gel compositions derived from succinoglycan. EP Patent 251 638, January 7, 1988.

Delgado, E., Keown, B., 2009. Low volatile phosphorous gelling agent. US Patent 7 622 054, assigned to Ethox Chemicals LLC (Greenville, SC), November 24, 2009.

Dobroskok, B.E., Gulyaeva, Z.G., Kubareva, N.N., Muslimov, R.K., Nizova, S.A., Terekhova, V.V., et al., 1992. Plugging composition for hydro-insulation of oil stratum – contains polydimethyldiallyl ammonium chloride, sodium salt of carboxy methyl cellulose, sodium chloride and water. SU Patent 1 758 209, assigned to Moscow Gubkin Oil Gas Inst., August 30, 1992.

Funkhouser, G.P., Frost, K.A., 1999. Polymeric compositions and methods for use in well applications. US Patent 5 960 877, assigned to Halliburton Energy Serv., October 5, 1999.

Garifullin, S.S., Gallyamov, I.M., Plotnikov, I.G., Shuvalov, A.V., 1996. Aluminum chloride-based gel-forming technologies. Neft Khoz (2), 32–35.

Gioia, F., Urciuolo, M., 2004. The containment of oil spills in unconsolidated granular porous media using xanthan/Cr(iii) and xanthan/Al(iii) gels. J. Hazard. Mater. 116 (1–2), 83–93.

Gross, J.M., 1987. Gelling organic liquids. EP Patent 225 661, assigned to Dowell Schlumberger Inc., June 16, 1987.

Gustov, B.M., Khatmullin, A.M., Asmolovskii, V.S., Zyurin, V.G., Saifutdinov, F.K., Lenchenkova, L.E., 1996. Field tests of gel technologies at the Arlan field. Neft Khoz (2), 36–38.

Harris, L.E., Holtmyer, M.D., Pauls, R.W., 1986. Method for fracturing subterranean formations. US Patent 4 622 155, assigned to Halliburton Co., November 11, 1986.

Hoskin, D.H., Rollmann, L.D., 1988. Polysilicate esters for oil reservoir permeability control. EP Patent 283 602, September 28, 1988.

Huddleston, D.A., 1989. Hydrocarbon geller and method for making the same. US Patent 4 877 894, assigned to Nalco Chemical Co., October 31, 1989.

Huddleston, D.A., 1992. Liquid aluminum phosphate salt gelling agent. US Patent 5 110 485, assigned to Nalco Chemical Co., May 5, 1992.

Jones, C.K., Williams, D.A., Blair, C.C., 1999. Gelling agents comprising aluminium phosphate compounds. GB Patent 2 326 882, assigned to Nalco Exxon Energy Chem. L, January 6, 1999.

Kosyak, S.V., Danyushevskij, V.S., Pshebishevskij, M.E., Trapeznikov, A.A., 1993. Plugging formation fluid transmitting channel – by successive injection of aqueous solution of polyacrylamide and liquid glass, buffer liquid and aqueous solution of polyacrylamide and manganese nitrate. SU Patent 1 797 645, February 23, 1993.

Kotelnikov, V.S., Demochko, S.N., Fil, V.G., Rybchich, I.I., 1992. Polymeric composition for isolation of absorbing strata – contains ferrochromo-lignosulphonate, water-soluble acrylic polymer and water. SU Patent 1 730 435, assigned to Ukr. Natural Gas Res. Inst., April 30, 1992.

Kuznetsov, V.L., Lyubitskaya, G.A., Kolesnik, E.I., Kazakova, E.N., Kurochkin, B.M., Lobanova, V.N., 1994. Plugging solution for isolating absorption zones in oil and gas wells – contains prescribed synthetic latex, water soluble salt of methacrylate-methacrylic acid copolymer as additive, and water. RU Patent 2 024 734, assigned to Drilling Tech. Res. Inst., December 15, 1994.

Kuznetsov, V.L., Lyubitskaya, G.A., Krayushkina, E.I., Kolesnik, E.I., Kazakova, E.N., Vystorop, V.K., et al., 1992. Plugging solution for oil and gas wells – contains polyisoprene or butadiene-styrene latex, bentonite or chalk as filler, polyoxypropylene as additive, and water. SU Patent 1 733 624, assigned to Rubber Latex Articles Res. and Drilling Tech. Res. Inst., May 15, 1992.

Leblanc, M.C.P., Durrieu, J.A., Binon, J.P., Fery, J.J., Provin, G.G.L., 1988. Process for treating an aqueous solution of acrylamide resin in order to enable it to gel slowly even at high temperature. GB Patent 2 197 655, May 25, 1988.

Leblanc, M.C.P., Durrieu, J.A., Binon, J.P.P., Provin, G.G., Fery, J.J., 1990. Process for treating an aqueous solution of acrylamide resin in order to enable it to gel slowly even at high temperature. US Patent 4 975 483, December 4, 1990.

Li, Y., Yang, I.C.Y., Lee, K.I., Yen, T.F., 1993. Subsurface application of alcaligenes eutrophus for plugging of porous media. In: Premuzic, E.T., Woodhead, A. (Eds.), Microbial Enhancement of Oil Recovery - Recent Advances: Proceedings of the 1992 International Conference on Microbial Enhanced Oil Recovery, vol. 39 of Elsevier Developments in Petroleum Science Series. Elsevier Science Publishing Co. Inc., New York, pp. 65–77.

Lukocs, B., Mesher, S., Wilson, T.P.J., Garza, T., Mueller, W., Zamora, F., et al., 2007. Non volatile phosphorus hydrocarbon gelling agent. US Patent Application 20070173413, assigned to Clearwater International, LLC, July 26, 2007.

Lyadov, B.S., 1992a. Gel-forming composition for isolating works in well – contains polyacrylamide, urotropin, water-soluble chromate(s) and water. SU Patent 1 730 432, assigned to Borehole Consolidation Mu., April 30, 1992.

Lyadov, B.S., 1992b. Polymeric solution for isolation of absorption strata – contains urea-formaldehyde and/or phenol formaldehyde resin and lignosulphonate. SU Patent 1 730 434, assigned to Borehole Consolidation Mu., April 30, 1992.

Maurer, R., Landry, M., 1990. Delayed-gelling compositions and their use for plugging subterranean formations. GB Patent 2 226 066, June 20, 1990.

Merrill, L.S., 1993. Fiber reinforced gel for use in subterranean treatment process. WO Patent 9 319 282, assigned to Marathon Oil Co., September 30, 1993.

Merrill, L.S., 1994. Fiber reinforced gel for use in subterranean treatment process. GB Patent 2 277 112, October 19, 1994.

Merrill, L.S., 1995. Fiber reinforced gel for use in subterranean treatment processes. US Patent 5 377 760, assigned to Marathon Oil Co., January 3, 1995.

Moradi-Araghi, A., 1995. Gelling compositions useful for oil field applications. US Patent 5 432 153, assigned to Phillips Petroleum Co., July 11, 1995.

Mumallah, N.A., 1987. Chromium (iii) propionate: a crosslinking agent for water-soluble polymers in real oilfield waters. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, San Antonio, TX, February 4–6, 1987.

Mumallah, N.A., 1990. Altering subterranean formation permeability. US Patent 4 917 186, April 17, 1990.

Mumallah, N.A.K., Shioyama, T.K., 1986. Process for preparing a stabilized chromium (iii) propionate solution and formation treatment with a so prepared solution. EP Patent 194 596, September 17, 1986.

Nanda, S.K., Kumar, R., Goyal, K.L., Sindhwani, K.L., 1987. Characterization of polyacrylamine Cr^{6+} gels used for reducing water/oil ratio. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, San Antonio, TX, February 4–6, 1987.

Ostryanskaya, G.M., Abramov, Y.D., Makarov, V.N., Osipov, S.N., Razhkevich, A.V., 1992. Gel-forming plugging composition – contains ligno-sulphonate, modified carboxymethyl cellulose, bichromate, calcium chloride and water. SU Patent 1 776 766, November 23, 1992.

Parusyuk, A.V., Galantsev, I.N., Sukhanov, V.N., Ismagilov, T.A., Telin, A.G., Barinova, L.N., et al., 1994. Gel-forming compositions for leveling of injectivity profile and selective water inflow shutoff. Neft Khoz (2), 64–68.

Perejma, A.A., Pertseva, L.V., 1994. Complex reagent for treating plugging solutions – comprises hydrolysed polyacrylonitrile, ferrochromolignosulphonate Cr-containing additive, waste from lanolin production treated with triethanolamine and water. RU Patent 2 013 524, assigned to N Caucasus Nat Gaz Res., May 30, 1994.

Rocha, C.A., Green, D.W., Willhite, G.P., Michnick, M.J., 1989. An experimental study of the interactions of aluminum citrate solutions and silica sand. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, Houston, TX, February 8–10, 1989, pp. 403–413.

Ryabokon, S.A., Goldshtein, V.V., 1989. Prospects of developing polymer plugging agents. Neft Khoz (5), 7–13.

Samuel, M., 2009. Gelled oil with surfactant. US Patent 7 521 400, assigned to Schlumberger Technology Corporation (Sugar Land, TX), April 21, 2009.

Seright, R.S., 1991a. Effect of rheology on gel placement. SPE Reserv. Eng. 6 (2), 212–218.

Seright, R.S., 1991b. Impact of dispersion on gel placement for profile control. SPE Reserv. Eng. 6 (3), 343–352.

Smith, J.E., 1995. Performance of 18 polymers in aluminum citrate colloidal dispersion gels. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, San Antonio, TX, February 14–17, 1995, pp. 461–470.

Soreau, M., Siegel, D., 1986. Injection composition for filling or reinforcing grounds. GB Patent 2 170 838, August 13, 1986.

Soreau, M., Siegel, D., 1990. Application of a gelling agent for an alkali-silicate solution for sealing and consolidating soils (verwendung eines geliermittels fuer zum abdichten und verfestigen von boeden bestimmte alkalisilikatloesung). DE Patent 3 506 095, assigned to Soc. Francaise Hoechst, May 31, 1990.

Ventresca, M.L., Fernandez, I., Navarro-Perez, G., 2009. Reversible gelling system and method using same during well treatments. US Patent 7 638 467, assigned to Intevep, S.A. (Caracas, VE), December 29, 2009.

Wang, X., Qu, Q., Dawson, J.C., Gupta, D.V.S., 2010. Thermal insulation compositions containing organic solvent and gelling agent and methods of using the same. US Patent 7 713 917, assigned to BJ Services Company (Houston, TX), May 11, 2010.

TRADENAMES

TABLE 8.5 Tradenames in References

Tradename Description	Supplier
Aculyn™ 28 Hydrophobically-modified polyacrylate (Wang et al., 2010)	Rohm and Haas
Fracsol™ Hydrocarbon fracturing fluid	Trysol Corp. (Delgado and Keown, 2009)
Polybor® Polymeric borate (Wang et al., 2010)	U.S. Borax of Valencia

Chapter 9

Filter Cake Removal

Well drill-in and servicing fluids are employed in the course of drilling, which typically include fluid loss control fluids. These fluids make up a comparatively small portion of the total, but sufficient to form a filter cake so as to plug off thief zones.

In general, well drill-in and servicing fluids are formulated to form a fast and efficient filter cake on the walls of a wellbore within a producing formation, in order to minimize leak-off and damage, which often contains an inorganic and an organic portion. This arises because drill-in fluids are typically composed of either starch or cellulose polymers, xanthan polymers, and sized calcium carbonate or salt particulates.

Before the production starts, the filter cake must be removed (Munoz, 2009). Insufficient degradation of the filter cake can significantly impede the flow capacity at the wellbore wall. Partially dehydrated, gelled drilling fluid and filter cake must be displaced from the wellbore annulus to achieve a successful primary cement job.

Conventional methods of filter cake removal consist of contacting and washing with suitable fluids, or it can be removed by special formulations of the drilling fluid, which often contains an acid-soluble particulate solid bridging agent. The filter cake formed by such a fluid is contacted with a strong acid to dissolve the bridging agent. This method is somewhat dangerous, because the strong acid may corrode the metallic surfaces of the completion equipment, thereby causing premature damage.

Another method of filter cake removal utilizes a water-soluble particulate solid bridging agent in the fluid. The bridging agent is contacted with an aqueous salt solution that is undersaturated with respect to the bridging agent. If this procedure is used, the bridging agents may require a comparatively long period of time to dissolve. The presence of a gelling agent may prevent the salt solution from contacting the water-soluble bridging agents.

A further method for filter cake removal is to contact it with a combination of an acid and an oxidizer. The acid may be used to degrade the inorganic portion

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of the filter cake, while the oxidizer may be employed to degrade the organic portion (Munoz, 2009).

BRIDGING AGENTS

Magnesium oxide, manganese oxide, calcium oxide, lanthanum oxide, cupric oxide, and zinc oxide can be used in combination with hydroxyethyl cellulose as fluid loss agents, and xanthan as suspension aid for solid particle bridging agents.

In addition to the bridging agent, the drilling or servicing fluid may also include an oxidizer, which is deposited in the filter cake and activated by ammonium chloride (NH_4Cl) in the cleaning solution to degrade the polymer in the filter cake. Magnesium peroxide in an encapsulated form is the most suitable oxidizer.

These compounds should be soluble in a clean-up solution containing a quaternary organic ammonium salt, or simply ammonium chloride (Todd et al., 2002). The solubilities of some selected particulate bridging agents are shown in Table 9.1. A chelating agent such as citric acid or its salts is also included in the clean-up solution.

Production engineers have been reluctant to use particle bridging because of the possibility of particle transport into the formation, resulting in formation damage, or costly and often ineffective stimulation treatments, but an example has been developed that quickly and effectively controls the fluid loss in a wide range of permeabilities and pore diameters (Johnson, 1994).

Water-soluble organic polymers, such as hydroxethyl cellulose, have been used to slow down the leak-off rate of clear brines into permeable formations. Fluid loss or leak-off, however, can be effectively controlled only by bridging the pore openings with rigid or semirigid particles of sufficient size and number.

The filter cake formed in this process is highly dispersible in the produced fluid and thus is effectively removed by putting the well into production. No acid treatment or other removal techniques are required. The primary bridging agent in this fluid is a sized calcium carbonate with particle sizes capable of initiating bridging pore diameters in excess of 100 μ.

Degradable Bridging Agents

Bridging agents made up from a degradable material can enhance filter cake removal. In this way, a self-degrading filter cake is formed. The bridging agent is suspended in a treatment fluid, and, as it begins to form a filter cake within the subterranean formation, the bridging agent becomes distributed throughout the resulting filter cake. After a certain period of time, the material degrades, which in turn causes the degradable material to be removed from the filter cake. As a result, voids are created in the filter cake that allow the produced fluids to flow more freely (Munoz and Eoff, 2010).

TABLE 9.1 Solubilities of Some Particulate Bridging Agents (Todd et al., 2002)

Particulate Bridging Agent	Aqueous Ammonium Salt Clean-up Solution	Solubility/ [g/100 ml]
Magnesium oxide	4 M ammonium chloride	1.6
Magnesium oxide	8 M ammonium acetate	2.8
Magnesium oxide	1.3 M ammonium chloride plus 1 M sodium citrate	2.8
Magnesium carbonate	8 M ammonium acetate	2.2
Magnesium carbonate	4 M ammonium chloride plus 0.4 M trisodium salt of nitrilotriacetic acid	2.9
Anhydrite ($CaSO_4$)	4 M ammonium chloride	1.7
Anhydrite ($CaSO_4$)	8 M ammonium acetate	2.9
Lime ($Ca(OH)_2$)	1.3 M ammonium chloride	3.0
Zinc oxide	4 M ammonium chloride	3.0
Zinc oxide	1.3 M ammonium chloride plus 0.8 M sodium citrate	2.9
Zinc carbonate	4 M ammonium chloride	2.4
Lanthanum oxide	0.36 M diammonium salt of ethylene diamine tetraacetic acid (EDTA)	2.2
Manganese hydroxide	4 M ammonium chloride	1.5

A polymeric bridging agent consists of polylactides, commonly synthesized by a ring opening polymerization of cyclic lactide monomers. Lactic acid belongs to the group of hydroxy acids, which are shown in Figure 17.18.

Lactide units are chiral, which allows degradation rates and physical and mechanical properties to be adjusted. Poly(*L*-lactide) is a semicrystalline polymer with a relatively slow hydrolysis rate, which could be desirable in applications where a slow degradation of the degradable material is desired. In contrast, poly(*D*,*L*-lactide) is a more amorphous polymer with a correspondingly faster hydrolysis rate. This may be suitable for applications where a more rapid degradation may be appropriate.

The various stereoisomers of lactic acid may be used as they are, or they can be combined. It may also be copolymerized with ε-caprolactone, 1,5-dioxepan-2-one, or trimethylene carbonate to tailor the desired properties. Yet another possibility is to control the desired properties via the molecular weight or to use blends of different molecular weights. Oligomeric lactic acid can be used as plasticizer.

TABLE 9.2 Dissolvable Bridging Agents (Todd, 2009b)

Compound
Magnesium citrate
Magnesium tartrate
Calcium citrate
Calcium tartrate
Calcium succinate
Calcium malate
Bismuth citrate

Other types of degradable polymers include polyanhydrides, such as polyadipic anhydride, polysuberic anhydride, polysebacic anhydride, and polydodecanedioic anhydride.

The bridging agents are contacted with an acidic breaker solution, e.g., dilute aqueous acetic acid (Munoz and Eoff, 2010) so that they can be destroyed by hydrolysis. Another possibility is to use delayed-release acid compositions, or enzymatic degradation, which may be achieved by the use of lactate oxidase (Munoz, 2010).

Dissolvable Bridging Agents

Similarly to degradable bridging agents, dissolvable bridging agents are helpful in removing filter cakes. They are based on salts of hydroxy acids (Todd, 2009b). Suitable examples are listed in Table 9.2.

The particle size of the bridging agent is 1–200 μ, and they should have a specific gravity sufficiently different from that of the drill solids in order to permit separation on the basis of gravity (Todd, 2009b). Alternatively, they can be dissolved EDTA compounds.

DEGRADATION BY ACIDS

In permeable carbonate formations, hydrochloric acid treatments are usually utilized to remove formation damage and the mud filter cake produced by drilling operations.

Citric Acid

An aqueous solution of citric acid and potassium chloride, alkali metal formate, acid tetraphosphate, alkaline earth chloride, and alkali metal thiophosphate has been reported as a composition for dissolving filter cake deposits left by the drilling mud in wellbores (Kristiansen, 1994).

The composition is useful as an additive for clearing stuck pipe in wellbores and as a fixer spacer for cementing pipe in wellbores. It can also be used as a well stimulation fluid in oil and gas production wells, where it is effective for dissolving filter cake that blocks pores in the production formation.

Horizontal Well Acid Breaker

Horizontal completions in unconsolidated formations can be enhanced by a hydrochloric acid (HCl) breaker system for well clean-up. Typically, the use of HCl in open-hole environments is avoided because of wellbore stability concerns, but it successfully removes salt fluid loss control materials in wells without noticeable hole collapse (Ali et al., 1993).

Acetic Acid

A case study was reported regarding the use of acetic acid (Nasr-El-Din et al., 2001). A large-scale acetic acid-based stimulation treatment was developed to remove drilling mud filter cake in vertical wells in a carbonate reservoir in Saudi Arabia. The wellbore stability of this weakly consolidated carbonate formation can be easily reduced by contact with HCl-based compositions. Laboratory testing indicated that the formation was mechanically weak, became brittle upon contact with acids, and produced large amounts of fine particles that can cause severe damage.

A chloride-free acid formula was therefore required to minimize the interference with the pulsed-neutron logs. A special acid treatment was needed to reduce the damage and maintain the integrity of the formation. Laboratory tests were performed with both regular and emulsified acetic acid and an auxiliary chemical, mainly EDTA. Pressure buildup tests after the treatment indicated that the acid was successful in removing the filter cake in all cases investigated. No fine particles nor any type of emulsion was observed in the well flowback samples.

Acid Generating Coatings

For sand control operations, gravel particles can be coated with an acid-releasing degradable material. This procedure is helpful during subsequent clean up. Coating is a straightforward procedure (Todd and Powell, 2006).

Preparation 9–1: Polylactic acid is dissolved in methylene chloride. This solution is then mixed with particulate sand. Afterwards, the solvent is stripped from the coated sand in vacuo in order to create a free flowing coated sand. The coated sand contains a 2% coating of polylactic acid. ■

As an alternative, polyglycolic acid has been used for coating of sand by coating as a melt (Lee, 2006).

Preparation 9–2:

1. A mixture consisting of 380 g of 20–40 mesh industrial quartz sand from Unimin Corporation, and 190 g of technical grade 65–70% glycolic acid solution from J. T. Baker was mixed together in a 2–liter crystallizing dish.

2. The dish was placed on a hot plate and heated under a ventilated hood. A temperature of at least 210–220°F was maintained for about 8–10 hours.

3. The mixture was stirred frequently until it turned into a light-brown colored, somewhat viscous and sticky mixture.

4. At this point, heating was stopped.

5. The mixture was cooled to room temperature while stirring. Large aggregates formed during cooling were broken up into individual grains using a mortar and pestle.

6. The loose polyglycolic acid coated sand grains were sieved through a 60-mesh screen to remove fine-grained, uncoated material. The product was used for the filter cake clean-up test. ■

Table 9.3 illustrates the generation of acidic components from a coated sand from procedure Preparation 9–2. Each fluid was exposed to brine at 60°C for 4 d. The acid release was characterized by the change in pH. As can readily be seen from the table, the use of polyglycolic acid coated sand with divalent brines is more beneficial than freshwater.

Acidic Foam

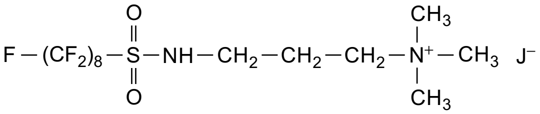
Foams tend to inhibit fluid flow and end the loss of fluids into the subterranean formation even if some portion of the filter cake mass has been prematurely broken. This allows continued dissolution of the rest of the filter cake. Hence, even if an acid acts more effectively at a specific section of the horizontal wellbore, fluid loss will still be arrested by the presence of the foam in these

TABLE 9.3 Generation of Acidic Components by Various Fluids

	Uncoated	Coated
	Sand	
Fluid	pH	pH
Fresh water	9.1	2.9
1.2 $kg\,l^{-1}$ NaCl Brine	8.1	1.6
1.5 $kg\,l^{-1}$ NaBr Brine	8.3	1.6
1.4 $kg\,l^{-1}$ $CaCl_2$ Brine	6.1	<0.1
1.7 $kg\,l^{-1}$ $CaBr_2$ Brine	4.8	<0.1

TABLE 9.4 Surfactant Foam Composition (Chan, 2009)

Component	%
Hydrochloric acid	3–10
Citric acid	5–20
Cationic fluorocarbon surfactant	0.1–0.5
n-Hexanol	0.1–2
Cocoamido propyl betaine	0.5–2
Alkyl polyglycoside	0.5–2



$$F-(CF_2)_8-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-NH-CH_2-CH_2-CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{N^+}}}-CH_3\quad J^-$$

FIGURE 9.1 FLUORAD™ FC 754.

areas. Removal of filter cake from a horizontal wellbore is performed as follows (Chan, 2009):

1. Forming a stable aqueous acidic foam, the foam should be stable at 95°C,
2. Positioning the aqueous acidic foam in the horizontal wellbore, and
3. Retaining the aqueous acidic foam in the horizontal wellbore for 2–4 h.

An example of such a surfactant foam composition is shown in Table 9.4. Cationic fluorocarbon surfactants consist of an insoluble fluorocarbon tail and a water-soluble moiety (Chan, 2009). For example, FLUORAD™ FC 754 is *N*,*N*,*N*-trimethyl[3-(perfluorooctanesulfonylamino)propyl]ammoniumiodide, which is shown in Figure 9.1.

The alcohol promotes the formation of microemulsions once the surfactant foam has been spent, and it becomes mixed with oily fluids, such as crude oil and condensate from the formation. The foam may be produced in situ by alternately injecting slugs of air and the composition through the horizontal wellbore.

ORTHOESTERS

Orthoesters find use in various oil field applications, including the delayed delivery of acids that eventually degrade filter cakes (Schriener and Munoz, 2009). Orthoester compositions generate acids that are capable of degrading the acid-soluble portion of a filter cake.

TABLE 9.5 Orthoesters for Delayed Acid Delivery (Schriener and Munoz, 2009)

Ortoester Compound	Boiling Point/[°C]
Trimethyl orthoacetate	107
Triethyl orthoacetate	142
Tripropyl orthoacetate	
Triisopropyl orthoacetate	
Polyorthoacetates	
Trimethyl orthoformate	101
Triethyl orthoformate	146
Tripropyl orthoformate	106 (40 mmHg)
Triisopropyl orthoformate	65 (18 mmHg)
Polyorthoformates	
Trimethyl orthopropionate	121
Triethyl orthopropionate	155

Tripropyl orthoformate is a commonly used example, however, a variety of orthoesters and orthoester polymers have been claimed to be usable. These are summarized in Table 9.5.

The presence of water is required to allow the orthoester to hydrolyze and produce an acid. Inhibitor bases, including sodium hydroxide, potassium hydroxide, amines, e.g., hexamethylenetetramine, and sodium carbonate are added to the orthoester to delay the generation of the acid (Schriener and Munoz, 2009).

ENZYMATIC DEGRADATION

Enzymes are promising candidates for clean-up operations because they can degrade the polymeric components of a filter cake. Thus the permeability of the rock is re-established. The particular properties of the enzymes are (Battistel et al., 2010):

1. High specificity, which allows activity to be accurately controlled with respect to the polymeric substrate,
2. Catalytic efficiency, which allows a high reaction rate per mole of reacted product to be obtained, under optimum conditions, and
3. Activity under bland conditions.

Damaging materials such as filter cakes and very viscous fluids within a subterranean formation of a wellbore can be removed by enzyme treatment (Tjon-joe Pin et al., 1994), which degrades polysaccharide-containing filter cakes and their damaging fluids by reducing their viscosity. The degraded filter cake and damaging fluid can then be removed from the formation back to the well surface.

The enzymes used act specifically on a given type of polysaccharide and are active at low to moderate temperatures. The enzymes attack only specific linkages in filter cakes and damaging fluids and are active in the pH range of 2 to 10.

Enzymes are available to degrade crosslinked hydroxypropylated starch and xanthan gum polymer systems (Beall et al., 1997; Moore et al., 1996). They are efficient in reducing the near-wellbore damage induced by the starch polymer, eventually returning permeabilities to 80–98% without the use of acid systems.

The use of enzymes as breakers allows the optimization well completion operations, so reducing the damage caused by fracturing during drilling. Unlike acids and other chemical oxidants, enzymes do not interact with the formation rock and the metals present, thus making undesirable secondary reactions impossible (Battistel et al., 2010).

An enhanced process for the degradation of scleroglucan or xanthan gums has been developed. Cellulase enzymes obtained specifically from *Trichoderma reesei* and glucosidase obtained from *Aspergillus niger* are used (Battistel et al., 2010).

PEROXIDES

Hydrogen Peroxide

A reagent for removing clay deposits based on an aqueous solution of H_2O_2 and Na_2CO_3 in a concentration range of 15–30 $g\,l^{-1}$ and 75–150 $g\,l^{-1}$, or a solution of sodium bicarbonate and HCl in a concentration range of 60–80 $g\,l^{-1}$ and 3.5–4.0 $g\,l^{-1}$ has been reported (Bulanov et al., 1992). Injection is followed by a holding time of preferably 2–5 h. Clay layer breakup products are washed out with a wash solution such as petroleum and circulating water.

Metal Peroxides

Mixture containing polysaccharide polymers and certain bridging particles and alkaline earth metal peroxides and zinc peroxide in an acidic aqueous solution successfully removes filter cake (Dobson and Mondshine, 1995; Mondshine and Benta, 1993). On soaking, a loosely adherent mass is left behind on the walls of the borehole that can be removed with a wash solution in which the bridging particles are soluble.

Magnesium Peroxide in Filter Cake

Magnesium peroxide is very stable in an alkaline environment, and remains inactive when added to polymer-based drilling fluids, completion fluids, or workover fluids. Because it is a powdered solid, it becomes an integral part of the deposited filter cake (Dobson and Kayga, 1995), which can be activated by a mild acid soak. This treatment produces hydrogen peroxide, which decomposes into oxygen and hydroxyl radicals (OH·) when catalyzed by a transition metal.

These highly reactive OH· species attack positions at the polymers that are resistant to acid alone, thus realizing significant improvements in filter cake removal. Magnesium peroxide is used as a breaker in alkaline water-based systems, especially in wells with a bottom hole temperature of 150°F (65°C) or less, when drilling into a pay-zone, underreaming, and in lost circulation pills, and fluid loss pills for gravel prepacks.

DEGRADATION BY OLIGOSACCHARIDES

A gelled and dehydrated drilling fluid or filter cake can be removed from the walls of wellbores by injecting an aqueous sugar solution (Weaver et al., 1996). This solution is kept in contact with the filter cake for long enough to cause the disintegration of the gelled drilling fluid and the filter cake. The whole composition is then displaced from the wellbore. Monosaccharide, disaccharide, and trisaccharide sugars can be used, and surface active agents, such as a blend of non-ionic ethoxylated alcohols or a mixture of aromatic sulfonates, can be added.

BREAKING BY EMULSIONS

Some water-in-oil emulsions are highly efficient in breaking the residual emulsion inside the filter cake, decreasing cake cohesion and reducing cake adherence to the formation face (Javora et al., 2009).

They act like a demulsifier to break oil-based drilling mud (OBM) or synthetic OBM water-in-oil emulsions and thus changes the adherence of the filter cake to the wellbore and formation.

When the emulsion is specifically formulated, the emulsion may pass the *no-sheen* requirement for use in Gulf of Mexico applications, where the emulsion must not produce a silvery or iridescent sheen on the surface of sea water (Javora et al., 2009).

In particular, the emulsion used should provide excellent particle suspension capacity in order to prevent particulates from redepositing within the well, e.g., on tubings, casings, or the formation surface.

The internal (or discontinuous) phase of the water-in-oil emulsion is water, and the external phase is a hydrophobic organic solvent. *D*-Limonene is a preferred organic solvent. Preferred surfactants are fatty acids, e.g., caprylic or capric acids, but several other types have been considered (Javora et al., 2009).

Suitable dispersing agents include organophosphate esters, such as (2-ethylhexyl) orthophosphate. The effectiveness of the concept of weakening the filter cakes has been tested muds in laboratory experiments (Javora et al., 2009).

Surfactant Nanotechnology

The removal of residues from OBMs in a wellbore is important, since brines contaminated with an OBM can adversely affect the productivity of a reservoir. All OBM residues can be removed by a series of solvent and surfactant treatments, but such treatments result in large disposal volumes, and incomplete water-wetting of the casing or formation by the surfactant may emerge. A recently developed method relies on surfactant nanotechnology in a high-density brine in order to form a microemulsion upon contact with oil (Zanten and Ezzat, 2010).

OBM filter cake with an acid-degradable weighting agent can also be removed and the reservoir becomes water-wet if the surfactant is used in conjunction with an acid precursor. Microemulsion technology is also suitable for remediation, as emulsion blockages can be removed (Zanten and Ezzat, 2010).

The issues of microemulsions have been described in detail (Fanun, 2008; Harrison, 2004), and their classification goes back to Winsor (1948). It is defined as a system of oil, water, and amphiphile that is a single phase, optically isotropic and thermodynamically stable liquid solution.

Single phase microemulsions are used to improve the removal of filter cakes formed during drilling with OBMs. The microemulsion removes oil and solids from the deposited filter cake (Jones et al., 2010). In addition, microemulsions find use in enhanced oil recovery operations (Santanna et al., 2009).

SPECIAL ISSUES

Manganese tetroxide

Manganese tetraoxide (Mn_3O_4) has been recently used as a weighting material for water-based drilling fluids. It has a specific gravity of $4.8\,g\,cm^{-3}$, making it suitable in muds for drilling deep gas wells. The filter cake formed by this mud also contains Mn_3O_4 (Moajil et al., 2008).

Several articles concerning the use of manganese tetroxide with other additives in drilling fluid formulations have reported negative effects on the reservoir performance. The permeability of reservoirs is reduced when they are contacted with such drilling fluids, meaning special and expensive stimulation techniques have been proven to be necessary.

Unlike $CaCO_3$, Mn_3O_4 is a strong oxidant (Moajil et al., 2008), hence the use of HCl is not recommended for the removal of the filter cake. Various organic acids, chelating agents, and enzymes, have been tested at temperatures up to 150°C.

Research has been presented which indicates that a drilling fluid formulation containing manganese tetroxide causes a minimal reduction of the permeability

TABLE 9.6 Drilling Fluid Formulation with Manganese Tetroxide (Al-Yami, 2009)

Ingredient	lbs bbl^{-1}	kg m^{-3}
Fresh water (95.2%)	0.952	2.7
Bentonite	4.0	11.4
Xanthan biopolymer	1.5	4.3
Starch with biocide	6.0	17.1
Hydrated lime	0.25	0.7
Manganese tetroxide	80.0	228.2

of the reservoir formation with respect to hydrocarbon flow (Al-Yami, 2009). These formulations are particularly useful for wells that are otherwise difficult to stimulate. A return permeability of 90% or greater was achieved without the need for acidizing treatments.

In order to achieve these performance levels, the formulation must possess certain rheological, density, temperature, and fluid loss properties. Such a formulation is shown in Table 9.6. Recall that manganese tetroxide has a density of 4.7 $g\,cm^{-3}$.

In comparison to a synthetic mud based on alkalis salts of formic acid, where a return permeability is 66% of the initial volume of oil injected, in a manganese tetroxide based mud a return permeability is 93% (Al-Yami, 2009).

Multiply Active Compositions

In many oil field applications, fluid loss additives and filter cakes are both needed during a treatment, but after the treatment they need to be removed entirely (Willberg and Dismuke, 2009). To degrade the acid-soluble particulate portion of the drill-in fluid filter cake, a conventional delayed-release acid system is usually used.

Oxidizers are used to degrade the polymeric portions of filter cakes, but they are not able to degrade the acid-soluble portion of a filter cake, so this usefulness is limited to cases where the bridging particles that comprise the particulate portion of the filter cake are small enough to flowback.

Filter cake degradation compositions comprise a delayed-release oxidizer component, which will release an acid-consuming component, and a delayed-release acid component that will release an acid derivative (Todd, 2009a). When a filter cake degradation composition is added to a wellbore, the acid-consuming component interacts with acids in such a way that the acids do not in turn interact with the acid-soluble portion of the filter cake for a period of time. This delays degradation of the acid-soluble portion of the filter cake. Thus, the integrity of the filter cake may not be jeopardized for a desired delay period. In addition, the reaction between the acid-consuming component and the acid derivative generates a peroxide that ultimately can degrade the polymeric portion of the filter cake.

Calcium peroxide CaO_2 is a solid with a yellowish color. It is insoluble in water, but it dissolves in acids, e.g., acetic acid, to form hydrogen peroxide. The hydrogen peroxide can then interact with the polymer in the filter cake to ultimately degrade at least a portion of its polymeric portion.

Orthoesters or polymers of hydroxy acids are used as delayed-release acid components. Compounds suitable as delayed-release oxidizers are magnesium peroxide, MgO_2 or calcium peroxide, CaO_2. The delayed-release oxidizer components may be encapsulated (Todd, 2009a).

Self-destructing Filter Cake

Self-destructing filter cake compositions are formulated from a mixture of particulate solid acid-precursors, and particulate solid acid-reactive materials. The solid acid-precursors hydrolyze and dissolve in the presence of water, generating acids that then dissolve the solid acid-reactive materials (Willberg and Dismuke, 2009).

The cyclic dimer of lactic acid, which has a melting point of 95–125°C or the cyclic dimer of glycolic acid are examples of suitable solid acid-precursors. Variants are polymers of these compounds. Particulate solid acid-reactive materials include calcium carbonate, aluminum hydroxide, or magnesia, which can be coated with a hydrolysis-delaying material (Willberg and Dismuke, 2009).

The compositions are used in oil field treatments such as drilling, completion, and stimulation. Here they disappear when no longer needed without the use of mechanical means or the injection of additional fluids.

Oscillatory Flow

A physical method to remove filter cake can be applied wherein a fluid is oscillated in the annulus prior to cementing (Keller, 1986, 1987), the direction of flow of the fluid in the annulus being changed at least twice. This removes the drilling mud and the filter cake from the annulus. After this oscillatory flow treatment, the cement slurry is pumped into the annulus.

REFERENCES

Al-Yami, A.S.H.A.-B., 2009. Non-damaging manganese tetroxide water-based drilling fluids. US Patent 7 618 924, assigned to Saudi Arabian Oil Company (Dhahran, SA), November 17 2009.

Ali, S.A., Sanclemente, L.W., Sketchler, B.C., Lafontaine-McLarty, J.M., 1993. Acid breakers enhance open-hole horizontal completions. Pet. Eng. Int. 65 (11), 20–23.

Battistel, E., Bianchi, D., Cobianco, S., Fornaroli, M., 2010. Process for the enzymatic removal of filter-cakes produced by water-based drilling and completion fluids. US Patent Application 20100069266, assigned to ENI S.P.A., Rome IT, March 18 2010.

Beall, B.B., Brannon, H.D., Tjon-Joe-Pin, R.M., O'Driscoll, K., 1997. Evaluation of a new technique for removing horizontal wellbore damage attributable to drill-in filter cake. In: Proceedings Volume, 4th Annu. India Oil & Nat. Gas Corp India Oil & Gas Rev Symp. (Mumbai, India, 8/18–19/97), pp. 53–65.

Bulanov, N.I., Monastyrev, V.A., Balakin, V.V., Pavlenko, A.N., Voropanov, V.E., 1992. Well bottom zone treatment with improved efficiency – includes injection of reagent breaking up clay crust for removal by flush solution stream. SU Patent 1 761 944, assigned to Oil Gas Res. Inst., September 15 1992.

Chan, A.F., 2009. Method and composition for removing filter cake from a horizontal wellbore using a stable acid foam. US Patent 7 514 391, assigned to Conocophillips Company (Houston, TX), April 7 2009.

Dobson Jr., J.W., Kayga, P.D., 1995. Magnesium peroxide breaker system improves filter cake removal. Pet. Eng. Int. 68 (10), 49–50.

Dobson, J.W., Mondshine, T.C., 1995. Well drilling and servicing fluids which deposit an easily removable filter cake. EP Patent 672 740, assigned to Texas United Chem. Co. Llc., September 20 1995.

Fanun, M. (Ed.), 2008. Microemulsions: Properties and Applications, Vol. 144 of Surfactant Science Series. CRC Press, Boca Raton, FL.

Harrison, J., 2004. Microemulsion technology for surfactants, Speciality Chemicals Mag. 24 (10), 32–36 [electronic:] http://surfaceactive.squarespace.com/storage/2006prsas_stl_specialitychemicals_magazine_nov2004.pdf.

Javora, P.H., Beall, B.B., Vorderburggen, M.A., Qu, Q., Berry, S.L., 2009. Method of using water-inoil emulsion to remove oil base or synthetic oil base filter cake. US Patent 7 481 273, assigned to BJ Services Company (Houston, TX), January 27 2009.

Johnson, M.H., 1994. Completion fluid-loss control using particulates. In: Proceedings Volume, SPE Formation Damage Contr. Int. Symp. (Lafayette, LA, 2/9–10/94), pp. 319–320.

Jones, T.A., Clark, D.E., Quintero, L., 2010. Microemulsions to convert OBM filter cakes to wbm filter cakes having filtration control. US Patent 7 709 421, assigned to Baker Hughes Incorporated (Houston, TX), May 4 2010.

Keller, S.R., 1986. Flow method and apparatus for well cementing. GB Patent 2 172 629, assigned to Exxon Production Research Co., September 24 1986.

Keller, S.R., 1987. Oscillatory flow method for improved well cementing. CA Patent 1 225 018, assigned to Exxon Production Research Co., August 04 1987.

Kristiansen, K., 1994. Composition for use in well drilling and maintenance. WO Patent 9 409 253, assigned to Gait Products Ltd. and Kristiansen, Kastholm, April 28 1994.

Lee, L.-J., 2006. Acid-coated sand for gravel pack and filter cake clean-up. US Patent 7 132 389, assigned to M-I LLC (Houston, TX), November 7 2006.

Moajil, A.M.A., Nasr-El-Din, H.A., Al-Yami, A.S., Al-Aamri, A.D., Al-Agil, A.K., 2008. Removal of filter cake formed by manganese tetraoxide-based drilling fluids. In: SPE International Symposium and Exhibition on Formation Damage Control, Society of Petroleum Engineers, Lafayette, Louisiana.

Mondshine, T.C., Benta, G.R., 1993. Process and composition to enhance removal of polymercontaining filter cakes from wellbores. US Patent 5 238 065, assigned to Texas United Chemical Corp., August 24 1993.

Moore, W.R., Beall, B.B., Ali, S.A., 1996. Formation damage removal through the application of enzyme breaker technology. In: Proceedings Volume, SPE Formation Damage Contr. Int. Symp. (Lafayette, LA, 2/14–15/96), pp. 135–141.

Munoz Jr., T., 2009. In-situ filter cake degradation compositions and methods of use in subterranean formations. US Patent 7 553 800, assigned to Halliburton Energy Services, Inc. (Duncan, OK), June 30 2009.

Munoz Jr., T., 2010. Methods of degrading filter cakes in subterranean formations. US Patent 7 648 946, assigned to Halliburton Energy Services, Inc. (Duncan, OK), January 19 2010.

Munoz Jr., T., Eoff, L.S., 2010. Treatment fluids and methods of forming degradable filter cakes comprising aliphatic polyester and their use in subterranean formations. US Patent 7 674 753, assigned to Halliburton Energy Services, Inc. (Duncan, OK), March 9 2010.

Nasr-El-Din, H.A., Lynn, J.D., Taylor, K.C., 2001. Lab testing and field application of a large-scale acetic acid-based treatment in a newly developed carbonate reservoir. In: Proceedings Volume, SPE Oilfield Chem. Int. Symp. (Houston, TX, 2/13–16/2001).

Santanna, V., Curbelo, F., Castro Dantas, T., Dantas Neto, A., Albuquerque, H., Garnica, A., 2009. Microemulsion flooding for enhanced oil recovery. J. Pet. Sci. Eng. 66 (3–4), 117–120.

Schriener, K., Munoz Jr., T., 2009. Methods of degrading filter cakes in a subterranean formation. US Patent 7 497 278, assigned to Halliburton Energy Services, Inc. (Duncan, OK), March 3 2009.

Tjon-joe Pin, R.M., Brannon, H.D., Rickards, A.R., 1994. Method of dissolving organic filter cake obtained in drilling and completion of oil and gas wells. WO Patent 9 401 654, assigned to BJ Services Co., January 20 1994.

Todd, B.L., 2009a. Filter cake degradation compositions and methods of use in subterranean operations. US Patent 7 598 208, assigned to Halliburton Energy Services, Inc. (Duncan, OK), October 6 2009.

Todd, B.L., 2009b. Methods and fluid compositions for depositing and removing filter cake in a well bore. US Patent 7 632 786, assigned to Halliburton Energy Services, Inc. (Duncan, OK), December 15 2009.

Todd, B.L., Powell, R.J., 2006. Compositions and methods for degrading filter cake. US Patent 7 080 688, assigned to Halliburton Energy Services, Inc. (Duncan, OK), July 25 2006.

Todd, B.L., Reddy, B.R., Fisk Jr., J.V., Kercheville, J.D., 2002. Well drilling and servicing fluids and methods of removing filter cake deposited thereby. US Patent 6 422 314, assigned to Halliburton Energy Serv. Inc., July 23 2002.

Weaver, J., Ravi, K.M., Eoff, L.S., Gdanski, R., Wilson, J.M., 1996. Drilling fluid and filter cake removal methods and compositions. US Patent 5 501 276, assigned to Halliburton Co., March 26 1996.

Willberg, D., Dismuke, K., 2009. Self-destructing filter cake. US Patent 7 482 311, assigned to Schlumberger Technology Corporation (Sugar Land, TX), January 27 2009.

Winsor, P.A., 1948. Hydrotropy, solubilisation and related emulsification processes. Trans. Faraday Soc. 44, 451–471.

Zanten, R.V., Ezzat, D., 2010. Surfactant nanotechnology offers new method for removing oil-based mud residue to achieve fast, effective wellbore cleaning and remediation. In: SPE International Symposium and Exhibiton on Formation Damage Control, Society of Petroleum Engineers, Lafayette, Louisiana.

Chapter 10

Cement Additives

The state of the art in cementing technology (Hervot et al., 1993; Lyons, 1996; Nelson, 1990) and recent developments have been sketched out in the literature (Crook and Calvert, 2000; Sweatman, 2011), and discussions of the details of special cement formulations can be found in several monographs (Edmeades and Hewlett, 2003; Odler, 2000).

The movement of gas from the subterranean zone through the cement slurry, during and after primary cementing is addressed, as gas migration, which can cause severe problems; for example, high volume loss of gas from a high pressure zone to a low pressure zone and the failure of the cement to seal the annulus.

Gas migration is caused by the behavior of the cement slurry during the transition phase, in which the cement slurry changes from being a true hydraulic fluid to a highly viscous mass with some solid characteristics. When first placed in the annulus, the cement slurry acts as a true liquid and thus transmits hydrostatic pressure, but it may lose this ability during the transition phase. The reasons for this may be (Dao et al., 2005):

- Loss of fluid from the slurry to the subterranean zone; and
- Development of static gel strength, i.e., stiffness, in the slurry.

When pressure is exerted on the formation by the cement, the slurry falls below the pressure of the gas in the formation, and the gas initially migrates through the cement slurry forming flow channels in the cement slurry, which allow further migration of the gas, even after the slurry has set.

Various techniques have been developed for eliminating undesirable gas migration, such as consecutive placements of the slurry or the application of special fluid loss agents. These techniques cause the passages in the cement to be plugged.

Alternatively, gelling agents can be added to the cement composition. These materials migrate from the cement composition into the surrounding subterranean zone, forming a barrier of a crosslinked gel. This gel inhibits gas migration into the cement.

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CEMENTING TECHNOLOGIES

There are two basic kinds of activities in cementing, namely, primary and secondary cementing. Primary cementing fixes the steel casing to the surrounding formation, and secondary cementing is for filling formations, sealing, water shutoff, etc.

Primary Cementing

The main purposes of primary cementing are:

- Supporting vertical and radial loads to the casing,
- Isolating porous formations,
- Sealing subsurface fluid streams, and
- Protecting the casing from corrosion.

Secondary Cementing

Secondary cementing refers to cementing operations that are intended to use cement in maintaining or improving the operation of the well. Two general cementing operations belong to this class, namely squeeze cementing and plug cementing.

Squeeze Cementing

Squeeze cementing is used for the following purposes:

- Repairing a faulty primary cementing operation,
- Stopping intolerable loss of circulation fluid during drilling operations,
- Sealing abandoned or depleted formations,
- Repairing leaks of the casing, and
- Isolating a production zone by sealing adjacent unproductive zones.

The slurry used in these operations should be designed to allow the fluid loss of the formation to be squeezed into the respective formation. Low-permeability formations can have a formulation of the slurry with an American Petroleum Institute (API) fluid loss (API RP 13B-1, 1997) of 200–400 $\mathrm{ml\,h^{-1}}$, whereas high-permeability formations require a slurry with 100–200 $\mathrm{ml\,h^{-1}}$ water loss. A high-pressure squeeze operation with a short duration requires an accelerator.

Thick slurries will not fill a narrow channel well, so squeeze cement slurries should be rather thin. Dispersants should be added for this reason. High compressive strength is not necessary for these types of slurries.

Plug Cementing

Plug cementing is used for plugging abandoned wells for environmental reasons. A kick-off plug is used to plug off a section of the borehole. The plug uses a hard surface to assist the kick-off procedure. Plug cementing is also used in drilling operations if extensive circulation loss is encountered. The plug is set in the region of the thief zone and pierced again with the bit.

It is often necessary to shut off water flows in open-hole completion operations and in production. Additional cementation methods are used to provide an anchor for testing tools or for other maintenance operations.

BASIC COMPOSITION OF PORTLAND CEMENT

Cement is made from calcareous and argillaceous rock obtained from quarries. Thus from the chemical viewpoint, the main components are carbonates and silicates. The raw materials used for cement are given in Tables 10.1 and 10.2.

Manufacturing

Grinding and Mixing

There are two processes for manufacturing cements: the dry process and the wet process. The dry process is cheaper than the wet process, but in practice more

TABLE 10.1 Raw Calcareous Materials

Material	Remarks
Limestone	$CaCO_3$, sedimentary rock formed by the accumulation of shells or corals
Cement rock	Sedimentary rock with composition similar to industrial cement
Chalk	Soft limestone
Marl	Loose deposit consisting mainly of $CaCO_3$
Alkali waste	Obtained from chemical plants

TABLE 10.2 Raw Argillaceous Materials

Material	Remarks
Clay	Hydrous aluminum silicates
Shale	Consists of clay, mud, and silt, mainly aluminum silicates
Slate	Dense fine-grained rock containing mainly clay
Ash	Contains silicates; secondary product

difficult to control. Limestone and clay materials are crushed, either dry or in water slurry, and stored in separate containers. The composition is analyzed and the contents are blended according to the result of the analysis to achieve the desired properties. Blends obtained from the wet process must be dried to some extent. The blend is ground to a mesh size of 100–200 (i.e., 0.15–0.07 mm) (ASTM C184-94E1, 2001; ASTM C786-96, 2001; ASTM E11-01, 2001).

Burning

The blends are heated in a long rotary kiln. In the first stage of heating, free water evaporates at temperatures exceeding 900°C. Calcium carbonate caustifies to calcium oxide (CaO), which starts reacting with aluminum silicates and the materials liquify. Heating continues to a final temperature of 1500°C. When the material is cooled it forms irregular-shaped solids called *clinkers*. Small amounts of gypsum (1–3%) are added to these clinkers to prevents flash setting and control the basicity, which is due to CaO.

A commercial product is actually a blend of different cements to produce a more constant quality. A typical chemical composition of Portland cement is given in Table 10.3.

Active Components in Cements

There are four active chemical compounds in cement formulations, given in Table 10.4.

Chemistry of Setting

The setting reactions involve tricalcium silicate ($3\,CaO \times SiO_2$) and dicalcium silicate ($2\,CaO \times SiO_2$), which react with water molecules to form calcium

TABLE 10.3 Chemical Composition of Portland Cement (Falbe and Regitz, 1995)

Compound	%
CaO	60–69
SiO_2	18–24
$Al_2O_3 + TiO_2$	4–8
Fe_2O_3	1–8
MgO	<5
K_2O, Na_2O	<2
SO_3	<3

TABLE 10.4 Active Components in Cement Formulations

Component	Formula	Remarks
Tricalcium aluminate	$3\,CaO \times Al_2O_3$	Hydrates quickly, responsible for strength of cement in early stage; setting time can be controlled by addition of gypsum
Tricalcium silicate	$3\,CaO \times SiO_2$	Responsible for strength in all stages
Dicalcium silicate	$2\,CaO \times SiO_2$	Responsible for final strength
Tetracalcium aluminoferrite	$4\,CaO \times Al_2O_3 \times Fe_2O_3$	Little effect on physical properties

silicate hydrate ($3\,CaO \times 2\,SiO_2 \times 3\,H_2O$) and calcium hydroxide ($CaO \times H_2O = Ca(OH)_2$).

$$2(3CaO \times SiO_2) + 6(H_2O) \rightarrow 3\,CaO \times 2SiO_2 \times 3\,H_2O + 3\,CaO \times H_2O \quad (10.1)$$

$$2(2CaO \times SiO_2) + 4(H_2O) \rightarrow 13\,CaO \times 2SiO_2 \times 3\,H_2O + CaO \times H_2O \quad (10.2)$$

The stoichiometric amounts of water required for setting can be calculated from these equations. The hydration reactions are exothermic. Then the hydration rests. The inhibition period can last several hours. This behavior is important, because otherwise the proper placement of the cement would not be possible. After the inhibition period, hydration restarts and the cement starts to develop strength. The water uptake results in an amorphous gel with a variable stoichiometry. During setting, the volume changes because of molecular contraction, shrinkage, swelling, and so on.

Standardization of Cements

The API recognizes nine classes of well cements (API RP 13B-1, 1995). The classification is similar to ASTM C 150, Type I (ASTM C150-00, 2001). These classes are summarized in Table 10.5.

Mixing with Additives

The cement usually is mixed in the dry state with a wide variety of additives, depending on the application of the cement. These include accelerators, retarders, dispersants, extenders, weighting agents, gels, foamers, and fluid loss additives.

TABLE 10.5 Classes of Cements and Properties

Class	Depth [m]	Properties
A Portland	0–2000	General purpose
B Portland	0–2000	Sulfate resistant
C High early	0–2000	High early strength
D Retarded	2000–3000	General purpose or sulfate resistant
E Retarded	3000–4000	High temperature, high pressure; moderately or highly sulfate resistant
F Retarded	3000–5000	Extremely high temperature and high pressure; moderately or highly sulfate resistant
G Basic	0–2500	Covering a wide range of depth, temperatures and pressures; no additives besides $CaSO_4$; can be used with accelerators or retarders
H Basic	0–2500	Basic well cement; no additives besides $CaSO_4$; can be used with accelerators or retarders
J	3500–5000	Extremely high temperature and high pressure; no additives besides $CaSO_4$; can be used with accelerators or retarders

Important Properties of Cement Slurries and Set Cement

In cementing operations and applications, several properties are needed for proper use, which are given in brief in the following sections.

Specific Weight

Specific weight is one of the most important properties of a cement slurry. The specific weight of a certain dry cement regulates the minimum or maximum amount of water that can be added. The minimum amount of water, from the aspect of density, is greater than the stoichiometric quantity necessary for proper setting. If more than the maximum amount of water is used, pockets of free water will be formed in the set cement column. Typical amounts of water range from 38–46% in the final mixture.

Thickening Time

The thickening time covers the time over which the cement can be manipulated after mixing with water. It is similar to pot lifetime in thermoset resins. Viscosity increases with time after this point, because of the setting reaction. When the viscosity becomes too great, the slurry is no longer pumpable. It is therefore necessary to place the cement within a certain time after mixing, otherwise, serious

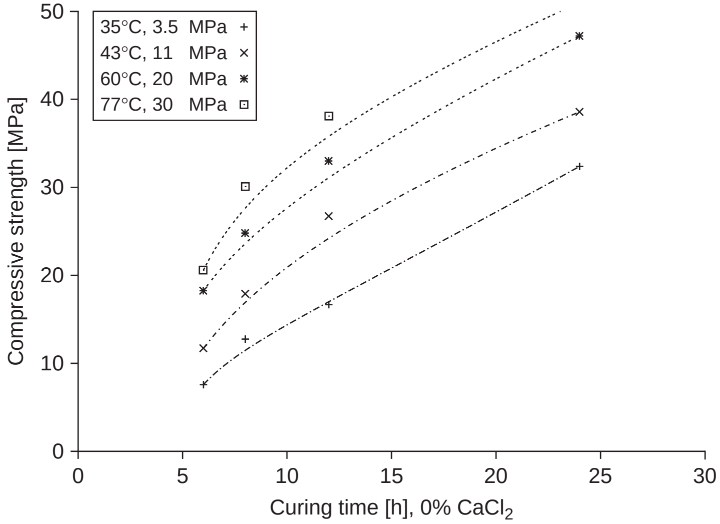


FIGURE 10.1 Influence of temperature and pressure on the comprehensive strength of an API Class H cement (Smith, 1976).

damage to the well could occur. An accurate knowledge of the time needed for the operation is necessary, taking the following factors into consideration:

- Mixing time,
- Displacing time (to bring down),
- Plug release time, and
- Safety time.

In general, the thickening time decreases with increasing temperature, hence it is important that the temperature conditions in the well are known.

Strength of the Set Cement

The strength of a cement usually refers to its compressive strength. The development of strength in the course of setting is shown in Figure 10.1. In general, the rate of setting increases with increasing temperature and pressure.

SPECIAL CEMENT TYPES

Resin Cement

Resin or polymer cements have been reviewed by (Chandra et al., 1996). They are materials made by replacing the cement at least partly with polymers. Cements can be modified by latex, dispersions, polymer powders, water-soluble polymers, liquid resins, and monomers. When the polymer is used in

TABLE 10.6 Properties of Polymer Cement in Comparison with Conventional Cement

Property	Change	Remarks
Abrasion resistance	++	
Impact resistance	+	
Tensile strength	+	
Flexural strength	+	Depends on curing methods
Compressive strength	0	
Gas migration	–	Porous structures remain, but a change in interfacial tension (IFT) occurs
Chemical resistance	+	
Acid, alkali, salt	++	Pure epoxide, furan, and acrylic cements
Organics, alkali	–	Pure polyester
Pore volume	–	
Freeze-thaw resistance	+	Pure polymer cements absorb essentially no water (ASTM C666-97, 2001)

+) Better
–) Worse
0) No change in comparison with conventional cement

small amounts, it modifies only the pore structure and does not behave like a binder.

The addition of polymer changes the properties of the set cement. The water-to-cement ratio is reduced as the polymer-to-cement ratio increases. This influences the mechanical properties, as indicated in Table 10.6.

Oil-based Cement

To prepare an oil-based cement, the cement is suspended in hydrocarbons instead of water. In this organic environment, no setting takes place and the cement particles remain fine, so they may penetrate into small pores. Setting starts when the cement particles come in contact with water, which takes place in the formation. Oil-based cements are mainly used as plugging and squeeze cements.

Cements with small particle size have found a number of uses in production and injection well casing repair jobs (Dahl et al., 1991). They are particularly useful for water shutoff jobs, because the hydrocarbon slurry sets only in the presence of water, so the oil producing sections of a reservoir remain relatively damage-free after water shutoff. Selective water shutoff with oil-based cement also has been used with polymers crosslinked by metal crosslinkers (Dalrymple et al., 1992; Maughmer and Dalrymple, 1992).

High-temperature Cement

High-temperature cement formulations are basically polymer concrete, consisting mainly of unsaturated polyesters or vinylester resins with allylphthalate as vinyl monomer (Justnes and Dahl-Jorgensen, 1994). Curing is achieved with peroxides, which decompose sufficiently fast at temperatures between 120°C and 200°C. Polymer concrete requires additional materials to compensate for the shrinkage.

Highly filled polymer composites, such as polymer concrete, suffer from setting stresses that are generated during the cure of the resin binder, when the polymerization shrinkage is hindered by the close packing of a filler and by aggregate particles. These stresses significantly decrease the strength of the cured composite.

Producing zero-shrinkage with strength enhancement can be achieved by dispersing small amounts of hydrated montmorillonite into the resin. Montmorillonite was found to be effective with three different resin binders: polyesters, epoxies, and acrylics. A mineral-resin interaction mechanism has been suggested (Haque, 1986). The organic molecules replace some of the ordered hydration water that is released by the mineral at the temperatures generated by the exothermic polymerization reaction. A binder used for plugging hot drill holes contains mainly phosphoric slag, trisodium phosphate, and NaOH (Bashev and Kadantseva, 1992).

Silica Flour and Silica Fume

Silica powder has been studied as a stabilizer for oil well cement at high temperatures (Zhang and Chen, 1993). Tests indicate that it can improve the stability and pressure resistance strength of cement. The manufacture of high-strength concrete (after 28 days the compressive strength is greater than 80 MPa) often involves the addition of ultra-fine particles together with large proportions of organic admixtures (De Larrard, 1989). Silica fumes were found to be the most effective additive.

Substitution of silica flour with varying proportions of silica fume affects the strength and the permeability of hardened cements (Grabowski and Gillott, 1989). The positive effect on the strength regression at increased temperatures is due to a greater rate of carbonation of the set cement (Milestone et al., 1986).

At 150°C carbonation is not controlled by permeability, but rather by the calcium hydroxide content. The optimal levels of silica addition for geothermal fluids, which contain high levels of CO_2, is ca. 15–20%. The coefficient of permeability was found to decrease with an increase in the degree of hydration. The use of silica fume was found to decrease the permeability only slightly (Banthia and Mindess, 1989).

Low-temperature Cement

A particular challenge in cementing is the development of compressive strength in a cement slurry within a reasonable time period at low temperatures. Cement blends, such as Portland or ultra-fine cement blends, have been used together with accelerators in order to obtain rapid setting of the cement and the development of sufficient compressive strength (Santra and Fitzgerald, 2009). Special formulations have been developed for cementing operations in arctic regions or for deep water applications (Boncan, 2001; Brothers, 1995; Griffith et al., 1996; Lartseva and Gordienko, 1992; Vasilchenko and Luginina, 1992).

At low temperatures, i.e., less than 25°C, an excessive amount of accelerator is needed to achieve the desired behavior of setting, which may result in cement compositions that rapidly form viscous gels with a premature loss of pumpability.

Alternative formulations have been developed that do not suffer from these drawbacks. These compositions are based on magnesium oxide (Santra and Fitzgerald, 2009). Light-burned or caustic magnesia is produced by calcining at temperatures ranging from 700–1000°C. Light-burned magnesia is characterized by a high surface area, a low crystallinity, and a high degree of reactivity in comparison to other grades of burned MgO.

The thickening time may be adjusted by the addition of an inhibitor, such as sodium hexametaphosphate, so that the composition remains pumpable during downhole placement.

In low temperature formations, where the cement is subjected to freeze–thaw cycling, freezing point depressants must be added. Salts may serve as such, but traditional organic freezing point depressants, such as ethylene glycol, may also be added (Kunzi et al., 1993, 1994, 1995).

In the case of epoxide cements at temperatures lower than 20°C, the viscosity increases so much that pumping becomes difficult (Chan and Griffin, 1996). Small amounts of aromatic solvents reduce the viscosity satisfactorily. Ethylene glycol butyl ether also changes the IFT so that the polymer may penetrate into hairline cracks and fine capillaries. This is advantageous in preventing liquid or gas migration.

High-alumina Cement

High-alumina cement is a rapid-hardening cement made from bauxite and limestone. It is comparatively resistant to chemical attack. Milling retards the setting of aluminous cement (Scian et al., 1991). On the other hand, setting accelerators such as lithium carbonate compensate for milling. Compositions of high-alumina cement containing quartz or glass, calcium carbonate, microsilica, carbon black, iron oxide red mud or screened fly ash, and styrene-butadiene latex have been described (Baret et al., 1997; Villar et al., 1997, 2000).

Magnesian Cement

Innovations in cementing technology have made it possible to place a cement slurry across a given area, establish the desired seal, and subsequently remove the blockage by completely dissolving the cement using common oil field acids (Coats et al., 1996). This type of cement is referred to as magnesian cement or magnesium oxychloride cement.

Magnesian cement is completely soluble in hydrochloric acid. Retarded acid-soluble well cements contain magnesium oxide, magnesium chloride, additional borate, and sucrose as a set retarder. Low density compositions are foamed with appropriate amounts of gas (King and Totten, 1993; Totten et al., 1994).

Fiber Cement

Fiber-containing cement was initially developed as a high-strength material that could be used to line a borehole (Van Vliet et al., 1995). Several relatively simple and cheap spin-off applications have been identified, such as its use in cement plugs for borehole stabilization and as a lost circulation material. Several companies are already applying or offering fiber cement for these purposes in the field, in both organic fibers and metal fibers (Cheyrezy et al., 1999; Le Roy-Delage et al., 1999; Stewart et al., 1996, 1997).

The benefits of carbon fiber technology have been demonstrated in the building industry, but have not been investigated for improving set cements in gas and oil wells. A great potential exists for a technological breakthrough in difficult cementing operations. A fourfold increase in toughness and a 50% increase in compressive strength can be obtained through the addition of carbon fiber. Carbon fibers are, however, very expensive, so their benefits may be jeopardized by the high price.

Carbon fiber oxidized by a hot NaOH solution appears to have a potential for use as reinforcement in high-temperature cementitious material systems (Pittman et al., 1996; Sugama et al., 1988). It has been found that active carboxylic acid and sodium carboxylate functional groups introduced on the fiber surfaces by extensive oxidation react preferentially with Ca^{2+} ions released from cement in a hydrothermal environment at 300°C. This interfacial interaction leads to a linkage between the fiber and the cement matrix, thereby enhancing the bond strength.

Fibers may also have disadvantages. An increase in the number of fibers in the cement leads to an increase in its porosity and permeability, resulting in a decrease in compressive strength. During the acid treatment of the formation, the fibers in the cement can be easily dislodged and extracted from cracks as smooth flakes, leaving pore spaces (Trabelsi and Al-Samarraie, 1999).

Acid Gas Resistant Cement

High rate acid gas injection wells pose a significant challenge for the design of cementing systems. The resistance of Portland cement to carbon dioxide is a significant problem. A CO_2-resistant Portland system has been developed by limiting the cement concentration and reducing the total system permeability by use of specialty sized particles (Benge, 2005).

Permeable Cement

For the majority of oil well applications it is desirable for the cement to have a very low permeability, but there are some applications in which permeable cements are considered as useful. Typically, such applications are those in which only mechanical support to the formation or the casing is needed, i.e., for poorly consolidated producing zones that require stabilization (Danican et al., 2010). Such permeable cement compositions contain a hollow particulate material, such as microspheres, which allow the formation of a permeable structure. High contents of foam that can make the slurry difficult to place are avoided.

Microspheres are typically formed from aluminosilicate or other glass-like materials. They break down in the cement during setting due to chemical reactions and thermal instability, which imparts porosity to the material (Danican et al., 2010). A typical material has hollow spheres of average sizes around 50–350 μ.

Salt-water Stable Latex Cement

Cement slurries containing a latex emulsion may coagulate when contacted with a salt solution, so forming a gelled mixture that is no longer useful as a cement sealant. However, special formulations of cement slurries have been developed that are stable to salt water.

In these formulations the latex must be premixed with a stabilizer until a homogenous solution is formed, after which it can be safely contacted with salt water. Suitable latex stabilizers are ethoxylated nonyl phenol and oligo ethoxylated iso-dodecyl alcohol ether sulfate (Lewis et al., 2009b), which are actually surfactants.

Settable Drilling Fluids

Aqueous-based drilling fluids can be converted into settable drilling fluids by the addition of cement kiln dust (Roddy et al., 2008).

Basically, a settable drilling fluid should be formulated so that it is compatible with the drilling fluid that remains in the wellbore. The use of a such a fluid may alleviate the problems associated with the disposal of used drilling fluid. Several examples of formulation of such types of drilling fluids have been presented (Roddy et al., 2008).

CLASSIFICATION OF CEMENT ADDITIVES

Cement additives have been classified into six categories (Bourgoyne, 1986). In fact, this classification is crude. The World Oil Cementing Supplements regularly review commercially available cementing additives in certain *World Oil* issues (Anonymous, 1995, 1997, 1998, 1999). In these publications comprehensive listings of cementing products and additives available from major suppliers can be found, grouped into functional categories as shown in Table 10.7.

Commercially available products can also be readily found on the World Wide Web. Individual compounds may emerge in more than one of the categories listed in Table 10.7, for example, rubber particles reduce the density of the slurry and are also suitable as lost circulation additives.

Fluid loss refers to the filtration of certain components of the fluid into the formation. Lost circulation is the total material lost into high-permeability

TABLE 10.7 Classification of Cement Additives

Additives for Cementing
Basic cements
Accelerators and salts
Extenders and density-reducing additives
Silica to reduce or prevent high-temperature strength retrogression
Dispersants
Bond improving and expanding agents
Retarders
Fluid loss additives
Antigas migration agents
Antifoam and defoaming agents
Additives and mixtures to reduce or prevent lost circulation
Density-increasing or weighting agents
Free water control and solid suspending agents
Spacers and chemical washes or preflushes
Specialty cement blends

thief zones. Table 10.8 gives a summary of additives to control special problems (Lyons, 1996).

Light-weight Cement

Adding low-density materials reduces the density of a cement composition. These additives are referred to as *extenders*, because they reduce the density of the cement itself, at the cost of other desirable properties, such as set strength. Generally they are not chemically inert, but may be reactive. Light-weight additives are summarized in Table 10.9.

Bentonite

Bentonite is used in secondary cementing operations (Sirenko et al., 1995), since it can reduce the specific weight of the slurry if used at high percentages. It is dry blended to the cement in levels of up to 25%. The addition of bentonite requires more water.

This additive also increases the viscosity of the slurry, and in high amounts it is known to increase the permeability and reduce the final strength of the cement. Therefore high concentrations of bentonite are not recommended.

Furnace Slag

A furnace slag cement slurry can have a density of 1500–1600 $\text{kg}\,\text{m}^{-3}$. A combination of silica flour and furnace slag may be used to achieve service temperatures exceeding 200°C (Ganguli et al., 1997). A gas may be suitable as a foaming agent (Chatterji et al., 1996).

TABLE 10.8 Summary of Additives to Control Special Problems

Purpose	Action or Agents
Gel strength additives	Preparation of spacers
Permeability control	Silica flour, gas bubble–producing additives
Corrosion control	Various nitrogen compounds, polyoxylated amines, amides, and imidazolines
Radioactive traces	Helpful in finding the region of actual placement of the cement
Bactericides	Paraformaldehyde, sodium chromate
Strength increasers	Nylon, metal fibers
Defoamers	Controlled inclusion of air during mixing
Encapsulation	Controlled release of various additives (Reddy et al., 2001)

TABLE 10.9 Light-weight Cement Additives

Compound Class	Remarks	References
Bentonite	Increases viscosity	
Furnace slag cement	High service temperatures	Lu et al. (1997)
Porous glass particles		Jamth (1998), Zhang and Wang (1989)
Gilsonite	Soluble in organic solvents	
Pozzolan	Inexpensive	Heathman and Crook (1994a, 1994b)
Silica fume	Substitute for natural pozzolan	Müller and Dillenbeck (1991), Squyres and Lopez (1990)
Rubber		Le Roy-Delage et al. (2000)
Polyacrylonitrile		Logvinenko et al. (1997)
Hydroxyethyl cellulose (HEC)	Free-fluid inhibitor	Stephens (2001), Stephens and Pereira (2001)
Expanded polystyrene (PS)		Boles and Boles (1998)
Perlite	Much additional water	Nahm et al. (1993)
Coal	No additional water	Ekshibarov and Khasanov (1992)
Diatomaceous earth	No increase of viscosity	
Hollow aluminosilicate microspheres		Kukacka and Sugama (1994, 1995)

Hollow Glass Microspheres

Glass beads with diameters of 2–200 μ and densities of 600–700 kg m^{-3} can be mixed with a cement slurry in certain proportions to form a low-density glass bead slurry.

Laboratory experiments show that the slurry is effective for improving cementing quality in low-pressure and low-permeability formations. Low-density cement with hollow microspheres is often not stable because of the comparatively low plastic viscosity (Ma, 1993), which must exceed 40 MPa to give adequate cement quality and eliminate fluid channeling.

When porous glass particles are used, they are filled with water. The cement slurry will absorb extra water from the pores of the porous particles, thus counteracting the shrinkage during setting (Jamth, 1998).

Ceramic Microspheres

Materials formed by acid-base reactions between calcium aluminate compounds and phosphate-containing solutions yield high-strength, low-permeability, CO_2 resistant cements when cured in hydrothermal environments. The addition of hollow aluminosilicate microspheres to the uncured matrix constituents yields slurries with densities as low as approximately 1200 kg m^{-3}, which cure to produce materials with properties meeting the criteria for well cementing. These formulations also exhibit low rates of carbonation. The cementing formulations are pumpable at temperatures up to 150°C.

Ceramic microspheres for cementing applications may replace blast furnace slag and Portland cement in any well cementing operation. They are a useful well cementing constituent that may be successfully implemented in differing temperature dependent processes, such as the steam injection technique employed for heavy crude oil extraction. They are manufactured by the following steps (Quercia et al., 2010):

- Grinding industrial slag,
- Feeding into a vibration feeder,
- Heating with a gas/oxygen mix flame to 1200–2500°C, and
- Spheroidizing by propelling away from the burner.

As the pyrolized particles are propelled away from burner, they begin to rapidly cool in air and are spheroidized. The microspheres settle at a distance from the burner that is dependent on their diameters. The composition of typical slags is summarized in Table 10.10.

Lightweight cement slurries can be formulated using ceramic microspheres that are resistant to elevated temperatures and thermal cycling, such as are used in steam injection techniques (Quercia et al., 2010).

Gilsonite

Gilsonite, a solid hydrocarbon, was introduced to the oil industry in 1957 as a cement additive (Slagle and Carter, 1959). Gilsonite (Uintaite) is an asphalt

TABLE 10.10 Typical Composition of Slags (Quercia et al., 2010)

Oxide	Blast Furnace [%]	Iron-nickel Reduction [%]	Iron-nickel Smelting [%]
CaO	19–42	50–60	0–1
SiO_2	32–40	14–60	40–50
Al_2O_3	11–30	10–15	2–5
MgO	8–19	7–10	30–40
Fe_2O_3	0–5	3–15	10–20
SO_3	1–5	1–10	0–1
K_2O	0–1	0–1	0–1
Na_2O	0–15	0–1	0–1
NiO	0	0–1	0–1
Others	1–2	0–1	0–4

with a density of 1,050–1,150 $kg\,m^{-3}$, a melting point of 140–160°C, and an ultimate composition of approximately 85% C, 10% H, 2.5% N, 1.5% O. It is soluble in organic solvents and occurs naturally in Utah and Colorado. More details are given in chapter 1.

The unique properties of Gilsonite, such as low specific gravity, particle-size distribution, impermeability, resistance to corrosive fluids, chemical inertness, and low water requirements result in slurries with exceptional bridging properties, low slurry weight, compatibility with other slurry additives, and relatively high compressive strength.

Pozzolan

Pozzolan is a very finely ground pumice or fly ash with a specific gravity that is only slightly less than cement, so only a slight reduction of the specific weight can be achieved. On the other hand, pozzolan is inexpensive, so it has been proposed in several formulations. Silica fume has been proposed as a substitute for natural pozzolan.

Silica fume is a pozzolanic material composed of extremely fine, amorphous spheres produced as a by-product in the manufacture of silicon metals. It has a high water demand and it is more reactive than natural pozzolan or fly ash, but it increases the compressive strength significantly.

Rubber

Addition of rubber particles at levels of 30–100% to cement with a grain size of approximately 40–60 mesh (0.4–0.25 mm) will produce a light-weight cement with a low permeability.

These compositions are advantageous for cementing zones that are subjected to extreme dynamic stresses, such as perforation zones and the junctions of branches in a multi-sidetrack well. Recycled, expanded PS lowers the density of a hydraulic cement formulation and is an environmentally friendly solution for downcycling waste materials.

Coal

Coal has been used as a very low gravity additive. Coal does not require a significant amount of additional water when added to the cement.

Diatomaceous Earth

Diatomaceous earth has a lower specific gravity than bentonite, but it will not increase the viscosity of the slurry. Diatomaceous earth concentrations of up to 40% have been used.

Perlite

Expanded perlite requires a large amount of water when added to the slurry. It is often used in a blend with volcanic glass fines, or with pozzolan, along with bentonite. Without additional bentonite, perlite tends to separate and float to the upper part of the slurry.

Foam Cement

Foam cement is a special class of light-weight cement. The gas content of foamed cement can be up to 75% by volume. When cement compositions need to be foamed, a foaming additive must be included (Reddy and Riley, 2004).

The cement can be foamed by direct injection of the additive air, or any suitable inert gas, such as nitrogen, or even a mixture of such gases can be used, but nitrogen is the most common.

Alternatively cement can be foamed by a gas generated that is by a reaction between the cement slurry and an foaming additive, present in the cement in particulate form. For example, hydrogen gas can be generated in situ as the product of a reaction between a high pH slurry and fine aluminum powder.

A typical foamed cement composition contains a hydraulic cement, an aqueous rubber latex in an amount of up to 45%, a latex stabilizer, a defoaming agent, a gas, a foaming agent, and a foam stabilizer (Chatterji et al., 1997a, 1998).

Foamed cement compositions may negatively impact aquatic life, and one or more of the components could be flammable, thereby increasing the cost of shipping (Chatterji et al., 2007).

Foamed high-temperature applications are based on calcium phosphate cement (Brothers et al., 1999). If a foaming additive in particulate form is used, aluminum powder, gypsum blends, and deadburned magnesium oxide are preferred. Preferred foaming additives comprising aluminum powder are commercially available under the tradenames GAS-CHEK® and SUPER CBL.

A blend containing gypsum is also commercially available under the tradename MICROBOND™, additives comprising deadburned magnesium oxide are available under the tradename MICROBOND™ M and MICROBOND™, all from Halliburton Energy Services (Reddy and Riley, 2004). The stability of the foam is achieved by the addition of surfactants, as shown in Table 10.12.

Density-increasing or Weighting Agents

Weighting agents (Table 10.11) are added to increase the density of the cement, typically to combat high bottom hole pressures. Common additives are powdered iron, ferromat, powdered magnetite, and barite. Hematite can be used to increase the density of a mixture up to 2200 $kg\,m^{-3}$ (19 lb/gal), but requires the addition of some water.

Ilmenite has a specific gravity of 4700 $kg\,m^{-3}$ and does not require the addition of water when added to the slurry. It has a minimal effect on the thick-

TABLE 10.11 Weighting Agents for Cement

Compound class	Remarks
Ilmenite	No additional water
Hematite	Some water
Barite	Still more water
Manganese compounds	

TABLE 10.12 Surfactants for Foam Cement

Surfactant	References
Alkyl sulfates and alkyl ether sulfates	Chatterji et al. (2007) and Savoly and Elko (1995)
Alkylpolyoxyalkylene sulfonates	Bour and Childs (1992)
Polyoxyethylene	Onan et al. (1997)
Cocoamidopropyl dimethylamine oxide	Chatterji et al. (2006)

ening time and compressive strength. Barite requires more water than hematite, resulting in a decrease in the compressive strength of the set cement.

Control of Thickening and Setting Time

Often it is necessary to influence the setting time, either by accelerators or by retarders. If a cement is to be placed into a shallow depth, then acceleration will be desirable to avoid unnecessary waiting times. On the other hand, in a deep formation more open time is required, which may require the addition of retarders.

Cement Retarders

Examples of retarders also referred to as *set retarders* are shown in Table 10.13. Cements with retarders to prevent rapid setting may be used in the high-temperature and high-pressure environments of deep wells. Lignosulfonate and certain carbohydrate derivatives, such as welan gum, xanthan gum, cellulose, and polyanionic cellulose are common retarders.

Carrageenan, a high molecular weight polysaccharide derived from seaweed, produces an exceptionally stable storable liquid that is superior to typical storable cement slurries. These gums are ionic, linear polysaccharides composed of repeating galactose units that may be sulfated or unsulfated. Carrageenan can be κ-carrageenan, ι-carrageenan, or λ-carrageenan.

ι-carrageenan is employed most commonly, but mixtures are also possible. The properties of the individual carrageenan types primarily depend on the number and position of sulfate groups on the repeating galactose units. In the presence of excess cations, κ-carrageenan and ι-carrageenan form gels (Rae et al., 2001). The structure of carrageenan is shown in Figure 10.2. Carrageenan is also used as a thickener in food applications, such as ice cream.

Cement Accelerators

Cement accelerators are shown in Table 10.13. The most common accelerators are calcium chloride and sodium chloride. Calcium chloride may be used in concentrations up to 4% in wells with bottom hole temperatures less than 50°C. Calcium chloride tends to increase the final strength under pressure conditions.

Sodium chloride can be used as an accelerator in formulations that are bentonite free. The maximal bottom hole temperature is 70°C. In concentrations above 5%, the effectiveness is reduced. Saturated sodium chloride solutions act as retarders.

Special grades of gypsum hemihydrate are blended with Portland cement to give reduced thickening and setting times. Gypsum requires significantly more water addition. The maximal application temperatures are 70–80°C. Sodium silicate is used for cement slurries with diatomaceous earth. It can be used up to 7%.

TABLE 10.13 Cement Retarders

Compound Class	References
Scleroglucan	Cartalos et al. (1994)
Copolymer of isobutene and maleic anhydride (MA)	Livsey and Shaunak (1987)
Amino-*N*-[alkylidene] phosphonic acid derivatives	Nelson (1987)
Alkanolamine-hydroxy carboxy acid salts (e.g., tartaric acid and ethanolamine)	Chatterji et al. (1997b) and Davis et al. (1998)
Phosphonocarboxylic acids	Davis et al. (1999a, 1999b)
Dicyclopentadiene bismethylamine methylenephosphonate	Crump and Wilson (1988)
Lignosulfonate derivatives	Detroit (1995) and Detroit and Sanford (1989)
Carbohydrates grafted with vinyl polymers	Eoff (1993)
Carboxymethyl hydroxyethyl cellulose	
Wellan gum[a]	Rakitsky and Richey (1992)
Borax based	Casabonne et al. (1994)
Carrageenan	Rae et al. (2001)
Polyethylene amine derivatives and amides	Rodrigues (1994, 1995), Rodrigues and Eoff (1994)
Copolymers from maleic acid, 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) and others[b]	Rodrigues (1995)
Ethylene diamine-tetramethylene phosphonic acid, polyoxyethylene phosphonic acid, or citric acid[c]	Michaux (1999)
Polyacrylic acid phosphinate[c]	Cowan et al. (1996)

a) *Coadditive for retarded formulations*
b) *When bentonite is used, calcium–sodium–lignosulfonate is the best retarder for such cement slurries*
c) *High-alumina cement*

The addition of sodium sulfate to Portland cement accelerates hardening and increases the mobility of the solution. Chloride-free accelerators have been developed. Trihydroxybenzoic acid is a weak accelerator that eliminates the dormant period in the curing process, as does 4,5-dihydroxy-*m*-benzenedisulfonate. The recommended amount of dry cement is 0.1–5.0%

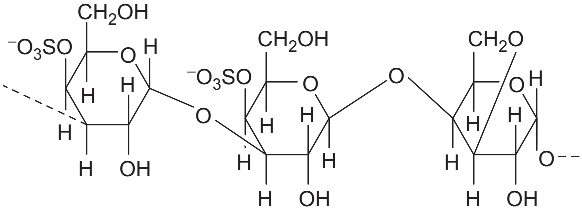


FIGURE 10.2 κ-Carrageenan.

TABLE 10.14 Cement Accelerators

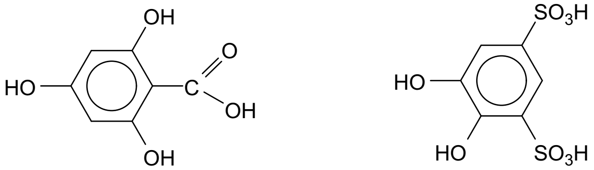
Compound	References
Propylene carbonate[a]	Liotta and Schwartz (2000)
Sodium and calcium chlorides[b]	Khlebnikov et al. (1997)
Aluminum oxide and aluminum sulfate	Akhrimenko et al. (1997)
Sodium sulfate	Tsytsymushkin et al. (1991c)
Calcium chloride	Cai et al. (1994)
2,4,6-Trihydroxybenzoic acid	Fry et al. (1992)
Disodium 4,5-dihydroxy-*m*-benzenedisulfonate[c]	Fry et al. (1992)
Formic acid esters	Bloys et al. (1991, 1992) and Carpenter and Wilson (1991)
Formamide	Bloys et al. (1991, 1992) and Carpenter and Wilson (1991)
Monoethanolamine	Carpenter and Wilson (1990)
Diethanol amine	Carpenter and Wilson (1990)
Triethanol amine	Carpenter and Wilson (1990)

a) Also has thixotropic properties
b) Waste of isopropylbenzene production by the alkylation method
c) Chloride-free set accelerator

(Fry et al., 1992). Some cement accelerators are listed in Table 10.14 and shown in Figure 10.3.

Zeolites

It is generally possible to accelerate or retard the setting time by using conventional cement additives, but special properties can be achieved by using zeolites.



2,4,6-Trihydroxybenzoic acid 4,5-Dihydroxy-*m*-benzenedisulfonic acid

FIGURE 10.3 Cement accelerators.

TABLE 10.15 Zeolites for Use in Oil Field Operations (Luke et al., 2008)

Name	Description
Analcime	Hydrated sodium aluminum silicate
Bikitaite	Lithium aluminum silicate
Brewsterite	Hydrated strontium barium calcium aluminum silicate
Chabazite	Hydrated calcium aluminum silicate
Clinoptilolite	Hydrated sodium aluminum silicate
Faujasite	Hydrated sodium potassium calcium magnesium aluminum silicate
Harmotome	Hydrated barium aluminum silicate
Heulandite	Hydrated sodium calcium aluminum silicate
Laumontite	Hydrated calcium aluminum silicate
Mesolite	Hydrated sodium calcium aluminum silicate
Natrolite	Hydrated sodium aluminum silicate
Paulingite	Hydrated potassium sodium calcium barium aluminum silicate
Phillipsite	Hydrated potassium sodium calcium aluminum silicate
Scolecite	Hydrated calcium aluminum silicate
Stellerite	Hydrated calcium aluminum silicate
Stilbite	Hydrated sodium calcium aluminum silicate

These pozzolanic materials may be activated with alkali or Portland cement in the presence of sufficient water.

Other properties of zeolite-containing compositions, such as compressive strength development, early strength, rheology, and density are of industrial interest (Fyten et al., 2007). Zeolites that have been claimed to be suitable for use in oil field operations are summarized in Table 10.15. Chabazite and clinoptilolite are particularly useful zeolites (Luke et al., 2008).

Intergrinding zeolite and cement clinker provides a bimodal distribution of particle size in the grind, and produces increased strength in the resultant material, in particular at longer set times. However, an increased compressive strength of the interground set material was not observed when hand-ground gypsum was added to the slurry of the interground clinker and zeolite material (Luke et al., 2008).

Viscosity Control

The viscosity of a cement affects its pumping properties. The viscosity must be kept low enough to ensure pumpability of the slurry during the entire operation period. In deep wells, because of the increased temperature, the viscosity decreases, which leads to an undesirable flow characteristics. This effect can be serious, because the viscosity follows the Arrhenius law.

Viscosifying additives are often used in well cement compositions to prevent the settling of solids in the cement compositions after they are placed in a subterranean zone. Viscosifying additives have been utilized successfully at subterranean temperatures of up to about 190°C, but at higher temperatures conventional viscosifying additives cannot prevent thermal thinning. This results in the settling of solids in cement compositions, which results in defective cementing and failure of the set cement to provide zonal isolation (Reddy and Riley, 2004).

Some of the additives used for viscosity control also may act as accelerators. Additives for viscosity control are shown in Table 10.16.

TABLE 10.16 Additives for Viscosity Control

Compound	References
Latex	Brothers (1992)
Scleroglucan[a]	Cartalos et al. (1994)
Calcium lignosulfonate[b]	
Phenol-formaldehyde resin modified with furfuryl alcohol[c]	Noik and Rivereau (1998)
Hectorite clay[d]	Carpenter et al. (1999)
Sulfonic acid copolymer, castor oil[e]	Bin Ibrahim et al. (2001a, 2001b)

a) High-temperature viscosifying additive
b) Also retarder
c) Polymer cement
d) Thixotropic cement
e) Multifunctional additive

Thermal Thinning

To combat the effect of thermal thinning, latex is added to a cement slurry without a latex stabilizing surfactant, resulting in a slurry that has low mixing viscosity and good solid-suspension properties at downhole temperatures. The latex emulsion inverts or breaks downhole, thereby providing the necessary viscosity and gel strength to compensate for thermal thinning and to keep the solids suspended in the cement slurry.

The inverted latex emulsion coagulates, forming rubber-like particles that increase the viscosity and gel strength of the cement slurry. No additional viscosifying agents are required to prevent the solids from settling.

Dispersants

The use of surface active agents in cements has two main goals; they act as retarding agents and dispersing agents. Dispersants improve the rheological properties, which facilitates blending at high densities without the need for excess water. They also enhance the flow behavior of the cement slurry and allow it to be pumped into a turbulent flow regime, thereby effecting a better bonding between the well casing and the rock formation.

Dispersants may, however, exhibit side effects: They enhance the action of fluid loss additives and the effectiveness of the retarder. Dispersants are widely used as oil field chemicals, in many other activities. The applications in the field of cementing technology are summarized in Table 10.17, and some ingredients are shown in Figure 10.4.

A number of dispersing agents have been utilized in cement compositions, particularly those used for primary and remedial cementing in oil and gas wells (Lewis and Szymanski, 2007). Organic acids, such as gluconic acid and citric acids are strong set-retarding agents, so their presence in a cement composition prevents it from setting for a relatively long period of time.

The set-retarding characteristics of lignosulfonates can be substantially eliminated by blocking the phenolic hydroxy group content. This can be achieved by reacting the lignosulfonate with, for example, propylene oxide.

Other commonly used dispersants include polynapthalene sulfonate, polyβ-naphthol sulfonate, and polymelamine sulfonate. While such dispersants function very well in cement compositions, they can be environmentally unacceptable, especially in offshore operations (Lewis and Szymanski, 2007).

Biodegradable dispersants that are based on starch have been described (Reddy and Eoff, 2007). These are basically sulfite adducts of an oxidized starch.

Expansion Additives

During setting, cement normally undergoes shrinkage, but this can be combated by adding expandable swelling additives into the matrix. Expanding cement is

TABLE 10.17 Dispersants

Dispersant	References
Polyoxyethylene sulfonate[a]	Childs and Burkhalter (1992), Heathman and Cromwell (1994)
Acetone formaldehyde cyanide resins	Cowan and Eoff (1993) and Eoff (1994)
Polyoxethylated octylphenol[b]	Gopalkrishnan (1993a,b), Gopalkirshnan and Roznowski (1993)
Copolymers of MA and 2-hydroxypropyl acrylate[c]	
Allyloxybenzene sulfonate or allyloxybenzene phosphonate[d]	Carpenter and Johnson (1997)
Ferrous lignosulfonate, ferrous sulfate, and tannic acid	Lindstrom and Riley (1994)
Alkali lignosulfonate[e]	Chatterji et al. (2000a, 2000b)
Acetone, formaldehyde polycondensate[f]	Onan et al. (1994a, 1994b)
Sulfonated napththalene formaldehyde condensate	Bray and Wood (1992), Crema and Kucera (1991), Crema et al. (1991b), Dilullo Arias et al. (1999), Miano et al. (1995)
2,4-Pentanedione-1,5-sodium disulfonate	Lewis and Szymanski (2007)
Melamine sulfonate polymer	Moran and Moran (1998)
Polyvinyl sulfonate	Moran and Moran (1998)
Styrene sulfonate polymer	Moran and Moran (1998)
Polyethyleneimine phosphonate	Crema et al. (1991a)
Casein with polysaccharides	Vijn (2001)
Dialdeyhde starch	Reddy and Eoff (2007)

a) For squeeze cementing
b) Non-ionic surfactant, 1–3 k Dalton
c) 1–20 k Dalton
d) As copolymer with various vinyl monomers
e) Blocked phenolic hydroxy group, biodegradable
f) For dispersing silica fume

used in water shutoff technology and plugging. Expansion additives should not be confused with the additives used for foam cement.

A series of test methods and procedures have been developed to measure these phenomena (API TR 10TR2, 1997). Cracks should be avoided because

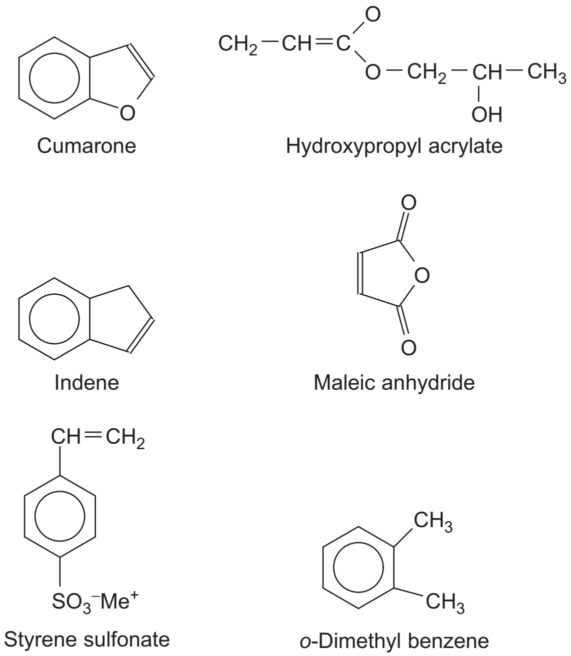


FIGURE 10.4 Components in dispersants.

these increase the permeability of the cement. The expansion of the cement, without the formation of macro-fissures, depends on the time at which the expanding additives (e.g., CaO or MgO) crystallize out (Danjuschewskij and Ghofrani, 1991; Ghofrani, 1997; Ghofrani et al., 1992).

Cement expansion should occur predominantly in the setting phase of plastic deformability of the cement matrix to fill in existing cavities. A certain, controlled amount of expansion should also occur in the higher strength phase of the matrix (Ghofrani and Plack, 1993). The expansion characteristics of CaO and MgO (Ghofrani and Werner, 1993) depend on the thermal history of burning, which can be optimized for specific requirements.

Deadburned magnesium oxide is suitable as an expanding additive (Cheung, 1998b, 1998a, 1999). The expansion occurs by a hydration mechanism. The additive is particularly effective when used at setting temperatures greater than approximately 150°C. Enhanced adhesion of expanded cements can be achieved by the addition of urea-formaldehyde resins (Taradymenko et al., 1993).

Set Strength Enhancement

Dialkanol aminoalkyl phenols as admixtures enhance the strength (Gartner and Kreh, 1993) of a cement if added in very small amounts, and they do not affect the initial properties of the fluid. They do not cause set acceleration or early set strength enhancement but provide enhanced compressive strength in later stages.

Addition of small amounts of potassium ferriocyanide and nitrilo trimethyl phosphonic acid promotes the formation of complex compounds and thus increases the strength of cement rock (Tsytsymushkin et al., 1991b).

Fibers

A mixture of a reactive aluminum silicate and a fibrous mineral, such as wollastonite (Mueller et al., 2001), improves the compressive strength, flexural strength, and tensile strength compared to conventional cement compositions. Wollastonite is typically available as very fine fibers or microfibers with diameters similar to those of cement particles (typically approximately 25–40 μ) and a fiber length typically between 0.4 and 0.6 mm.

Alternatively, the cement composition may include consolidating fibers, such as those of nylon or polypropylene. These reduce the potential for cement debris to be formed under high-stress conditions. Consolidating fibers are typically added to a cement composition in levels of between 0.25 and 5.0 pounds per sack.

Adhesion Improvement

A cement slurry additive consisting of methyl cellulose, a melamine-formaldehyde resin, and trioxane has been proposed for better bonding of cement to the casing string (Akhrimenko et al., 1992). Bisphenol-A epoxide resins, with amine-based curing agents, sand filler, and a mixture of *n*-butanol and dimethyl benzene as a diluent, have been proposed as additives to increase the adhesion properties of cement (Fan et al., 1996).

Quaternary ammonium salts (C_{10} to C_{18} alkyl benzyl dimethyl ammonium chloride) added at 40 ppm, and 2% of sodium chloride effect an increase in the strength of the cement rock, and in the adhesion properties, by 50–80% (Tsytsymushkin et al., 1991a).

Fluid Loss Control

Fluid loss control agents, also known as filtration control additives, are used in well cement compositions to reduce the fluid loss to permeable formations or zones into or through which the cement compositions are pumped. In primary cementing, the loss of fluid, i.e., water, to permeable subterranean formations can result in the premature gelation of the cement composition. Bridging of the annular space between the permeable formation or zone and the pipe string that is being cemented prevents the cement composition from being placed over the entire length of the annulus (Reddy and Riley, 2004).

Filtration control additives are added to cements for the same reason that they are used in drilling fluids. Untreated cement slurries, however, have much greater filtration rates than untreated drilling muds, so it is very important to limit the loss of water from a slurry into a permeable formation for several reasons:

- To minimize the hydration of water sensitive formations,
- To allow sufficient water to be available for cement hydration,
- To avoid a modification of the slurry properties, i.e., rheology, density, thickening time, and
- To avoid a bridging of the annular gap.

However, the mechanism of action of filtration control additives is not yet completely understood. Examples are bentonite, latex, and various organic polymers.

A mixture of a copolymer and a homopolymer has been suggested as a viscosifying and fluid loss controlling additive for well cement compositions. The copolymer is made from (Reddy and Riley, 2004):

1. Comonomers, which are calcium tolerant, of anionic nature, and disperse basic cement slurries;
2. Comonomers that may hydrolyze in basic cement slurries to generate anionic carboxylate groups that bind with calcium, viscosify the slurries, and prevent settling in the slurries; and
3. Comonomers, which generate non-ionic pendant groups on the polymer upon hydrolysis in basic cement slurries to prevent polymer precipitation.

Examples of the first type of comonomer are AMPS, vinylsulfonate, allyl sulfonate, 3-allyloxy-2-hydroxy-1-propanesulfonic acid, and their salts.

Examples of the second type of comonomer are selected from acrylonitrile, acrylamide (AAm), *tert*-butyl acrylate, *N*,*N*-dialkylacrylamide, *N*-vinylpyrrolidone, AMPS, and acrylic esters. Other fluid loss additives for cements are summarized in Table 10.18.

Water-soluble, AAm *tert*-butylsulfonic-acid-based copolymers are commonly used to provide fluid loss control for oil well cement slurries. Welan gum can negatively impact the effectiveness of these copolymers because it competes with the polymer for the adsorption sites on the surfaces of cement and silica (Plank et al., 2009a). Their impact generally depends on their anionic charge density, the quality of their anchor group to the cement or silica surface, and their concentration.

Water-soluble azo compounds serve as radical initiators for polymerization, e.g., 2,2′-azobis(*N*,*N*′-dimethylene isobutyramidine)dihydrochloride, 2,2′-azobis(2-amidinopropane)dihydrochloride, and 2,2′-azobis[2-methyl-*N*-(2-hydroxyethyl)propionamide]. Azo initiators decompose thermally into radicals, thus initiating polymerization in situ. The azo initiator is combined with the aqueous solution containing the monomer (Dao et al., 2005).

TABLE 10.18 Fluid Loss Additives for Cements

Compound	References
Water-soluble polymers[a]	Rae and Brown (1988)
Gilsonite[b]	
AMPS-based fluid loss additives[c]	Müller (1992)
Styrene-butadiene latex[d]	Gopalkrishnan (1993b)
Anionic aromatic polymers[e]	Brothers and Deblanc (1989)
Polynapthalene sulfonate and acrylic terpolymer	Kieffer et al. (1987)
Polyvinyl acetate[f]	Moran and Moran (1998)
Copolymers of acrylic acid and long side chain acrylic esters and several similar materials (e.g., methacrylics)	Audibert-Hayet et al. (2001)
Hydrophobically modified hydroxypropyl guar	Audibert et al. (2001)

a) General purpose
b) Also density reducer
c) Various other advantages
d) Also has thixotropic properties
e) Low bottom hole temperatures
f) With a dispersing sulfonated polymer and surfactant

Comonomers of the third type are *N*-alkyl-*N*-vinylalkanamides such as *N*-methyl-*N*-vinylacetamide, allyl glycidyl ether, or vinylacetate (Chatterji et al., 2001; Reddy and Riley, 2004). The copolymerization of AMPS with conjugate monomers yields a fluid loss agent whose properties include minimal retardation, salt tolerance, high efficiency, thermal stability, and excellent solids support (Chatterji et al., 2001).

The ratio of the comonomers is selected such that the copolymer does not viscosify the slurries excessively under ambient conditions. Upon undergoing hydrolysis reactions in the cement slurries during placement, the polymer will continuously generate sufficient carboxylate groups at downhole temperatures to react with the calcium ions present and viscosify the slurries to counteract thermal thinning. Thus, the higher the downhole temperature, the greater the thermal thinning of cement slurries and the greater the rate of slurry viscosification due to carboxylate-generating hydrolysis reactions.

Different homopolymers can be used in combination with the above described copolymer. For example, it has been found that the polymer can be used in a synergistic mixture with other homopolymers. The above described copolymer can be used advantageously in admixture with polyvinylpyrrolidone or polyacrylamide for preventing particle settling in cement slurries (Reddy and Riley, 2004).

Polyvinyl alcohol (PVA) works by reducing the permeability of the filter cake by coalescence of hydrated PVA microgel particles, which then form a polymer film. At temperatures above 38°C, the non-crosslinked PVA starts to dissolve in water the formation of a film is no longer possible. So above this temperature, and fluid loss control cannot be not achieved (Plank et al., 2009b). However, the addition of an acetone-formaldehyde-sulfite polycondensate as dispersant extends the temperature range at which PVA can successfully used.

Anionic aromatic polymers have been identified that simultaneously impart improved fluid loss control and adequate rheologic properties to salt-rich cement slurries. They can even be used at low bottom hole circulating temperatures.

Commonly, fluid loss control additives or friction reducers cannot be used in salt-rich systems when circulating temperatures are below 65°C, because they cause excessive retardation of the setting time. Anionic aromatic polymer systems, however, still display acceptably short thickening times (<6 h) and good early strength development when circulating temperatures are as low as 50°C.

Certain natural-based polymers have been used as fluid loss control additives in cementing operations including HEC, carboxymethylhydroxyethyl cellulose, and copolymers of AMPS and AAm or *N*,*N*-dimethylacrylamide. In addition, graft copolymers with a lignin or lignite backbone and AMPS, acrylonitrile, and *N*,*N*-dimethylacrylamide as grafted moieties have been used.

A graft copolymer with a backbone of a humic acid salt and similar monomers as mentioned before have been developed recently. These include AMPS and AAm, acrylic acid, vinylphosphonic acid, diallyldimethylammonium chloride, and the corresponding salts (Lewis et al., 2009a).

Gilsonite is active as a fluid loss additive because it reduces the permeability of cement. Latex additives also act as fluid loss additives as well as bonding aids, gas migration preventers, and matrix intensifiers. They improve the elasticity of the cement and its resistance to corrosive fluids (Jones and Carpenter, 1991). A styrene-butadiene latex in combination with non-ionic and anionic surfactants shows less fluid loss. The styrene-butadiene latex is added in an amount of up to 30% of the dry cement. The ratio of styrene to butadiene in the latex is typically 2:1. In addition, a non-ionic surfactant, octylphenol ethoxylate and polyethylene oxide, or an anionic surfactant, a copolymer of MA, and 2-hydroxypropyl acrylate can be added in amounts of up to 2% (Gopalkrishnan, 1993a).

Clay Control Additives

Cementing technology can be improved in wells with zones containing clays or shales that are sensitive to fresh water cement filtrate. Sodium chloride and potassium chloride (KCl) have been the primary materials of choice to yield a filtrate that damages these zones less.

The unfavorable effects of salt on cement have been extensively documented; in particular, the negative impact of KCl. Quaternary ammonium salts of aliphatic tertiary amines have been tested as alternatives

(Dillenbeck and Nelson, 1992; Dillenbeck et al., 1993; Patel et al., 2001). These additives impart superior clay-controlling properties without the undesirable side effects of either sodium or potassium chloride.

Anti-gas-migration Agents

Gas channeling can occur during the setting of a cement slurry. The formation of channels is dependent on the setting characteristics, and additives can influence this. During the setting period of a cement, two time cycles of cement expansion and contraction are observed (Talabani and Hareland, 1995a, 1995b). This is due to the individual contribution of each component in the cement mixture. To obtain the optimal tightness of the cement, the final contraction is crucial for blocking gas migration. Ironite sponge, synthetic rubber powder, and anchorage clay have been tested (Talabani and Hareland, 1995b; Talabani et al., 1999) as permeability reducers. These materials are environmentally safe and inexpensive. Proper amounts of these additives can be used to optimize the compressive strength and to eliminate both microfractures and the formation of a microannulus. A copolymer of AMPS, *N*-vinylacylamide, and AAm reduces gas channeling (Ganguli, 1992).

Carbon black may serve as a low-cost additive for controlling the gas migration in cement slurries (Calloni et al., 1995a). It is intended as a suitable substitute for polymer latex and silica fume and has been tested in field applications (Calloni et al., 1995b; Moroni et al., 1997). The concentration of carbon black varies from 2–20 parts, based on the weight of the dry cement (Miano et al., 1995). The particle size varies from 10–200 nm. A surfactant, for example, formaldehyde-condensed naphthalene sulfonate or sulfonated cumarone or indene resins, is necessary for its dispersion.

A mixture of lignosulfonates, alkali-treated brown coal, and minor amounts of organic silicon compounds was found to reduce the permeability of cements (Kuksov et al., 1992). The additives may interact with the crystallization centers of the cement slurry and form a gel system in its pores and capillaries, thus reducing the permeability and increasing its isolating capability. Furthermore, it is claimed that the additive retards the setting rate of cement up to 200°C and increases the resistance to corrosive media.

Phosphorated aluminum powder reacts with calcium hydroxide in the cement slurry during setting, and produces hydrogen. The gas swells the cement slurry, preventing the channeling of oil, gas, and water (Bortsov et al., 1997; Wang, 1996).

Corrosion Inhibitors

Ground water with high salinity, high CO_2 content, and sulfate-reducing bacteria corrodes the cement by dissolution, chemical, and expansion actions. By improving the permeability of the cement and by reducing the content of $Ca(OH)_2$, anticorrosion effects can be promoted.

Addition of silica flour changes the proportion of calcium and silica and the composition of the hydrates. Homogeneity, tightness, small pore channels, and low permeability improve the cement strength and anticorrosion effects (Liao et al., 1996). Hydrazine chloride has been proposed for inhibiting the corrosion of the casing (Tsytsymushkin et al., 1993).

Other Chemical Attack

Portland cement is susceptible to corrosion by CO_2 and H_2S. The chemical attack by CO_2 is called *carbonation*. A microsampling technique has been developed to study CO_2 corrosion in cements, because it is difficult to monitor by common test procedures (Bruckdorfer, 1985). This technique is also advantageous as an accelerated testing method. A polymer-modified cement has been tested in field studies (Getzlaf, 1998). The addition of silica also improves chemical resistance, in particular brine corrosion (Barlet-Gouedard and Maroy, 1999).

Use of Waste from Other Industrial Branches

Proper waste management becomes more important with increasing amounts of waste being created by modern civilization. In cementing technology, wastes from various sources can be used. These activities may be subdivided into two main classes:

- Use of wastes as raw material or secondary fuel in cement manufacture and
- Direct use of wastes as additives for oil well cements.

We discuss several issues in detail here, some of which were mentioned briefly in previous sections.

Cement Manufacture with Wastes

In the manufacture of Portland cement, many otherwise-waste materials can be used, either as a substitute for the traditional raw material, or as a secondary fuel (e.g., used tires) (Caveny et al., 1998; Schreiber and Yonley, 1993). In particular, drilling wastes can be introduced into the clinker burning process (Hundebol, 1994).

A mutual benefit will emerge for both waste disposal and cement manufacturers. The cement manufacturing companies reduce their demand for traditional raw materials and save the limited capacity of landfills and other waste-treatment industries.

Waste water-based drilling fluids can be solidified by adding cement mixtures (Terry et al., 1994), in particular, those with low-quality blast furnace slags (Benge and Webster, 1994; Cowan and Hale, 1995; Cowan and Smith, 1993; Saasen et al., 1994). Such mixtures have already been applied in wells at temperatures from approximately 4–315°C. The disposal of rock cuttings is achieved by (McCarthy et al., 1995):

- Combining the cuttings with water and blast furnace slag;
- Injecting the slurry into the annulus surrounding a wellbore casing; and
- Solidifying the cuttings, water, and slag.

TABLE 10.19 Use of Waste in Cementing Technology

Waste Type	References
Water-based drilling fluids[a]	Benge and Webster (1994), Cowan and Hale (1995), Cowan and Smith (1993)
Oil-based drilling muds containing water[b]	Carpenter (1994), Kanakamedala and Islam (1995)
Rock cuttings[c]	Hale (1994)
Slags from nonferrous metal industries[d]	Rakhmatullin et al. (1992)
Slags from nonferrous metal industries[e]	Kurbanov et al. (1993), Lartseva and Gordienko (1992), Negomedzyanov et al. (1995), Zeltser et al. (1992)
Waste from silicon production	Kvashenkin (1993)
Sludge waste from nonferrous metal industries[f]	Klyusov et al. (1996)
Waste from titanium and magnesium industries[g]	Klyusov et al. (1995)
Waste from semiconductor production	Angelopulo et al. (1991)
Waste from soda production	Blazhevich et al. (1992), Khlebnikov et al. (1997), Kurochkin et al. (1992), Malyarchuk et al. (1992), Mosienko et al. (1997b), Ovchinnikov et al. (1995), Shatov and Sharafutdinov (1997), Shatov et al. (1996a,b,c, 1995)
Production wastes from organic chemicals[h]	Frago and Powell (1994), Mosienko et al. (1997a), Perejma and Pertseva (1994), Perejma et al. (1995), Zhukhovitskij et al. (1992)
Polymer wastes[i]	Brothers et al. (1998), Khisaeva et al. (1992), Kurochkin et al. (1996)

a) With low-quality blast furnace slags
b) Moderate-strength cement
c) No removal of drilling fluids; less drilling fluids to be disposed
d) Nickel slag
e) Aluminum slag and Magnesium sludge
f) Contains chlorides, as accelerator
g) MA, sebacic acid
h) Rubber

Solidification in blast furnace slag cement is inexpensive (McCarthy et al., 1995). The slag is compatible with both oil-based and water-based drilling mud. Drilling fluids, therefore, do not need to be removed from the drilling cuttings prior to solidification in the wellbore annulus (Hale, 1994).

Disposal of Oil Sludge

The proper disposal of oil sludge is one of the fundamental problems of petroleum production. Increasingly stringent environmental control regulations, lack of final disposal sites, and high costs involved in disposal have resulted in limited oil sludge disposal options. Two options for disposing the oil sludge have been evaluated (Kanakamedala and Islam, 1995):

- The use of solid-liquid centrifugal separation and
- The use of oil sludge as a cementing material.

If the initial oil concentration in the sludge is high, then high-temperature centrifugation with a biodegradable surfactant is recommended to lower the concentration to a reasonable value. The resulting solid extract can be mixed with cement to obtain a product of a quality that is suitable for masonry.

The major potential uses of wastes in cementing technology are summarized in Table 10.19.

REFERENCES

Akhrimenko, V.E., Aleksandrova, E.A., Tkachenko, Z.N., Dmitriev, E.A., Derevenets, F.N., Abramov, S.A., 1997. Effect of aluminum compounds on setting time of cement slurry and strength of set cement. Stroit Neft Gaz Skvazhin Sushe More (10–11), 30–32.

Akhrimenko, V.E., Kuksov, A.K., Levin, E.M., 1992. Oil, gas well cementing additive – has added melamine formaldehyde resin for better bonding of cement to casing. SU Patent 1 709 072, assigned to Borehole Reinforc Res. Inst., January 30, 1992.

Angelopulo, O.K., Ali, A.K., Dzhabarov, K.A., Rusaev, A.A., Konovalov, E.A., Bojko, I.V., 1991. Plugging solution contains plugging portland cement, waste from semiconductors production containing dispersed silica, chloride(s), carbonate(s), phosphate(s) and water. SU Patent 1 700 202, assigned to Moscow Gubkin Oil Gas Inst., December 23, 1991.

Anonymous, 1995. Cementing products and additives. World Oil 216 (3 (Suppl)), C–3 – C–18.

Anonymous, 1997. Cementing products and additives. World Oil 218 (3 (Suppl)), C3, C5–C6, C8, C10–C12, C14, C16–C18.

Anonymous, 1998. Cementing products and additives. World Oil 219 (3), 87–99.

Anonymous, 1999. Cementing products and additives. World Oil 220 (3), 87–102.

API RP 13B-1, 1995. Recommended practice for field testing water-based drilling fluids. API Standard RP 13B-1, API Spec 10A. American Petroleum Institute, Washington, DC.

API RP 13B-1, 1997. Standard procedure for field testing water-based drilling fluids. API Standard API RP 13B-1. American Petroleum Institute, Washington, DC.

API TR 10TR2, 1997. Technical report on shrinkage and expansion in oilwell cements. API Standard API TR 10TR2. American Petroleum Institute, Washington, DC.

ASTM C150-00, 2001. Standard specification for portland cement. ASTM Standard, Book of Standards, vol. 04.01 ASTM C150-00. ASTM International, West Conshohocken, PA.

ASTM C184-94E1, 2001. Standard test method for fineness of hydraulic cement by the 150-μm (No. 100) and 75-μm (No. 200) sieves. ASTM Standard, Book of Standards, vol. 04.01 ASTM C184-94E1. ASTM International, West Conshohocken, PA.

ASTM C666-97, 2001. Standard test method for resistance of concrete to rapid freezing and thawing. ASTM Standard, Book of Standards, vol. 04.02 ASTM C666-97. ASTM International, West Conshohocken, PA.

ASTM C786-96, 2001. Standard test method for fineness of hydraulic cement and raw materials by the 300-μm (No. 50), 150-μm (No. 100), and 75-μm (No. 200) sieves by wet methods. ASTM Standard, Book of Standards, vol. 04.01 ASTM C786-96. ASTM International, West Conshohocken, PA.

ASTM E11-01, 2001. Standard specification for wire cloth and sieves for testing purposes. ASTM Standard, Book of Standards, vol. 14.02 ASTM E11-01. ASTM International, West Conshohocken, PA.

Audibert, A., Argillier, J.F., Pfeiffer, U., Molteni, G., 2001. Well cementing method using hmhpg [hydrophobically modified hydroxy propyl guar] filtrate reducer. US Patent 6 257 336, assigned to Inst. Francais Du Petrole and Soc. Lamberti SPA, July 10, 2001.

Audibert-Hayet, A., Noik, C., Rivereau, A., 2001. Copolymer additives for cement slurries intended for well bores. GB Patent 2 359 075, assigned to Inst. Francais Du Petrole, August 15, 2001.

Banthia, N., Mindess, S., 1989. Water permeability of cement paste. Cement Concrete Res. 19 (5), 727–736.

Baret, J.-F., Dargaud, B., Villar, J., Michaux, M., 1997. Cementing compositions and application of such compositions to cementing oil (or similar) wells. CA Patent 2 207 885, assigned to Schlumberger Ca. Ltd., December 18, 1997.

Barlet-Gouedard, V., Maroy, P., 1999. Cementing compositions and application thereof to cementing oil or analogous wells. WO Patent 9 901 397, assigned to Sofitech NV, Schlumberger Canada Ltd., and Dowell Schlumberger SA, January 14, 1999.

Bashev, F.P., Kadantseva, K.I., 1992. Binder for cements used to plug oil and gas drilling holes – contains phosphoric slag, sodium hydroxide and trisodium phosphate. SU Patent 704 030, assigned to Cement Equip Res. Inst., March 07, 1992.

Benge, G., 2005. Cement designs for high-rate acid gas injection wells. In: International Petroleum Technology Conference. International Petroleum Technology Conference, Doha, Qatar.

Benge, O.G., Webster, W.W., 1994. Evaluation of blast furnace slag slurries for oilfield application. In: Proceedings Volume, Iadc/SPE Drilling Conf. (Dallas, 2/15–18/94), pp. 169–180.

Bin Ibrahim, S., Huizenga, R., Oakley, D., Sithamparam, K., 2001a. Multifunctional additive to cement slurries. WO Patent 0 166 487, assigned to Sofitech NV, Schlumberger Canada Ltd., and Dowell Schlumberger SA, September 13, 2001.

Bin Ibrahim, S., Sithamparam, K., Huizenga, R., Oakley, D., 2001b. Multifunctional additive to cement slurries. EP Patent 1 132 354, assigned to Sofitech NV, September 12, 2001.

Blazhevich, V.A., Khisaeva, D.A., Umetbaev, V.G., 1992. Plugging solution – contains Portland cement, liquid waste from soda production and water and has reduced hardening time and increased strength. SU Patent 1 776 762, assigned to Bashkir Oil Ind. Res. Inst., November 23, 1992.

Bloys, J.B., Carpenter, R.B., Wilson, W.N., 1991. Accelerating set of retarded cement. US Patent 5 005 646, assigned to Atlantic Richfield Co., April 09, 1991.

Bloys, J.B., Carpenter, R.B., Wilson, W.N., 1992. Accelerating set of retarded cement. CA Patent 2 046 714, assigned to Atlantic Richfield Co., January 13, 1992.

Boles, J.L., Boles, J.B., 1998. Cementing compositions and methods using recycled expanded polystyrene. US Patent 5 736 594, assigned to BJ Services Co., April 07, 1998.

Boncan, V.C.G., 2001. Low temperature curing cement for wellbores. GB Patent 2 353 523, assigned to BJ Services Co., February 28, 2001.

Bortsov, V.P., Baluev, A.A., Bastrikov, S.N., 1997. Plugging solution for oil and gas wells – contains portland cement, expanding additive, water and additionally aluminium powder, surfactants and plasticiser. RU Patent 2 082 872, assigned to Sibe Oil Ind. Res. Inst., June 27, 1997.

Bour, D.L., Childs, J.D., 1992. Foamed well cementing compositions and methods. US Patent 5 133 409, assigned to Halliburton Co., July 28, 1992.

Bourgoyne, A.T., 1986. Applied Drilling Engineering, Volume 2 of SPE Textbook Series. Society of Petroleum Engineers, Richardson, TX.

Bray, W.S., Wood, W.R., 1992. Well cementing method using a dispersant and fluid loss intensifier. US Patent 5 105 885, assigned to BJ Services Co., April 21, 1992.

Brothers, L.E., 1992. Composition and method for inhibiting thermal thinning of cement. US Patent 5 135 577, assigned to Halliburton Co., August 04, 1992.

Brothers, L.E., 1995. Low temperature set retarded well cement compositions and methods. US Patent 5 472 051, assigned to Halliburton Co., December 05, 1995.

Brothers, L.E., Brennels, D.C., Childs, J.D., 1999. Light weight high temperature well cement compositions and methods. US Patent 5 900 053, assigned to Halliburton Energy Serv., May 04, 1999.

Brothers, L.E., Deblanc, F.X., 1989. New cement formulation helps solve deep cementing problems. Pet. J. Technol. 41 (6), 611–614.

Brothers, L.E., Onan, D.D., Morgan, R.L., 1998. Well cement compositions containing rubber particles and methods of cementing subterranean zones. US Patent 5 779 787, assigned to Halliburton Energy Serv., July 14, 1998.

Bruckdorfer, R., 1985. Carbon dioxide corrosion resistance in cements. In: Proceedings Volume, vol. 2, 36th Annu. Cim. Petrol. Soc. & Can. Soc. Petrol. Geol. Tech. Mtg. (Edmonton, Can, 6/2–5/85), pp. 517–525.

Cai, C., Yang, S., Ai, W., 1994. Application of accelerant $CaCl_2$ in watercut wells in Liaohe oilfield. Pet. Drill. Tech. 22 (1), 9–11, 68.

Calloni, G., Moroni, N., Miano, F., 1995a. Carbon black: a low cost colloidal additive for controlling gas migration in cement slurries. In: Proceedings Volume, Offshore Mediter Conf. (Ravenna, Italy, 3/15–17/95), pp. 563–574.

Calloni, G., Moroni, N., Miano, F., 1995b. Carbon black: a low cost colloidal additive for controlling gas migration in cement slurries. In: Proceedings Volume, SPE Oilfield Chem. Int. Symp. (San Antonio, 2/14–17/95), pp. 145–153.

Carpenter, R.B., 1994. Cement slurries for wells. US Patent 5 372 641, assigned to Atlantic Richfield Co., December 13, 1994.

Carpenter, R.B., Bloys, J.B., Johnson, D.L., 1999. Cement composition containing synthetic hectorite clay. WO Patent 9 902 464, assigned to Atlantic Richfield Co. and Arco British Ltd., January 21, 1999.

Carpenter, R., Johnson, D., 1997. Method and cement-drilling fluid cement composition for cementing a wellbore. WO Patent 9 748 655, assigned to Atlantic Richfield Co., December 24, 1997.

Carpenter, R.B., Wilson, W.N., 1990. Method of accelerating set of cement by washover fluid containing alkanolamine. US Patent 4 976 316, assigned to Atlantic Richfield Co., December 11, 1990.

Carpenter, R.B., Wilson, W.N., 1991. Accelerating the set of cement compositions in wells. EP Patent 0 448 218, assigned to Atlantic Richfield Co., September 25, 1991.

Cartalos, U., Lecourtier, J., Rivereau, A., 1994. Use of scleroglucan as high temperature additive for cement slurries. US Patent 5 301 753, assigned to Inst. Francais Du Petrole, April 12, 1994.

Casabonne, J.M., Jowe, M., Nelson, E., 1994. High-temperature petroleum-cement retarders, cement slurries, and associated cementation procedures (retardateurs haute temperature pour ciments petroliers, laitiers de ciments et procedes de cimentation correspondants). FR Patent 2 702 472, assigned to Dowell Schlumberger SA, September 16, 1994.

Caveny, B., Ashford, D., Hammack, R., Garcia, J.G., 1998. Tires fuel oil field cement manufacturing. Oil Gas J. 96 (35), 64–67.

Chan, K.S., Griffin Jr., T.J., 1996. Low temperature, low rheology synthetic cement. US Patent 5 547 027, assigned to Dowell Schlumberger Corp., August 20, 1996.

Chandra, S., Justnes, H., Ohama, Y., 1996. Concrete Polymer Composites, The Polymeric Materials Encyclopedia. CRC Press, Inc., Boca Raton, FL.

Chatterji, J., Brenneis, D.C., King, B.J., Cromwell, R.S., Gray, D.W., 2006. Foamed cement slurries, additives and methods. US Patent 7 013 975, assigned to Halliburton Energy Services, Inc. (Duncan, OK), March 21, 2006.

Chatterji, J., Brenneis, D.C., King, B.J., Cromwell, R.S., Gray, D.W., 2007. Foamed cement compositions, additives, and associated methods. US Patent 7 255 170, assigned to Halliburton Energy Services, Inc. (Duncan, OK), August 14, 2007.

Chatterji, J., Brennels, D.C., Gray, D.W., Lebo, S.E., Dickman, S.L., 2000a. Cement compositions and biodegradable dispersants therefor. US Patent 6 019 835, assigned to Halliburton Energy Serv., February 01, 2000.

Chatterji, J., Griffith, J.E., Totten, P.L., King, B.J., 1996. Lightweight well cement compositions and methods. US Patent 5 588 489, assigned to Halliburton Co., December 31, 1996.

Chatterji, J., King, B.J., Totten, P.L., Onan, D.D., 1997a. Resilient well cement compositions and methods. US Patent 5 688 844, assigned to Halliburton Co., November 18, 1997.

Chatterji, J., Lebo, S.E., Brenneis, C.D., Dickman, S.L., Gray, D.W., 2000b. Cement compositions comprising modified lignosulphonate. EP Patent 985 645, assigned to Halliburton Energy Serv. and Lignotech USA Inc., March 15, 2000.

Chatterji, J., Morgan, R.L., Davis, G.W., 1997b. Set retarded cementing compositions and methods. US Patent 5 672 203, assigned to Halliburton Co., September 30, 1997.

Chatterji, J., Totten, P.L., King, B.J., Onan, D.D., 1998. Well cement compositions. EP Patent 816 300, assigned to Halliburton Energy Serv., January 07, 1998.

Chatterji, J., Zamora, F., King, B.J., McKinley, R.J., 2001. Well cementing method. EP Patent 1 065 186, assigned to Halliburton Energy Serv., January 03, 2001.

Cheung, P.S., 1998a. Expanding additive for cement composition. CA Patent 2 224 201, assigned to Nalco Exxon Energy Chem. Lp., June 10, 1998.

Cheung, P.S., 1998b. Expanding additive for cement composition. GB Patent 2 320 246, assigned to Nalco Exxon Energy Chem. L, June 17, 1998.

Cheung, P.-S., 1999. Expanding additive for cement composition. US Patent 5 942 031, assigned to Nalco Exxon Energy Chem. Lp., August 24, 1999.

Cheyrezy, M., Dugat, J., Boivin, S., Orange, G., Frouin, L., 1999. Concrete comprising organic fibres dispersed in a cement matrix, concrete cement matrix and premixes. WO Patent 9 958 468, assigned to Bouygues SA, Lafarge SA, Rhone Poulenc Chimie, Cheyrezy, Marcel, Dugat Jerome, Boivin Sandra, Orange Gilles, and Frouin, Laurent, November 18, 1999.

Childs, J.D., Burkhalter, J.F., 1992. Fluid loss reduced cement compositions. GB Patent 2 247 234, assigned to Halliburton Co., February 26, 1992.

Coats, A., Sas-Jaworsky II., A., St Clergy, J., 1996. Magnesian cement, ct (coiled tubing) offer benefits. Am. Oil Gas Report. 39 (3), 92–93.

Cowan, K.M., Eoff, L., 1993. Surfactants: Additives to improve the performance properties of cement. In: Proceedings Volume, SPE Oilfield Chem. Int. Symp. (New Orleans, 3/2–5/93), pp. 317–327.

Cowan, K.M., Hale, A.H., 1995. High temperature well cementing with low grade blast furnace slag. US Patent 5 379 840, assigned to Shell Oil Co., January 10, 1995.

Cowan, K.M., Nahm, J.J.W., Wyant, R.E., Romero, R.N., 1996. Alumina wellbore cement composition. US Patent 5 488 991, assigned to Shell Oil Co., February 06, 1996.

Cowan, K.M., Smith, T.R., 1993. Application of drilling fluids to cement conversion with blast furnace slag in Canada. In: Proceedings Volume, no. 93-601, Cade/caodc Spring Drilling Conf. (Calgary, Can, 4/14–16/93) Proc.

Crema, S.C., Kucera, C.H., 1991. Cementing compositions containing a copolymer as a fluid loss control additive. EP Patent 444 489, assigned to BASF Corp., September 04, 1991.

Crema, S.C., Kucera, C.H., Gousetis, C., Oppenlaender, K., 1991a. Cementing compositions containing polyethyleneimine phosphonate derivatives as dispersants. EP Patent 444 542, assigned to BASF Corp., September 04, 1991.

Crema, S.C., Kucera, C.H., Konrad, G., Hartmann, H., 1991b. Fluid loss control additives for oil well cementing compositions. US Patent 5 025 040, assigned to BASF Corp., June 18, 1991.

Crook, R.J., Calvert, D.G., 2000. Cement technology: Pt 1: Improvements in techniques and equipment address cement issues. Oil Gas J. 98 (40), 60–66.

Crump, D.K., Wilson, D.A., 1988. Cement compositions containing set retarders. CA Patent 1 234 582, assigned to Dow Chemical Co., March 29, 1988.

Dahl, J., Harris, K., McKown, K., 1991. Uses of small particle size cement in water and hydrocarbon based slurries. In: Proceedings Volume, 9th Kansas Univ. et al Tertiary Oil Recovery Conf. (Wichita, Kans, 3/6–7/91), pp. 25–29.

Dalrymple, E.D., Dahl, J.A., East, L.E., McOwn, K.W., 1992. A selective water control process. In: Proceedings Volume, SPE Rocky Mountain Reg Mtg. (Casper, Wyo, 5/18–21/92), pp. 225–230.

Danican, S., Drochon, B., James, S., Ding, B., 2010. Permeable cements. US Patent 7 717 176, assigned to Schlumberger Technology Corporation (Sugar Land, TX), May 18, 2010.

Danjuschewskij, S.V., Ghofrani, R., 1991. Volume changes in cement slurries and set cements (Volumenänderungen erhärtender Zementschlämme). Erdöl Erdgas Kohle 107 (11), 447–455.

Dao, B., Biezen, E., Vijn, J.P., Pham, T., 2005. Process for controlling gas migration during well cementing. US Patent 6 936 574, assigned to Halliburton Energy Services, Inc. (Duncan, OK), August 30, 2005.

Davis, G.W., Chatterji, J., Morgan, R.L., 1998. Set retarded cememting compositions and methods. CA Patent 2 212 600, assigned to Halliburton Energy Serv. Inc., February 07, 1998.

Davis, K.P., Smith, A.C., Williams, M.J., 1999a. Cement setting modifiers. GB Patent 2 327 417, assigned to Albright & Wilson Ltd., January 27, 1999.

Davis, K.P., Smith, A.C., Williams, M.J., 1999b. Phosphonocarboxylic acids and their use as cement setting retarders. EP Patent 0 899 246, assigned to Albright & Amp and Wilson UK Ltd., March 03, 1999.

De Larrard, F., 1989. Ultrafine particles for the making of very high strength concretes. Cement Concrete Res. 19 (2), 161–172.

Detroit, W.J., 1995. Nitric acid oxidized lignosulfonates. US Patent 5 446 133, assigned to Lignotech USA Inc., August 29, 1995.

Detroit, W.J., Sanford, M., 1989. Solubilized lignosulfonate derivatives. US Patent RE32 895, assigned to Reed Lignin, Inc., March 28, 1989.

Dillenbeck, R.L., Nelson, S.G., 1992. New clay-controlling technology addresses problems encountered in cement design and performance. In: Proceedings Volume, SPE Rocky Mountain Reg Mtg. (Casper, Wyo, 5/18–21/92), pp. 641–647.

Dillenbeck, R.L., Nelson, S.G., Hall, B.E., Porter, D.S., 1993. Clay control additive for cement compositions and method of cementing. US Patent 5 232 497, assigned to Western Co. North America, August 03, 1993.

Dilullo Arias, G.F., Rae, P.J., Mueller, D.T., 1999. Multi-functional additive for use in well cementing. WO Patent 9 916 723, assigned to BJ Services Co., April 08, 1999.

Edmeades, R.M., Hewlett, P.C., 2003. Cement admixtures. In: Hewlett, P.C. (Ed.), Lea's Chemistry of Cement and Concrete, fourth ed. Butterworth-Heinemann, Oxford, pp. 841–905.

Ekshibarov, V.S., Khasanov, T.R., 1992. Oil well casing cement – containing 20 to 60 weight per cent of lightweight additive by-product from hydraulic washing of brown coal. SU Patent 1 731 939, assigned to Cent. Asia Gas Ind. Des. Inst., May 07, 1992.

Eoff, L., 1993. Set retarding additives, cement compositions and methods. US Patent 5 264 470, assigned to Halliburton Co., November 23, 1993.

Eoff, L., 1994. Acetone/formaldehyde/cyanide resins. US Patent 5 290 357, assigned to Halliburton Co., March 01, 1994.

Falbe, J., Regitz, M., 1995. CD Römpp Chemie-Lexikon, Version 1. Thieme Verlag, Stuttgart.

Fan, S., Yuan, S., Ye, Y., 1996. A laboratory study of adhesion agent of er type for casing cementing. Jianghan. J. Pet. Inst. 18 (2), 1996. 77–80.

Frago, H.W., Powell, R.D., 1994. Re-use of certain oil exploration and production waste as supplemental fuel in the manufacture of cement. In: Abstracts Volume, Annu. Aapg-Sepm-Emd-Dpa-Deg Conv (Denver, 6/12–15/94), p. 151.

Fry, S.E., Totten, P.L., Childs, J.D., Lindsey, D.W., 1992. Chloride-free set accelerated cement compositions and methods. US Patent 5 127 955, assigned to Halliburton Co., July 07, 1992.

Fyten, G.C., Luke, K., Rispler, K.A., 2007. Cementitious compositions containing interground cement clinker and zeolite. US Patent 7 303 015, assigned to Halliburton Energy Services, Inc. (Duncan, OK), December 4, 2007.

Ganguli, K.K., 1992. Control of gas flow through cement column. US Patent 5 099 922, assigned to Western Co. North America, March 31, 1992.

Ganguli, K.K., Kattenburg-Schuler, R., Leatherdale, S.T., Porat, A.J., Zaslavsky, G., 1997. Lightweight thermally stable cement compositions and method of use. WO Patent 9 749 644, assigned to BJ Services Co. and Nowsco Well Services Ltd., December 31, 1997.

Gartner, E.M., Kreh, R.P., 1993. Cement additives and hydraulic cement mixes containing them. CA Patent 2 071 080, assigned to Grace (w R) & Co., January 20, 1993.

Getzlaf, D., 1998. Field studies illustrate merits of fcrs (flexible corrosion-resistant sealant). Am. Oil Gas Report. 41 (13), 95–96, 105.

Ghofrani, R., 1997. Development of CaO- and MgO-swelling cements into usage maturity for cementation of natural gas underground storage wells and natural gas production wells, DMGK Res Rep 444-3, Clausthal Tech. Univ.

Ghofrani, R., Marx, C., Wolschendorf, H., 1992. Swelling (expanding) cements based on CaO and MgO (Quellzemente auf der Basis von CaO und MgO). Erdöl Erdgas Kohle 108 (1), 9–11.

Ghofrani, R., Plack, H., 1993. Conditions for successful use of CaO and MgO expanding cements in annulus cementations (Voraussetzungen für den erfolgreichen Einsatz von CaO- und MgO-Quellzementen bei Ringraumzementationen). In: Proceedings Volume, DMGK Spring Conf. (Celle, Ger, 5/13–14/93), pp. 87–100.

Ghofrani, R., Werner, K.C., 1993. Effect of the calcination temperature and the duration of calcinations on the optimization of expanding efficiency of the additives CaO and MgO in swelling (expanding) cements (Optimierung der Expansionswirkung der Zusätze CaO und MgO in Quellzement). Erdöl Erdgas Kohle 109 (1), 7–9.

Gopalkirshnan, S., Roznowski, M., 1993. Additive composition for oil well cementing formulations. US Patent 5 258 072, assigned to BASF Corp., November 02, 1993.

Gopalkrishnan, S., 1993a. Additive composition for oil well cementing formulations. US Patent 5 252 128, assigned to BASF Corp., October 12, 1993.

Gopalkrishnan, S., 1993b. Additive composition for oil well cementing formulations. US Patent 5 258 428, November 02, 1993.

Grabowski, E., Gillott, J.E., 1989. Effect of replacement of silica flour with silica fume on engineering properties of the oilwell cements at normal and elevated temperatures and pressures. Cement Concrete Res. 19 (3), 333–344.

Griffith, J.E., Totten, P.L., King, B.L., Chatterji, J., 1996. Well cementing methods and compositions for use in cold environments. US Patent 5 571 318, assigned to Halliburton Co., November 05, 1996.

Hervot, T., Leverot, A., Lesgent, B., Philippot, J.N., Martin, M., Schaeffer, F., et al., 1993. Cementing Technology and Procedures. Editions Technip, Total, Gaz De France, Inst Francais Du Petrole, Paris, France .

Hale, A.H., 1994. Well drilling cuttings disposal. US Patent 5 341 882, assigned to Shell Oil Co., August 30, 1994.

Haque, E., 1986. Physicochemical interactions between montmorillonite and polymerizing systems: Effect on particle-reinforced composites, Ph.D. thesis. Rice University, Houston, TX.

Heathman, J.F., Cromwell, R.S., 1994. Well cementing. EP Patent 592 217, assigned to Halliburton Co., April 13, 1994.

Heathman, J.F., Crook, R.J., 1994a. Fine particle size cement compositions and methods. US Patent 5 346 012, assigned to Halliburton Co., September 13, 1994.

Heathman, J.F., Crook, R.J., 1994b. Fine particle size cement compositions. EP Patent 611 081, assigned to Halliburton Co., August 17, 1994.

Hundebol, S., 1994. Method and plant for manufacturing cement clinker. WO Patent 9 429 231, December 22, 1994.

Jamth, J., 1998. A cement slurry and a method for the production of such a cement slurry, as well as a use for a light weight filling material as an additive in a cement slurry. WO Patent 9 819 976, assigned to Veba A/S and Dennert Poraver GmbH, May 14, 1998.

Jones, R.R., Carpenter, R.B., 1991. New latex, expanding thixotropic cement systems improve job performance and reduce costs. In: Proceedings Volume, SPE Oilfield Chem. Int. Symp. (Anaheim, Calif, 2/20–22/91), pp. 125–134.

Justnes, H., Dahl-Jorgensen, E., 1994. Alternative cementing materials for completion of deep, hot oil-wells. WO Patent 9 412 445, assigned to Sinvent Assoc., June 09, 1994.

Kanakamedala, R.D., Islam, M.R., 1995. A new method of petroleum sludge disposal and utilization. In: Proceedings Volume, vol. 2, 6th Unitar et al Heavy Crude & Tar Sands Int. Conf. (Houston, 2/12–17/95), pp. 675–682.

Khisaeva, D.A., Blazhevich, V.A., Umetbaev, V.G., 1992. Plugging solution for isolation of absorption zones in boreholes – includes bentonite, calcium chloride, buckwheat husks and polymer reagent produced by interaction of polymethyl-methacrylate wastes with monoethanolamine. SU Patent 1 739 005, assigned to Bashkir Oil Ind. Res. Inst., June 07, 1992.

Khlebnikov, V.N., Umetbaev, V.G., Loginov, A.B., Nazmetdinov, R.M., Kamaletdinova, R.M., 1997. Use of salt-containing secondary resources as cement set accelerators. Neftepromysl Delo (12), 21–24.

Kieffer, J., Michaux, M., Rae, P., 1987. Additive for controlling the filtrate of well cementing slurries and corresponding cementing process (additif pour le controle du filtrat des laitiers de cementation de puits, et procede de cimentation correspondant). FR Patent 2 592 056, assigned to Dowell Schlumber Etud Fab, June 26, 1987.

King, B.J., Totten, P.L., 1993. Well cementing method using acid removable low density well cement compositions. US Patent 5 213 161, assigned to Halliburton Co., May 25, 1993.

Klyusov, A.A., Antipov, V.S., Krasnov, B.I., Novikov, N.K., 1995. Plugging solution for low temperature wells – contains plugging cement, water and molten chloride melt obtained as waste from titanium-magnesium production as complex chloride additive. RU Patent 1 091 616, assigned to Tyumen Nat Gases Res. Inst. and Tyumenniigiprogaz, September 20, 1995.

Klyusov, A.A., Shalyapin, M.M., Kalugin, Y.N., Kargapoltseva, L.M., 1996. Plugging solution for low temperature oil wells – contains plugging cement, water and hardening accelerator in form of sludge waste from production of metallic magnesium from carnallite. SU Patent 884 366, May 20, 1996.

Kukacka, L.E., Sugama, T., 1994. Lightweight CO_2-resistant cements for geothermal well completions, Brookhaven Nat Lab Rep BNL-60326, Brookhaven National Lab.

Kukacka, L.E., Sugama, T., 1995. Lightweight CO_2 resistant cements for geothermal well completions, Brookhaven Nat Lab Rep BNL-61259, Brookhaven National Lab.

Kuksov, A.K., Krezub, A.P., Mariampolskij, N.A., Ryabova, L. I., Lyshko, G.N., Loskutov, D.A., Zhmurkevich, E.I., 1992. Oil and gas borehole plugging solution reagent – contains brown coal treated with alkali, organic silicon compound and lignosulphonate. SU Patent 1 719 618, assigned to Borehole Consolidation Mu., March 15, 1992.

Kunzi, R.A., Vinson, E.F., Totten, P.L., Brake, B.G., 1993. Low temperature well cementing compositions and methods. CA Patent 2 088 897, August 06, 1993.

Kunzi, R.A., Vinson, E.F., Totten, P.L., Brake, B.G., 1994. Low temperature well cementing compositions and methods. US Patent 5 346 550, assigned to Halliburton Co., September 13, 1994.

Kunzi, R.A., Vinson, E.F., Totten, P.L., Brake, B.G., 1995. Low temperature well cementing compositions and methods. US Patent 5 447 198, assigned to Halliburton Co., September 05, 1995.

Kurbanov, Y.M., Nikashin, S.E., Kalugina, N.Y., 1993. Plugging solution for cementing oil and gas wells – contains plugging cement, aluminium slag from highly alloyed aluminium production, acrylic polymer or cellulose ether and water. SU Patent 1 789 665, assigned to Kama Deep Extrem Borehole, January 23, 1993.

Kurochkin, B.M., Khannanov, S.N., Saitgareev, R.Z., Kashapov, S.A., Sagidullin, I.A., 1996. Ways of effective use of rubber crumbs during plugging works in cased wells. Neftepromysl Delo (12), 19–21.

Kurochkin, B.M., Moskvicheva, N.T., Lobanova, V.N., Kateev, I. S., Khabibullin, R.A., 1992. Oil-well slurry for lost-circulation zone isolation. SU Patent 1 726 733, assigned to Inst. Burovoi Tekhnik, April 15, 1992.

Kvashenkin, V.B., 1993. Plugging solution for cementing low pressure oil and gas wells – contains plugging portland cement, waste of silicon production as the lightening additive and calcium chloride as mineral salt, and water. SU Patent 1 832 149, assigned to E Sibe Geolog. Geophy Min. Re, August 07, 1993.

Lartseva, L.S., Gordienko, S.Y., 1992. Grouting mortar. SU Patent 1 760 087, assigned to Kazakhsk Gni Pi Neftyanoj, September 07, 1992.

Le Roy-Delage, S., Dargaud, B., Baret, J.-F., 1999. Cementing compositions and use of such compositions for cementing oil wells or the like. WO Patent 9 958 467, assigned to Sofitech NV, Schlumberger Ca Ltd., Schlumberger Cie Dowell, Le Roy Delage, Sylvaine, Dargaud Bernard, and Baret, Jean Francois, November 18, 1999.

Le Roy-Delage, S., Dargaud, B., Baret, J.F., Thiercelin, M., 2000. Cementing compositions and the use of such compositions for cementing oil wells or the like. WO Patent 0 020 350, assigned to Sofitech NV, Schlumberger Canada Ltd., and Dowell Schlumberger SA, April 13, 2000.

Lewis, S., Chatterji, J., King, B., Brenneis, D.C., 2009a. Cement compositions comprising humic acid grafted fluid loss control additives. US Patent 7 576 040, assigned to Halliburton Energy Services, Inc. (Duncan, OK), August 18, 2009.

Lewis, S., Morgan, R., Gordon, C., Santra, A.K., 2009b. Salt water stable latex cement slurries. US Patent 7 576 042, assigned to Halliburton Energy Services, Inc. (Duncan, OK), August 18, 2009.

Lewis, S.J., Szymanski, M.J., 2007. Methods for cementing using compositions containing salts. US Patent 7 293 941, assigned to Halliburton Energy Services, Inc. (Duncan, OK), November 13, 2007.

Liao, G., Yang, Y., Wang, H., 1996. Effect on anti corrosion ability of oil well slurry using silica flour. Oil Drill. Prod. Technol. 18 (4), 31–34, 43, 106.

Lindstrom, K.O., Riley, W.D., 1994. Soil-cement compositions and their use. EP Patent 605 075, assigned to Halliburton Co., July 06, 1994.

Liotta Jr., F.J., Schwartz, S.A., 2000. Supported carbonic acid esters useful as set accelerators and thixotropic agents in cement. WO Patent 0 002 828, assigned to Arco Chem. Tech. and Lyondell Chemie Technologie Ne, January 20, 2000.

Livsey, I., Shaunak, R., 1987. Cement setting retarding agents. GB Patent 2 182 031, May 07, 1987.

Logvinenko, S.V., Bateev, D.E., Chernyak, Y.V., Osipov, V.V., Potapkin, V.P., 1997. Low density cement slurry preparation – comprises mixing cement with specified weight percentage of aqueous solution of polyacrylnitrile. RU Patent 2 072 026, January 20, 1997.

Lu, N., Jia, Z., Ma, H., Wang, W., Wu, D., 1997. Study and applications of low density furnace slag cement slurry system. Oil Drilling Prod. Technol. 19 (2), 37–40, 53, 107.

Luke, K., Fitzgerald, R.M., Zamora, F., 2008. Drilling and cementing with fluids containing zeolite. US Patent 7 448 450, assigned to Halliburton Energy Services, Inc. (Duncan, OK), November 11, 2008.

Lyons, W.C., 1996. Standard Handbook of Petroleum and Natural Gas Engineering, vol. 1–2. Gulf Publishing Co, Houston, TX.

Müller, D.T., 1992. Performance characteristics of vinylsulfonate-based cement fluid-loss additives. In: Proceedings Volume, SPE Rocky Mountain Reg Mtg. (Casper, Wyo, 5/18–21/92), pp. 609–617.

Müller, D.T., Dillenbeck III., R.L., 1991. The versatility of silica fume as an oilwell admixture. In: Proceedings Volume, SPE Prod. Oper. Symp. (Okla City, 4/7–9/91), pp. 529–536.

Ma, H., 1993. Study on the stability of low density cement with hollow microsphere. Drill. Fluid Completion Fluid 10 (1), 61–65, 76.

Malyarchuk, B.M., Pavlyuk, V.Y., Nijger, F.V., Tarasov, B.G., Tarabarinov, P.V., 1992. Composition for plugging flooded porous strata – contains clay, alumina cement, natural zeolite, calcined soda, polyacrylamide, alkyl resorcinol resin, pentaerythritol production waste and natural saline. SU Patent 1 776 764, assigned to Ivano Frank Oil Gas Inst., November 23, 1992.

Maughmer, R.E., Dalrymple, D., 1992. Treatment helps to decrease water. Am. Oil Gas Report. 35 (6), 114, 116, 118.

McCarthy, S.M., Daulton, D.J., Bosworth, S.J., 1995. Blast furnace slag use reduces well completion cost. World Oil 216 (4), 87–88, 90, 92, 94, 96.

Miano, F., Calloni, G., Moroni, N., Marcotullio, A., 1995. Cementitious composition for the cementation of oil wells. EP Patent 636 591, assigned to Eniricerche SPA and Agip SPA, February 01, 1995.

Michaux, M., 1999. Controlling setting in a high-alumina cement. WO Patent 9 933 763, assigned to Sofitech NV, Schlumberger Canada Ltd., and Dowell Schlumberger SA, July 08, 1999.

Milestone, N.B., Sugama, T., Kukacka, L.E., Carciello, N., 1986. Carbonation of geothermal grouts: Pt.1: CO2 attack at 150 C. Cement Concrete Res. 16 (6), 941–950.

Moran, L.K., Moran, L.L., 1998. Composition and method to control cement slurry loss and viscosity. US Patent 5 850 880, assigned to Conoco Inc. (Ponca City, OK), December 22, 1998.

Moroni, N., Calloni, G., Marcotullio, A., 1997. Gas impermeable carbon black cements: Analysis of field performances. In: Proceedings Volume, Vol. 2, E&P Forum et al Offshore Mediter Conf. (OMC 97) (Ravenna, Italy, 3/19–21/97), pp. 781–792.

Mosienko, V.G., Petrakov, Y.I., Nagornova, V.F., Nikiforova, V. N., 1997a. Complex additive for plugging solutions – contains modifying reagent in form of waste from production of sebacic acid, from stage of neutralising of sodium salts of fatty acids. RU Patent 2 074 310, assigned to Nevinnomyssk Novekotek En, February 27, 1997.

Mosienko, V.G., Petrakov, Y.I., Pedus, A.M., Nikiforova, V.N., 1997b. Complex additive to plugging solution – contains waste from production of sebacic acid, ammonium sulphate and carboxymethyl cellulose, reducing water separation, etc. RU Patent 2 078 908, assigned to N Caucasus Nat Gaz Res., May 10, 1997.

Mueller, D.T., Boncan, V.G., Dickerson, J.P., 2001. Stress resistant cement compositions and methods for using same. US Patent 6 230 804, assigned to BJ Services Co., May 15, 2001.

Nahm, J.J.W., Vinegar, H.J., Karanikas, J.M., Wyant, R.E., 1993. High temperature wellbore cement slurry. US Patent 5 226 961, assigned to Shell Oil Co., July 13, 1993.

Negomedzyanov, V.R., Bortsov, V.P., Denisov, V.S., Slepov, V.V., Volkova, S.S., 1995. Plugging composition for use in oil and gas extraction industry – contains portland cement and aluminium-containing additive in form of slag dust waste from aluminium production process. RU Patent 2 029 067, assigned to Sibe Oil Ind. Res. Inst., February 20, 1995.

Nelson, E.B., 1987. Well treating process and composition. CA Patent 1 216 742, January 20, 1987.

Nelson, E.B. (Ed.), 1990. Well Cementing, Vol. 28 of Elsevier Developments in Petroleum Science. Elsevier Science Publishing Co. Inc., New York.

Noik, C., Rivereau, A., 1998. Method and material for well cementing (methode et materiau pour la cimentation de puits). EP Patent 881 353, assigned to Inst. Francais Du Petrole, December 02, 1998.

Odler, I., 2000. Special Inorganic Cements, Vol. 8 of Modern Concrete Technology. E & FN Spon, London.

Onan, D.D., Terry, D.T., Brake, B.G., 1994a. Downhole cement composition. EP Patent 618 344, assigned to Halliburton Co., October 05, 1994.

Onan, D.D., Terry, D.T., Riley, W.D., 1994b. Set-activated cementitious compositions and methods. US Patent 5 332 041, assigned to Halliburton Co., July 26, 1994.

Onan, D.D., Webster, W.W., Griffith, J.E., 1997. Well cementing method. EP Patent 787 698, assigned to Halliburton Energy Serv., August 06, 1997.

Ovchinnikov, V.P., Shatov, A.A., Shulgina, N.Y., Ovchinnikov, P.V., 1995. Salt composition for regulating hardening processes of plugging agents. Neftepromysl Delo (11–12), 32–33.

Patel, A.D., Stamatakis, E., Davis, E., 2001. Shale hydration inhibition agent and method of use. US Patent 6 247 543, assigned to M I Llc., June 19, 2001.

Perejma, A.A., Pertseva, L.V., 1994. Complex reagent for treating plugging solutions – comprises hydrolysed polyacrylonitrile, ferrochromolignosulphonate Cr-containing additive, waste from lanolin production treated with triethanolamine and water. RU Patent 2 013 524, assigned to N Caucasus Nat Gaz Res., May 30, 1994.

Perejma, A.A., Tagirov, K.M., Ilyaev, V.I., Kovalev, A.A., 1995. Plugging solution for conducting well repair works, etc. – contains portland cement, polyacrylamide, specified stabilising additive, sodium sulphate waste from sebacic acid production and water. RU Patent 2 035 585, assigned to N Caucasus Nat Gaz Res., May 20, 1995.

Pittman, W., Maurer, W.C., Deskins, W.G., Sabins, F., Müller, D., 1996. Carbon-fiber technology for improved downhole cement performance: Final report, Gas Res Inst Rep GRI-96/0276, Gas Res Inst (August 1996).

Plank, J., Lummer, N.R., Dugonjic-Bilic, F., 2009a. Physico-chemical interactions perturbing the effectiveness of an atbs-based fluid loss polymer used in oil well cementing. In: SPE International Symposium on Oilfield Chemistry, Society of Petroleum Engineers, The Woodlands, Texas.

Plank, J., Lummer, N.R., Dugonjic-Bilic, F., Sadasivan, D., 2009b. Comparative study of the working mechanisms of different cement fluid loss polymers. In: SPE International Symposium on Oilfield Chemistry, Society of Petroleum Engineers, The Woodlands. Texas.

Quercia, G., Perera, Y., Blanco, A., Pereira, F., 2010. Ceramic microspheres for cementing applications. US Patent Application 20100144562, assigned to INTEVEP S.A. (Caracas, VE), June 10, 2010.

Rae, P., Brown, E., 1988. Polymer additives improve cementing in salt formations. Oil Gas J. 86 (49), 31–32, 35–36, 38.

Rae, P.J., Johnston, N., Dilullo, G., 2001. Storable liquid systems for use in cementing oil and gas wells. US Patent 6 173 778, assigned to BJ Services Co., January 16, 2001.

Rakhmatullin, T.K., Agzamov, F.A., Ivanov, V.V., Karimov, N. K., Tankibaev, M.A., Trenkenshu, N.V., 1992. Clinker-less binder composition – contains mixture of slag from melting of oxidised nickel ores and tails from enrichment of phosphorite ores. SU Patent 1 777 617, assigned to Kaza Oil Geolog. Survey, November 23, 1992.

Rakitsky, W.G., Richey, D.D., 1992. Rapidly hydrating welan gum. EP Patent 505 096, assigned to Merck & Co. Inc., September 23, 1992.

Reddy, B.R., Crook, R.J., Chatterji, J., King, B.J., Gray, D.W., Fitzgerald, R.M., Powell, R.J., Todd, B.L., 2001. Controlling the release of chemical additives in well treating fluids. US Patent 6 209 646, assigned to Halliburton Energy Serv., April 03, 2001.

Reddy, B.R., Eoff, L.S., 2007. Biodegradable dispersants for cement compositions and methods of cementing in subterranean formations. US Patent 7 273 100, assigned to Halliburton Energy Services, Inc. (Duncan, OK), September 25, 2007.

Reddy, B.R., Riley, W.D., 2004. High temperature viscosifying and fluid loss controlling additives for well cements, well cement compositions and methods. US Patent 6 770 604, assigned to Halliburton Energy Services, Inc. (Duncan, OK), August 3, 2004.

Roddy, C.W., Chatterji, J., Brenneis, D.C., King, B.J., 2008. Settable drilling fluids comprising cement kiln dust. US Patent 7 338 923, assigned to Halliburton Energy Services, Inc. (Duncan, OK), March 4, 2008.

Rodrigues, K.A., 1994. Cement set retarding additives, compositions and methods. US Patent 5 341 881, assigned to Halliburton Co., August 30, 1994.

Rodrigues, K.A., 1995. Cement set retarding additives, compositions and methods. US Patent 5 421 879, June 06, 1995.

Rodrigues, K.A., Eoff, L.S., 1994. Functionalized polymers containing amine groupings and their use as retarders in cement slurries. US Patent 5 368 642, assigned to Halliburton Co., November 29, 1994.

Saasen, A., Salmelid, B., Blomberg, N., Hansen, K., Young, S.P., Justnes, H., 1994. The use of blast furnace slag in North Sea cementing applications. In: Proceedings Volume, Vol. 1, SPE Europe Petrol. Conf. (London, UK, 10/25–27/94), pp. 143–153.

Santra, A.K., Fitzgerald, R., 2009. Cement compositions for low temperature applications. US Patent 7 530 394, assigned to Halliburton Energy Services, Inc. (Duncan, OK), May 12, 2009.

Savoly, A., Elko, D.P., 1995. Foaming agent composition and process. WO Patent 9 516 515, assigned to Henkel Corp., June 22, 1995.

Schreiber Jr., R.J., Yonley, C., 1993. The use of spent catalyst as a raw material substitute in cement manufacturing. ACS Pet. Chem. Div. Preprints 38 (1), 97–99.

Scian, A.N., Porto, L.J.M., Pereira, E., 1991. Mechanochemical activation of high alumina cements – hydration behavior: Pt.1. Cement Concrete Res. 21 (1), 51–60.

Shatov, A.A., Karimov, N.K., Mavlyutov, M.R., Agzamov, F.A., Gareev, A.T., Nazarenko, N.N., 1996a. Plugging solution for cementing oil and gas wells – contains portland cement, distiller liquid – waste from calcined soda production and additionally baryta. RU Patent 2 059 793, May 10, 1996.

Shatov, A.A., Karimov, N.K., Mavlyutov, M.R., Agzamov, F.A., Titov, V.M., Yakimtsev, V.V., 1996b. Plugging solution for oil and gas wells – containing portland cement, waste from calcined soda production and power station fly ash giving reduced cost and improved expansion properties. RU Patent 2 059 792, May 10, 1996.

Shatov, A.A., Karimov, N.K., Mavlyutov, M.R., Agzamov, F.A., Voronin, A.V., Maltseva, I.D., 1996c. Plugging solution for cementing oil and gas wells – contains portland cement, waste from production of calcined soda, water and additionally slag waste from metallurgical industry. RU Patent 2 059 791, May 10, 1996.

Shatov, A.A., Sergeev, V.N., Titov, V.M., Maltseva, I.D., Ovchinnikov, V.P., 1995. Plugging solution for oil and gas wells – includes cement, water, and additive in form of waste from calcined soda production containing calcium and sodium salts. RU Patent 2 030 557, assigned to Sterlitamak Petro Ind. Wks, March 10, 1995.

Shatov, A.A., Sharafutdinov, Z.Z., 1997. Plugging solution – contains portland cement and specified additive based on waste from production of calcined soda. RU Patent 2 072 027, assigned to Karbon Stock Co., January 20, 1997.

Sirenko, P.M., Bublikova, N.G., Kovalenko, V.D., Kostenko, D. A., 1995. Light heat-resistant plugging material – contains lightening-stabilising additive in form of bentonite clay powder, and additionally water absorption reducing agent. RU Patent 2 043 481, assigned to Ukr. Natural Gas Res. Inst., September 10, 1995.

Slagle, K.A., Carter, L.G., 1959. Gilsonite-a unique additive for oil-well cements. In: Drilling and Production Practice. American Petroleum Institute, Washington, DC.

Smith, D.K., 1976. Cementing. SPE Publications, The Woodlands. TX, 2nd Printing.

Squyres, J.W., Lopez, H., 1990. Silica fume as a strength enhancer in low density slurries. In: Proceedings Volume, 37th Annu. Southwestern Petrol. Short Courseass et al Mtg. (Lubbock, Texas, 4/18–19/90), pp. 47–53.

Stephens, M., 2001. Low density well cement compositions and method of use. US Patent 6 176 314, assigned to Phillips Petroleum Co., January 23, 2001.

Stephens, M., Pereira, B., 2001. Low density well cement compositions. WO Patent 0 105 727, assigned to Phillips Petroleum Co., January 25, 2001.

Stewart, R.B., Lohbeck, W.C.M., Gill, D.S., Baaijens, M.N., 1996. An expandable slotted tubing, fibre-cement wellbore lining system. In: Proceedings Volume, Annu. SPE Tech. Conf. (Denver, 10/6–9/96), pp. 127–134.

Stewart, R.B., Lohbeck, W.C.M., Gill, D.S., Baaijens, M.N., 1997. An expandable-slotted-tubing, fiber-cement wellbore-lining system. SPE Drilling Completion 12 (3), 163–167.

Sugama, T., Kukacka, L.E., Carciello, N., Galen, B., 1988. Oxidation of carbon fiber surfaces for improvement in fiber-cement interfacial bond at a hydrothermal temperature of 300 C. Cement Concrete Res. 18 (2), 290–300.

Sweatman, R., 2011. Well Cementing. Gulf Publishing Company, Houston, TX.

Talabani, S., Hareland, G., 1995a. Expansion-contraction cycles for cement optimized as a function of additives. In: Proceedings Volume, SPE Prod. Oper. Symp. (Oklahoma City, 4/2–4/95), pp. 277–284.

Talabani, S., Hareland, G., 1995b. New cement additives that eliminate cement body permeability. In: Proceedings Volume, SPE Asia Pacific Oil & Gas Conf. (Kuala Lumpur, Malaysia, 3/20–22/95), pp. 169–176.

Talabani, S., Hareland, G., Islam, M.R., 1999. New additives for minimizing cement body permeability. Energy Sources 21 (1–2), 163–176.

Taradymenko, Y.Y., Timovskij, V.P., Kushu, V.A., Akhrimenko, V. E., Karpenko, Y.G., 1993. Plugging solution – contains portland cement, calcium oxide-based expanding additive, water and additionally polymethylene-urea, to improve efficiency. SU Patent 1 799 999, assigned to Borehole Consolidation Mu., March 07, 1993.

Terry, D.T., Onan, D.D., Totten, P.L., King, B.J., 1994. Converting drilling fluids to cementitious compositions. US Patent 5 295 543, assigned to Halliburton Co., March 22, 1994.

Totten, P.L., Brake, B.G., Vinson, E.F., 1994. Retarded acid soluble well cement compositions and methods. US Patent 5 281 270, assigned to Halliburton Co., January 25, 1994.

Trabelsi, A.M.S., Al-Samarraie, L.S., 1999. Fiber content affects porosity, permeability, and strength of cement. Oil Gas J. 97 (18), 108, 110, 112, 114.

Tsytsymushkin, P.F., Khajrullin, S.R., Tarnavskij, A.P., Kovalenko, P.V., Kudryashova, Z.N., Iskhakov, R.M., Levshin, V. N., Sudakov, V.M., 1993. Plugging solution for oil and gas wells – contains plugging portland cement, nitrilo-trimethyl phosphonic acid, hydrazine hydrochloride and water and has corrosion-protective properties. RU Patent 2 002 037, October 30, 1993.

Tsytsymushkin, P.F., Khajrullin, S.R., Tarnavskij, A.P., Kudryashova, Z.N., Levshin, V.N., Mikhajlov, B.V., 1991a. Plugging solution for wells in salt-bearing deposits – contains plugging cement, sodium chloride, water and alkyl-benzyl-methyl-ammonium chloride as additive. SU Patent 1 700 201, assigned to Volgo Urals Hydrocarbon, December 23, 1991.

Tsytsymushkin, P.F., Khajrullin, S.R., Tarnavskij, A.P., Kudryashova, Z.N., Mikhajlov, B.V., 1991b. Plugging solution contains portland cement, sodium sulphate, potassium ferricyanide and nitrile-tri:methyl-phosphonic acid. SU Patent 1 700 204, assigned to Volgo Urals Hydrocarbon, December 23, 1991.

Tsytsymushkin, P.F., Khajrullin, S.R., Tarnavskij, A.P., Kudryashova, Z.N., Mikhajlov, B.V., 1991c. Plugging solution contains portland cement, sodium sulphate, potassium ferricyanide and nitrile-tri:methyl-phosphonic acid. SU Patent 1 700 204-A assigned to Volgo Ural Ni Pi Dobyche Perer, December 23, 1991.

Van Vliet, J.P.M., Van Kleef, R.P.A.R., Smith, T.R., Plompen, A. P., Kuijvenhoven, C.A.T., Quaresma, V., Raiturkar, A., Schoenmakers, J.M., Arentz, B., 1995. Development and field use of fibre-containing cement. In: Proceedings Volume, Vol. 4, 27th Annu. SPE et al Offshore Technol. Conf. (Houston, 5/1–4/95), pp. 183–197.

Vasilchenko, Y.V., Luginina, I.G., 1992. Binder for cementing low-temperature wells – contains modified lignosulphonate(s), potash and cement of specified composition, to increase bending strength of cement rock. SU Patent 1 749 199, assigned to Belgorod Constr. Mater Tech., July 23, 1992.

Vijn, J.P., 2001. Dispersant and fluid loss control additives for well cements, well cement compositions and methods. US Patent 6 182 758, assigned to Halliburton Energy Serv., February 06, 2001.

Villar, J., Baret, J.-F., Michaux, M., Dargaud, B., 1997. Cementing compositions and application of such compositions to cementing oil (or similar) wells. EP Patent 0 814 067, assigned to Sofitech NV, December 29, 1997.

Villar, J., Baret, J.-F., Michaux, M., Dargaud, B., 2000. Cementing compositions and applications of such compositions to cementing oil (or similar) wells. US Patent 6 060 535, assigned to Schlumberger Technology Corp., May 09, 2000.

Wang, W.J., 1996. The development and applications of cx-18 antichannelling agent. J Xi'an Pet. Inst. 11 (5), 6–7, 50–53.

Zeltser, P.Y., Chalykh, V.I., Chernyakhovskij, L.V., Smetanin, V.N., Kravchenko, V.I., Elkin, K.S., 1992. Method for preparation of light-weight oil-well slurry. SU Patent 1 728 471, assigned to Vostoch Sib Nii Geolog. and Ir Vi Alyuminievoj Magnievoj P, April 23, 1992.

Zhang, Y., Chen, L., 1993. High temperature stabilizer for oil well cement. Drill. Fluid Completion Fluid 10 (3), 58–61, 75–76.

Zhang, Y., Wang, Z., 1989. Experiments and applications of low density glass bead slurry. Pet. Drill. Tech. 17 (4), 48–51, 87.

Zhukhovitskij, V.B., Kolomoets, M.I., Zagrudnyj, A.M., 1992. Polymeric plugging solution contains urea-formaldehyde resin, expandable resol-phenol- formaldehyde resin containing surfactant and aluminium powder, and maleic anhydride production waste. SU Patent 1 728 473, assigned to Ukrgeologiya Min. Rscs Inst., April 23, 1992.

TRADENAMES

TABLE 10.20 Tradenames in References

Tradename Description	Supplier
FloBloc® 210 Polyvinyl alcohol (cement additive) (Moran and Moran, 1998)	Conoco, Inc.
GasStop™ HT Tannin grafted with acrylamide and 2-acrylamido-2-methylpropane sulfonic acid (Reddy and Riley, 2004)	Halliburton Energy Services, Inc.
Halad® (Series) Fluid loss control additive (Dao et al., 2005; Reddy and Riley, 2004)	Halliburton Energy Services, Inc.
HE™ 300 Polymer from 2-acrylamido-2-methylpropane sulfonic acid, *N*-vinylpyrrolidone, and acrylamide (Reddy and Riley, 2004)	Drilling Specialties Comp.
Hostadrill™ 2825 Polymer from 2-acrylamido-2-methylpropane sulfonic acid, acrylamide and *N*-vinyl-*N*-alkylamide (Reddy and Riley, 2004)	Clariant GmbH

TABLE 10.20 Tradenames in References–Cont'd

Tradename Description	Supplier
Hostamer™ 4706 Polymer from 2-acrylamido-2-methylpropane sulfonic acid,acrylamide and *N*-vinyl-*N*-alkylamide (Reddy and Riley, 2004)	Clariant GmbH
Hostamer™ V 4707 Polymer from 2-acrylamido-2-methylpropane sulfonic acid, acrylamide and *N*-vinyl-*N*-alkylamide (Reddy and Riley, 2004)	Clariant GmbH
Permseal® Polymerizable solution as cement additive (Dao et al., 2005)	Halliburton Energy Services, Inc.
PVP K™-90 Polyvinylpyrrolidone (Reddy and Riley, 2004)	ISP
SA™-541 Causticized hydroxypropyl guar surface treated with sodium borate (Reddy and Riley, 2004)	Halliburton Energy Services, Inc.
SCR™-100 Copolymer of 2-acrylamide-2-methylpropane sulfonic acid and acrylic acid (Reddy and Riley, 2004)	Halliburton Energy Services, Inc.
SCR™-500 Copolymer of 2-acrylamido-2-methylpropane sulfonic acid and itaconic acid (Reddy and Riley, 2004)	Halliburton Energy Services, Inc.

Chapter 11

Transport

Pipelines have a long history. In ancient times, they were used for water transport, examples of which are still visible at archeological sites. However, it is clear that these early constructions could not withstand high pressures. The advent of gas pipelines started between 1820 and 1830 with the distribution of town gas. Nowadays, pipelines are indispensable to the petroleum industries for the transport of various materials, including natural gas, crude oil of various types, and refined products.

The construction and operation of pipelines are described in the literature and are not a subject of oil field chemicals (Bourgoyne, 1986; Krass et al., 1979; McAllister, 2009; Mohitpour et al., 2000). In this chapter, the additives and chemicals that facilitate the transport of fossil fuel products will be discussed.

PRETREATMENT OF THE PRODUCTS

Certain requirements concerning the purity of the product to be transported must be fulfilled. For natural gas, the water content should be kept below a certain level to reduce hydrate formation, and the oxygen and sulfur must be controlled effectively. Some additive classes are presented in Table 11.1.

Pretreatment for Corrosion Prevention

Methods used to control presumptive corrosion include deaeration and dehydration. Carbon dioxide and hydrogen sulfide are the main corrosives in pipelines for natural gas, but they are only aggressive in the presence of water, so sweetening and drying the gas is useful to prevent corrosion. In oil pipelines, water emulsified in the crude oil can cause corrosion problems (Bromley et al., 1991), and emulsified crude oil in separated produced water is also an environmental and disposal problem.

Petroleum Engineer's Guide to Oil Field Chemicals and Fluids. DOI: 10.1016/B978-0-12-383844-5.00011-8

TABLE 11.1 Main Classes of Additives and Chemicals Used for Transport

Additive	Remarks
Drag reducers	For both liquid and gas transport
Pour point depressants	Reduce pour points of waxy crudes
Odorizing additives	For safety
Gas hydrate inhibitors	For gas and multiphase transport to prevent hydrate deposits
Surfactants	For multiphase transport of heavy crudes
Corrosion inhibitors	Both chemical inhibitors and biocides
Paraffin inhibitors	Prevent paraffin depositions

Natural Gas

Natural gas consists mainly of methane, although there are trace amounts of higher hydrocarbons, nitrogen, and even helium. It is usual practice to strip out higher hydrocarbons, such as ethane, propane, butane, and unsaturated hydrocarbons from natural gas if it is to be transmitted through pipelines.

The materials that are stripped out are then transported or stored separately, often as liquids. A typical composition of natural gas transmitted through pipelines is shown in Table 11.2.

The compressibility factor, z, of methane is always less than 1.0 in normal temperature ranges, i.e., between −40°C and 50°C. The compressibility factor decreases as the pressure rises or the temperature falls, hence less energy is needed to pump a given volume of methane at any given, normal temperature than it would be if the methane behaved like an ideal gas.

This effect is more marked at higher pressures. Similarly, as the pressure is increased at a constant temperature, more methane (measured at standard volume) can be stored in a given volume than would be predicted from the ideal gas equation.

Below 7 MPa, the dominant variable for the compressibility factor in the PVT equation is the molecular weight of the gas. At this pressure, the addition of ethane or propane increases the average molecular weight of the gas more rapidly than the z factor decreases. Thus there is an advantage to removing ethane, propane, etc., from the gas.

At pressures greater than 7 MPa it is advantageous to add substances such as C_2 or C_3 hydrocarbon compounds, carbon monoxide, hydrogen fluoride, ammonia, or a mixture of these with the natural gas. Ammonia without other additives is useful as an additive for gas storage at pressures down to about 5.5 MPa. Above a lower limit, which varies with the additive and the pressure, this results

TABLE 11.2 Composition of the Natural Gas Transmitted from Alberta, Canada to Ontario, Canada (Morris and Perry, 2001)

Component	%-vol
Methane	95.4
Ethane	1.97
Nitrogen	1.27
Carbon dioxide	0.55
Propane	0.51
i-Butane	0.17
n-Butane	0.08
i-Pentane	0.02
n-Pentane	0.01
n-Hexane	0.02

in a smaller $M_w \times z$ product, and therefore a decrease in the amount of power needed to compress the mixture for storage and to keep it compressed.

It is also advantageous to add ammonia, and sometimes carbon monoxide to natural gas to be transmitted through pipelines at pressures above 5.5 MPa. Hydrogen fluoride is also effective, but it is prohibitive because of its toxicity and corrosive properties.

The precise amount of each additive that can be added at any given pressure to yield beneficial results can be found by calculating the product of the molecular weight and the z factor of the resulting mixture $M_w \times z$, and comparing it with the product of the molecular weight and the z factor of the original natural gas. If $M_w \times z$ is smaller for the mixture than for the natural gas, energy can be saved in pumping and compression (Morris and Perry, 2001a).

In many cases the use of two or more additives has a synergistic effect, so an even smaller amount of each is needed than would be if only one were present, in order to produce the z factor over that of an equivalent standard volume of natural gas at the pressure and temperature involved.

When the mixture is pumped through a pipeline, however, an additional effect of ammonia emerges. The pumping stations that are installed at intervals along the pipeline compress the gas. Then, as it travels toward the next pumping station, it gradually loses pressure and expands.

Compression of the gas as it passes through the compressor station heats it, before it cools again, while passing through the pipeline, transferring some of its heat to the surrounding soil through the pipeline wall. Ammonia is a refrigerant, which absorbs heat as it expands. Thus when a gas mixture of ammonia and natural gas is compressed and then is subsequently allowed to flow through a gas pipeline, the ammonia cools the mixture as it expands. This is regarded as an additional advantage (Morris and Perry, 2001).

Sulfur Contamination of Refined Products

If refined products, such as gasoline, diesel, jet fuel, or kerosene, are transported in a pipeline, where at times sour hydrocarbon fluids have been transported, there may be an undesired enrichment of sulfur in the refined products. This can be avoided if the oxygen level of the transportant is maintained below 20 ppm (Falkiner and Poirier, 1996).

The dissolved oxygen level of the hydrocarbon product is controlled by reducing the amount of air injection employed in mercaptan or disulfide reduction, or by the use of oxygen scavengers prior to the introduction of the refined hydrocarbon product into the pipeline.

Demulsifiers

A gas containing entrained asphaltene is conditioned for pipeline transportation by injecting a surface active compound that consists of a mixture of a demulsifying agent, an antifoaming agent, a dispersant, an aromatic solvent, and an alcohol solvent. This prevents the formation of emulsion of asphaltene and hydrocarbons (Mendoza, 1995). A typical surface-active composition is shown in Table 11.3.

TABLE 11.3 Surface Active Composition for Conditioning a Gas Containing Entrained Asphaltenes

Action	Compound	% by wt
Demulsifying agent	Solution of a sulfonic acid, a phenolic resin, and alcohol	5 to 15
Antifoaming agent	Silicone	1 to 3
Dispersant	Imidazoline	10 to 40
Aromatic solvent	Benzene, toluene, xylene, residues of BTX distillation	10 to 60
Alcohol solvent	From methanol to hexanol	20 to 60

Heavy Crudes

The most relevant parameters in the pipeline transportation of heavy crude oil are velocity, viscosity, temperature, density, and pour point (Gerez and Pick, 1996). Heavy crude can be transported on trunk systems in a variety of modes, including segregation, blending, and batching.

Segregation requires separate pipelines, blending consists of mixing crudes, and batching refers to shipping the crude in discrete batches. There are a number of methods for enhancing the transportability of heavy crude, including oil-in-water emulsion formation, droplet suspension, dilution, the use of drag reducing additives, and heating.

Emulsions for Heavy Crudes

Oil-in-water emulsions provide a cost-effective alternative to the heating or diluting methods mentioned previously. A typical transport emulsion is composed of 70% crude oil, 30% aqueous phase, and 500–2,000 ppm of a stabilizing surfactant formulation (Rimmer et al., 1992).

Non-ionic surfactants are relatively insensitive to the salt content of the aqueous phase. Ethoxylated alkyl phenols have been used successfully for the formation of stable emulsions that resist inversion.

Activation of Natural Surfactants

The natural surfactants in crude oil can be activated by chemical treatment (Padron et al., 1995). This method has been shown to be effective for highly viscous crude oil from the *Orinoco Belt* that was traditionally transported either by heating or diluting. The surfactant's precursors are the carboxylic acids that occur in the crude oil.

Activation is initiated by an aqueous buffer solution (Padron, 1994, 1995) of either sodium hydroxide in combination with sodium bicarbonate or sodium silicate. Water-soluble amines also have been found to be suitable (Rivas et al., 1994). Multivalent inorganic salts, such as aluminum nitrate (Rodriguez et al., 1990) in quantities of around 30 ppm are additional stabilizers for the emulsion.

Low-temperature Transportation

In addition to the surfactant, a freezing point depressant can be added for low-temperature transportation. Possible depressants include salts, sugars, and alcohols such as glycerol (Gregoli and Olah, 1992).

CORROSION CONTROL

Coatings, cathodic protection, and chemical additives are extensively used to prevent internal and external pipeline corrosion. The excessive use of incompatible chemical additives has caused severe problems in gas-transporting systems.

The costs arising from these problems often exceed the costs of the chemicals themselves, so the careful evaluation and selection of chemical additives can minimize these problems and provides considerable scope for cutting costs (Wu, 1990).

Crude Oil Treatment

Some crude oils contain certain organic compounds that are corrosive, in particular naphthenic acid, which causes problems in transportation, refining, and processing. The naphthenic acid content can be reduced simply by treating with alcohol, such as methanol, to form the corresponding ester.

Treatment temperatures are preferably around 350°C, with pressures of about 100–300 kPa, which generally result from the system itself (Sartori et al., 2001).

Chemical Inhibition

Inhibitors may be classified according to their solution properties, as either oil-soluble, water-soluble, or dispersible inhibitors. Chemical inhibitors act as film formers to protect the surface of the pipeline. They are often complex mixtures. The majority of inhibitors used in oil production systems are nitrogenous and have been classified according to the broad groupings given in Table 11.4. Typical corrosion inhibitors are shown in Table 11.5 and in Figure 11.1. For details, see also Chapter 6.

Synergism with Drag Reducers

Copolymers of acrylamide and acrylic acid (AA) that are added as drag reducers also enhance the activity of corrosion inhibitors in brine solutions by decreasing turbulence, so that the corrosion inhibitor can contact the internal surface of

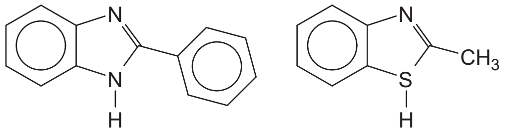
TABLE 11.4 Groupings of Corrosion Inhibitors Used in Transportation (McKerrell and Lynes, 1988)

Grouping
Amides or imidazolines
Salts of nitrogenous molecules with carboxylic acids (fatty acids, naphthenic acids)
Nitrogen quaternaries
Polyoxylated amines, amides, and imidazolines
Nitrogen heterocyclics

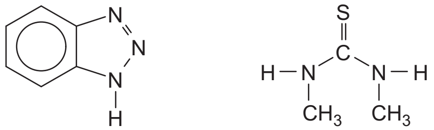
TABLE 11.5 Corrosion Inhibitors

Inhibitor	References
Glutaraldehyde[a]	El-Gamal and Gad (1997)
2-Phenylbenzimidazole and 2-methylbenzothiazole[b]	Koshel et al. (1988)
Benzotriazole and 1,3-dimethyl-2-thiourea	
Thiourea	
Sodium hexametaphosphate	
Tribasic sodium orthophosphate with polyurethane (PU) foam[c]	Bohon and Ruschau (2001)

a) Bacterial corrosion
b) Chemical corrosion
c) For external protection



2-Phenyl benzimidazole 2-Methyl-benzothiazole



Benzotriazole 1,3-Dimethyl-2-thiourea

FIGURE 11.1 Corrosion inhibitors.

the pipeline more thoroughly. Therefore the copolymer acts synergistically with corrosion inhibitors to increase their efficiency (Johnson et al., 1996).

The effect of a chemical drag reducer on oxygen corrosion of carbon steel has been investigated in a large-scale flow loop, which simulates a sea-water injection line. A drag reduction of up to 48% was achieved, and a reduction of corrosion occurred (McMahon et al., 1997).

Coatings

Coatings protect the wall material by preventing contact with aggressive substances. A coating is actually not an additive, but they are included for

TABLE 11.6 Coatings for Pipelines

Coating Material	Remarks	References
Bitumen	Oxidized bitumen with hexamethylenetetramine	Kashirskij et al. (1994)
Concrete	Styrene-butadiene copolymer latex additions on centrifugally cast concrete	Buchheit et al. (1993)
Epoxide resins	Glass fiber reinforced	Osborne (1993)
Polyethylene		Miyajima et al. (1993)
PP	External corrosion protection	Arai and Ohkita (1989)
PU foams	Insulating systems for high-temperature marine pipelines	Palmer and Wright (1991)
Polyurea		Kenworthy (2001)

completeness. A polyethylene coating with special antioxidant stabilizers has an excellent resistance to thermal oxidation at 80°C.

A polypropylene (PP) coating is suitable for external corrosion protection of steel line pipes at temperatures between −30°C and 120°C. Coatings are summarized in Table 11.6.

Alternative Plastic Materials

Fiber-reinforced epoxide pipes have many advantages for the petroleum industry. These pipes offer corrosion resistance, high strength-to-weight ratios, light weight, desirable electrical properties, dimensional stability, pressure and temperature stability in given ranges, and low maintenance costs.

PARAFFIN INHIBITORS

The techniques of paraffin removal and paraffin prevention have been reviewed (Heinze et al., 2001). Copolymers of ethylene with vinylacetate (Duncum et al., 1998a,b, 2000; Sharov et al., 1989) or polymers of *p*-nonylphenyl methacrylate and *p*-dodecylphenyl methacrylate (Handa et al., 1999) make good paraffin inhibitors. These materials lower the pour point of the oil.

It has been shown that it is necessary to use blends of copolymers of different compositions and molecular weights to obtain optimal efficiency for oils that differ in the content of *n*-paraffins and asphalt-resinous substances.

Polyacrylamide and wastes from the production of glycerol with a concentration of 400 $\mathrm{mg\,l^{-1}}$ of oil have also been claimed to be effective as paraffin inhibitors (Dzhanakhmedova et al., 1992).

TABLE 11.7 Pour Point Depressants

Chemicals	References
Copolymer of acrylic esters with allyl ethers[a]	Krull et al. (1998); Wirtz et al. (1994)
Urea and derivatives	Kissel (1997)
Homopolymer of acrylic esters	Meyer et al. (1995)
Grafted ethylene vinyl acetate polymer[b]	Balzer et al. (1995); Feustel et al. (2001)
Substituted fullerenes[c]	Schriver et al. (1995)

a) In amounts of several hundred ppm
b) Grafted with unsaturated dicarboxylic acid derivates
c) Fullerene–aniline, fullerene–phenol adducts

POUR POINT DEPRESSANTS

Some crude oils are so waxy that their transportation by cold pipelines is very difficult, especially in winter, due to their high pour points. The crystallization of waxes at lower temperatures causes reduced liquidity in waxy crude oils, which considerably hampers the transportation of crude oils through long distance pipelines.

Taking all the economic aspects into consideration, additive treatment, which depresses the pour point and improves the flow characteristics of the crude at lower temperatures, was found to be the most suitable method for transporting waxy crude oil (Sunil Kumar, 1989). Typical pour point depressants are shown in Table 11.7.

The pour point can alternatively be reduced by modifying the crude oil itself, for example, by cracking (Fung et al., 2002).

DRAG REDUCERS

Pipeline flow improvers, or drag reducing agents, have been utilized in the petroleum industry for many years (Almond, 1989). Their first application was to reduce downhole pressure loss during the pumping of the fluids downhole to fracture-tight formations.

One of the first large-scale pipeline applications to use them was to increase the throughput of crude oil on the Trans-Alaskan pipeline in 1979. Because of the reduction of the apparent viscosity, drag reducers are useful for reducing the energy required for pumping. They are discussed in more detail in Chapter 12, but some are shown here in Table 11.8 and Figure 11.2.

TABLE 11.8 Drag Reducers

Chemicals	References
Low-density polyethylene[a]	Aubanel and Bailly (1987)
Copolymer of a linear α-olefin with crosslinkers[b]	Gessell and Washecheck (1990)
Polyacrylamides[c]	Grabois and Lee (1991), Lee and Wiggins (1991), Majumdar et al. (1980)
Polyalkylene oxide[c]	Grabois and Lee (1991), Lee and Wiggins (1991), Majumdar et al. (1980)
Fluorocarbons[d]	Karydas (1988)
Polyalkylmethacrylates[e]	Malik et al. (1992, 1996), Ritter and Herold (1990), Ritter et al. (1989a,b)
Terpolymer of styrene, alkyl acrylate, and AA or methacrylic acid[f]	Naiman and Chang (1991)

a) *Olefin up to 10* mol-%
b) *α-Olefins are 1-hexene, 1-octene, 1-decene, and 1-dodecene; crosslinkers are divinylbenzene or organo-siloxanes with pendent vinyl groups*
c) *Water-soluble drag reducers for emulsions*
d) *For asphaltenic crude oils*
e) *Esters with C_{10} to C_{18} and ionic monomers; reduces friction in the flow of hydrocarbons by a factor of 5 at concentrations of 25 ppm*
f) *Styrene also includes* tert-*butylstyrene (drag reducer for hydrocarbon fluids)*

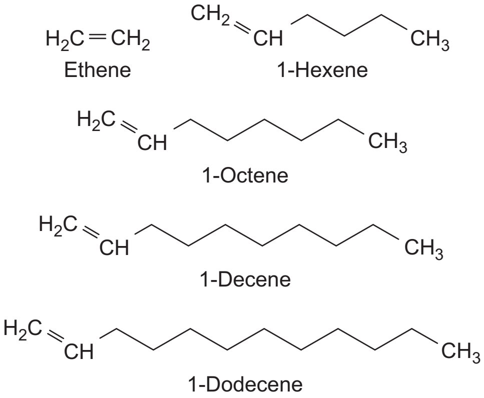


FIGURE 11.2 Monomers for poly(olefin)s as drag reducers.

Drag Reduction in Gas Transmission Lines

Drag reduction in gas transmission lines can be achieved by applying a thin chemical coating to the pipe's inner surface to reduce friction between the flowing gas and the pipe wall.

It is an important criterion that the additive can bond strongly onto metal surfaces and form a smooth film to mitigate the turbulence at the gas-solid interface (Li et al., 1997). Effective gas drag reducers have properties similar to corrosion inhibitors, lubricants, and surfactants. Fatty acid amines or amides exhibit these properties.

Synergism with Paraffin Deposition

In waxy crudes, the wax has a tendency to become deposited during storage in tanks, or while flowing through pipelines. Deposition in a pipeline severely affects its throughput, so the deposits have to be removed periodically by pigging operations.

The wax deposition behavior of Bombay high crude oil has been studied under different conditions using a cold disk-type assembly (Hameed et al., 1989). It was found that much less deposition occurs with additive-treated crude than with untreated crude under otherwise identical conditions. However, the deposits obtained from treated crude have slightly higher melting points and lower oil content. The wax separation temperature of crude oils can be determined from their viscosity behavior (Khan et al., 1991).

HYDRATE CONTROL

To avoid the plugging of production facilities by hydrates, it is usual practice to add thermodynamic inhibitors, such as methanol or glycol. A newer concept is the injection of low-dosage additives. These can be either kinetic inhibitors, which delay nucleation or prevent the growth of hydrate crystals, or hydrate dispersants, which prevent the agglomeration of hydrate particles and allow them to be transported within the flow (Huo et al., 2001; Palermo et al., 1997).

Hydrate control is discussed extensively in Chapter 13. Classes of hydrate control agents are shown in Table 11.9, and suitable additives are shown in Table 11.10 and in Figure 11.3.

ADDITIVES FOR SLURRY TRANSPORT

The slurry pipeline transport of minerals, the removal of the solids produced during the drilling of wells, and the removal of solids formed during the polishing and grinding of metals all use specific additives. Anionic, cationic, or nonionic surfactants, e.g., cetyltrimethyl ammonium chloride, dodecyl diphenyl oxide disulfonate, and soya bis[2-hydroxyethyl]amine (Rose et al., 1987) may be used to alter the viscosity.

TABLE 11.9 Classes of Additives for Hydrate Control (Goodwin, 1995)

Class	Remark
Thermodynamic inhibitors	Methanol or glycol modify stability range of hydrates
Antinucleants	Prevent nucleation of hydrate crystals
Growth modifiers	Control the growth of hydrate crystals
Slurry additives	Limit the droplet size available for hydrate formation
Anti-agglomerates	Dispersants that remove hydrates

TABLE 11.10 Additives for Hydrate Control for Pipelines

Additive	References
Methanol, glycol[a]	
Poly(*N*-vinyl-2-pyrrolidone)[b]	Sloan (1994)
Alkyl glycosides[c]	Reynhout et al. (1993)
L-Tyrosine and the methyl ester of *L*-tyrosine[d]	Duncum et al. (1993)

a) Thermodynamic inhibitor
b) Growth inhibitor
c) C_8–C_{18} alkyl glycoside with glucose, fructose, etc. For example, 1-O-octyl-β-D-glucopyranoside, dodecyl-β-maltoside
d) Amino acid

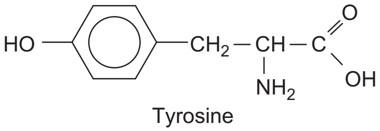
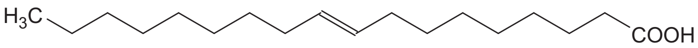
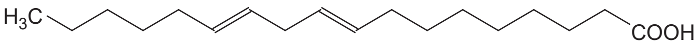


FIGURE 11.3 Tyrosine.

Fatty amines are prepared from the corresponding fats by conversion into the nitrile and hydrogenation. Soybean oil contains a mixture of various long chain acids, mostly oleic acid (9-octadecenoic acid), and linoleic acid (9,12-octadecadienoic acid), that is, C_{18} single and double unsaturated acids, respectively. Components for additives for slurry transport are shown in Figure 11.4. Fatty amines are highly active surfactants.



Oleic acid



Linoleic acid

FIGURE 11.4 Components for additives for slurry transport.

TABLE 11.11 Additives for Odorization (Fakhriev et al., 1994)

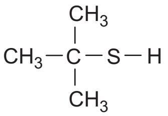
Additive
Ethylmercaptan
Diethyl disulfide
Mixture of ethylmercaptan, propylmercaptan, and butylmercaptans

CH_3-CH_2-SH

Ethylmercaptan

$CH_3-CH_2-CH_2-CH_2-SH$

n-Butylmercaptan



$$CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-S-H$$

tert-Butylmercaptan

$CH_3-CH_2-S-CH_2-CH_3$

Diethyl sulfide

$CH_3-CH_2-S-CH_2-CH_2-CH_3$

Ethylpropylsulfide

FIGURE 11.5 Additives for odorization.

ADDITIVES FOR ODORIZATION

Odorization of natural gas allows its presence to be detected in air before it reaches combustible levels. The most important compounds are given in Table 11.11 and Figure 11.5. The topic is detailed in Chapter 15.

CLEANING

Even carefully built pipelines have been found to contain up to 10 t of waste materials, mostly iron rust, sand, mud, and welding rods. Even shoes, gloves, and bottles have been removed from pipes. Cleaning can generally be achieved by pumping suitable solvents in pigging operations.

Gelled Pigs

Gelled fluid pigs will perform most of the functions of conventional pigs, but they have additional chemical capabilities, and they can be injected into a pipeline through a valve. However, for displacement by a gas, gel pigs must be propelled by a mechanical pig.

Most pipeline gels are water-based, but a variety of chemicals, solvents, and acids can be gelled. Gelled diesel, an organic gel, was first patented for pipeline use in 1973 (Purinton and Mitchell, 1987). The gels can be used for waste material removal, separation of products, placement of biocides and inhibitors, and removal of trapped mechanical pigs (Kennard and McNulty, 1992; Messner, 1991).

An ablating gelatin pig has been described for use in pipelines. Because of the properties of gelatin, the pig will ablate, thereby depositing a protective layer onto the wall of the pipe (Lowther, 1993). The pig can be molded outside the pipe or it can be formed in situ.

The pig is formed by mixing gelatin with a heated liquid and then allowing the mixture to cool to ambient temperature. Preferably, the liquid will contain a corrosion inhibitor or a drag reducer. In some applications, a slug of the treating solution is also passed through the pipeline between two ablating gelatin pigs. For high-temperature applications, a hardener may be added to increase the melting temperature of the pig.

REFERENCES

Almond, N.E., 1989. Pipeline flow improvers. In: Proceedings Volume, API Pipeline Conf., Dallas, April 17–18, 1989, pp. 307–311.

Arai, T., Ohkita, M., 1989. Application of polypropylene coating system to pipeline for high temperature service. In: Proceedings Volume, 8th BHRA Internal & External Protect of Pipes Int. Conf., Florence, Italy, October 24–26, 1989, pp. 189–201.

Aubanel, M.L., Bailly, J.C., 1987. Amorphous high molecular weight copolymers of ethylene and alpha- olefins. EP Patent 243 127, October 28, 1987.

Balzer, J., Feustel, M., Krull, M., Reimann, W., 1995. Graft polymers, their preparation and use as pour point depressants and flow improvers for crude oils, residual oils and middle distillates. US Patent 5 439 981, assigned to Hoechst AG, August 08, 1995.

Bohon, W.M., Ruschau, G.R., 2001. Method for inhibiting external corrosion on an insulated pipeline. US Patent 6 273 144, assigned to Atlantic Richfield Co., August 14, 2001.

Bourgoyne, A.T., 1986. Applied Drilling Engineering, Volume 2 of SPE Textbook Series. Society of Petroleum Engineers, Richardson, TX.

Bromley, M.J., Gaffney, S.H., Jackson, G.E., 1991. Oilfield emulsion control, techniques and chemicals used to separate oil and water. In: Proceedings Volume, Volume 3, Inst. Corrosion UK Corrosion 91 Conf., Manchester, UK, October 22–24, 1991.

Buchheit, R.G., Hinkebein, T.E., Hlava, P.F., Melton, D.G., 1993. The effects of latex additions on centrifugally cast concrete for internal pipeline protection. In: Proceedings Volume, Volume 4, 12th SPE/NACE Int. Corrosion Congr., Houston, September 19–24, 1993, pp. 2854–2864.

Duncum, S.N., Edwards, A.R., Osborne, C.G., 1993. Method for inhibiting hydrate formation. EP Patent 536 950, assigned to British Petroleum Co. Ltd., April 14, 1993.

Duncum, S.N., Hodgson, P.K.G., James, K., Osborne, C.G., 1998a. Inhibitors and their uses in oils. WO Patent 9 821 446, assigned to BP Exploration Oper. Co. Ltd., May 22, 1998.

Duncum, S.N., James, K., Osborne, C.G., 1998b. Wax deposit inhibitors. GB Patent 2 323 095, assigned to BP Exploration Oper. Co. Ltd., September 16, 1998.

Duncum, S.N., James, K., Osborne, C.G., 2000. Wax deposit inhibitors. US Patent 6 140 276, assigned to BP Exploration Oper. Co. Ltd., October 31, 2000.

Dzhanakhmedova, S.D., Pryanikov, E.I., Sulejmanova, S.A., Mamedov, K.K., Dubrovina, E.G., Indyukov, N.M., Sulejmanov, A.B., 1992. Composition for preventing asphaltene-resin- paraffin deposits – contains waste from production of synthetic glycerine, in mixture with polyacrylamide. SU Patent 1 761 772, September 15, 1992.

El-Gamal, I.M., Gad, E.A.M., 1997. Low temperature rheological behavior of umbarka waxy crude and influence of flow improver. Rev. Inst. Franc. Pet. 52 (3), 369–379.

Fakhriev, A.M., Latypova, M.M., Nasteka, V.I., Berdnikov, A.I., Klimov, V.Y., 1994. Odorising agent for compressed hydrocarbon gas – contains ethyl-mercaptan or mixed mercaptans, and additionally waste from process of oxidising de-mercaptanisation of light hydrocarbons. RU Patent 2 009 178, assigned to Hydro Carbon Raw Mat. Res. and Orenburg Gas Process Wks, March 15, 1994.

Falkiner, R.J., Poirier, M.A., 1996. Method for reducing elemental sulfur pick-up by hydrocarbon fluids in a pipeline. CA Patent 2 158 789, April 08, 1996.

Feustel, M., Krull, M., Oschmann, H.J., 2001. Additives for improving the cold flow properties and the storage stability of crude oil [additive zur verbesserung von kaltfliesseigenschaften und lagerstabilitaet von rohoelen]. WO Patent 0 196 503, assigned to Clariant International Ltd., December 20, 2001.

Fung, G.S., Depalm, P.E., Sharma, P., 2002. Pour point depression unit using mild thermal cracker. US Patent 6 337 011, assigned to Halliburton Energy Serv., January 08, 2002.

Gerez, J.M., Pick, A.R., 1996. Heavy oil transportation by pipeline. In: Proceedings Volume, Volume 2, 1st Asme et al Int. Pipeline Conf., Calgary, Can, June 9–13, 1996, pp. 699–710.

Gessell, D.E., Washecheck, P.H., 1990. Composition and method for friction loss reduction. US Patent 4 952 738, assigned to Conoco Inc., August 28, 1990.

Goodwin, S., 1995. Prediction, modelling and management of hydrates using low dosage additives: Pt.1: Additive types and operational implications. In: Proceedings Volume, IBC Tech. Serv. et al Advances in Multiphase Oper. Offshore Conf., London, UK, November 29–30, 1995.

Grabois, R.N., Lee, Y.N., 1991. Use of a water soluble drag reducer in a water/oil/gas system. US Patent 5 027 843, assigned to Conoco Inc., July 02, 1991.

Gregoli, A.A., Olah, A.M., 1992. Low-temperature pipeline emulsion transportation enhancement. US Patent 5 156 652, assigned to Canadian Occident Petrol. Ltd., October 20, 1992.

Hameed, M.S., Taha, E.J., Al-Jarrah, M.M.F., 1989. Observations on the effect of low molecular weights polyethylene-oxides on the flow of water in closed pipes and standard fittings. J. Pet. Res. 8 (1), 47–60.

Handa, S., Hodgson, P.K.G., Ferguson, W.J., 1999. Asphaltene precipitation inhibiting polymer for use in oils. GB Patent 2 337 522, assigned to BP Chemicals Ltd., November 24, 1999.

Heinze, L.R., Shahreyar, N., Baruah, B.M., 2001. A review of past 50 years of paraffin prevention and removal techniques as presented in the swpsc [southwestern petroleum short course]. In: Proceedings Volume, 48th Annu. Southwestern Petrol. Short Course Ass. Inc et al Mtg., Lubbock, TX, April 25–26, 2001, pp. 230–238.

Huo, Z., Freer, E., Lamar, M., Knauss, D.M., Sloan Jr., E.D., Sannigrahi, B., 2001. Hydrate plug prevention by anti-agglomeration. Chem. Eng. Sci. 56 (17), 4979–4991.

Johnson, J.D., Fu, S.L., Bluth, M.J., Marble, R.A., 1996. Inhibiting corrosion. GB Patent 2 299 331, assigned to Nalco Chemical Co., October 02, 1996.

Karydas, A., 1988. Use of organic fluorochemical compounds with oleophobic and hydrophobic groups in asphaltenic crude oils as viscosity reducing agents. EP Patent 256 979, February 24, 1988.

Kashirskij, A.I., Mulyukov, F.G., Popov, V.V., Rukhlin, Y.N., Svetov, A.Y., Glebov, A.V., Puryga, T.V., 1994. Bitumen composition for insulation of pipelines – contains oxidised bitumen and hexamethylenetetramine as additive, giving insulation layer with good mechanical strength and corrosion protection. RU Patent 2 021 309, assigned to S Oil Pipelines Control, October 15, 1994.

Kennard, M.A., McNulty, J.G., 1992. Conventional pipeline-pigging technology: Pt.2: Corrosion-inhibitor deposition using pigs. Pipes Pipelines Int. 37 (4), 14–20.

Kenworthy, T., 2001. Polyurea coatings for offshore oil rigs in the gulf of mexico. Mater. Perf. 40 (10), 40–42.

Khan, H.U., Handoo, J., Agrawal, K.M., Joshi, G.C., 1991. Determination of wax separation temperature of crude oils from their viscosity behaviour. Erdöl Erdgas Kohle 107 (1), 21–22.

Kissel, C.L., 1997. Method for reducing the pour point of an oil and compositions for use therein. US Patent 5 593 955, assigned to Entek Corp., January 14, 1997.

Koshel, K.C., Bhatia, J.S., Kumar, S., Samant, A.K., 1988. Corrosion problem in kalol injection water pipeline system and its control by using corrosion inhibitors. ONGC Bull. 25 (2), 115–133.

Krass, W., Kittel, A., Uhde, A., 1979. Pipelinetechnik: Mineralölfernleitungen, TÜV Handbücher Band 3. Verlag TÜV Rheinland, Köln.

Krull, M., von Halasz, S.P., Reimann, W., Balzer, J., Geiss, H., 1998. Copolymers of ethylenically unsaturated carboxylic acid esters with polyoxyalkylene ethers of lower, unsaturated alcohols as flow-improving agents for paraffin containing oils. US Patent 5 718 821, assigned to Hoechst AG, February 17, 1998.

Lee, Y.N., Wiggins, F.R., 1991. Activation of water-in-oil emulsions of friction reducing polymers for use in saline fluids. US Patent 5 067 508, assigned to Conoco Inc., November 26, 1991.

Li, Y.H., Chesnut, G.R., Richmond, R.D., Beer, G.L., Caldarera, V.P., 1997. Laboratory tests and field implementation of gas drag reduction chemicals. In: Proceedings Volume, SPE Oilfield Chem. Int. Symp., Houston, February 18–21, 1997, pp. 457–469.

Lowther, F.E., 1993. Method for treating tubulars with a gelatin pig. US Patent 5 215 781, assigned to Atlantic Richfield Co., June 01, 1993.

Majumdar, S., Holay, S.H., Singh, R.P., 1980. Adiabatic compressibility and solvation of drag reducing polymers in aqueous solutions. Eur. Polym. J. 16 (12), 1201–1206.

Malik, S., Shintre, S.N., Mashelkar, R.A., 1992. Process for the preparation of a new polymer useful for drag reduction in hydrocarbon fluids in exceptionally dilute polymer solutions. US Patent 5 080 121, assigned to Council Sci & Ind. Researc, January 14, 1992.

Malik, S., Shintre, S.N., Mashelkar, R.A., 1996. A polymer useful for drag reduction in hydrocarbon fluids and its preparations. EP Patent 471 116, assigned to Council Sci & Ind. Researc, March 06, 1996.

McAllister, E.W. (Ed.), 2009. Pipeline Rules of Thumb Handbook: Quick and Accurate Solutions to your Everyday Pipeline Problems, seventh ed. Gulf Professional Publishing, Elsevier Inc., Burlington.

McKerrell, E.H., Lynes, A., 1988. Development of an HPLC (high performance liquid chromatography) method for the determination of nitrogen containing corrosion inhibitors in a mixed hydrocarbon/glycol matrix. In: Proceedings Volume, no. 67, 3rd Royal Soc. Chem. Ind. Chem. in the Oil Ind. Int. Symp., Manchester, UK, April 19–20, 1988, pp. 212–222.

McMahon, A.J., Smith, P.S., Lee, Y., 1997. Drag reducing chemical enables increased sea water injection without increasing the oxygen corrosion rate. In: Proceedings Volume, NACE Int. Corrosion Conf., (Corrosion 97), New Orleans, March 9–14, 1997.

Mendoza, A.L., 1995. Surface active composition for conditioning a gas containing entrained asphaltenes. GB Patent 2 279 964, assigned to Corpoven SA, January 18, 1995.

Messner, S.F., 1991. Cleaning of pipelines with gel pigs (csotavvezetek tisztitasa geles csomala-wqe cokkal). Koolaj Foldgaz 24 (7), 219–222.

Meyer, G., Kessel, D., Rahimian, I., 1995. The effect of pour point depressants of the polyacrylate-type on crude oil (Wirkung von Stockpunkterniedrigern des Polyacrylat-Typs auf Rohöle). Erdöl Kohle-Erdgas-Petrochem. 48 (3), 135–137.

Miyajima, Y., Kariyazono, Y., Funatsu, S., Endo, E., 1993. Durability of polyethylene coated steel pipe at elevated temperature. In: Proceedings Volume, no. 7, 10th BHR Group Ltd et al Pipe Protect Int. Conf., Amsterdam, Netherland, November 10–12, 1993, pp. 183–190.

Mohitpour, M., Golshan, H., Murray, A., 2000. Pipeline Design & Construction: A Practical Approach. American Society of Mechanical Engineers, New York.

Morris, I., Perry, G., 2001. High pressure storage and transport of natural gas containing added C2 or C3, or ammonia, hydrogen fluoride or carbon monoxide. US Patent 6 217 626, assigned to JL Energy Transport Inc., April 17, 2001.

Morris, I., Perry, G., 2001a. Pipeline transmission method. US Patent 6 201 163, assigned to JL Energy Transport Inc., March 13, 2001.

Naiman, M.I., Chang, J.C., 1991. Methods and compositions for reduction of drag in hydrocarbon fluids. US Patent 4 983 186, assigned to Petrolite Corp., January 08, 1991.

Osborne, D., 1993. The development in the use of fre (fiber reinforced epoxy) pipe systems for industrial and offshore applications. In: Proceedings Volume, no. 7, 10th BHR Group Ltd et al Pipe Protect Int. Conf., Amsterdam, Netherland, November 10–12, 1993, pp. 27–45.

Padron, A., 1994. Stable emulsion of viscous crude hydrocarbon in aqueous buffer solution and method for forming and transporting same. CA Patent 2 113 597, assigned to Maraven SA, July 22, 1994.

Padron, A., 1995. Stable emulsion of viscous crude hydrocarbon in aqueous buffer solution and method for forming and transporting same. EP Patent 672 860, assigned to Maraven SA, September 20, 1995.

Padron, A., Castro, L., Zamora, G., 1995. Transportable and stable hydrocarbons in buffer solution dispersions. In: Proceedings Volume, Volume 2, 6th Unitar et al Heavy Crude & Tar Sands Int. Conf., Houston, February 12–17, 1995, pp. 587–596.

Palermo, T., Sinquin, A., Dhulesia, H., Fourest, J.M., 1997. Pilot loop tests of new additives preventing hydrate plugs formation. In: Proceedings Volume, 8th BHR Group Ltd et al Multiphase 97 Int. Conf., Cannes, France, June 18–20, 1997, pp. 133–147.

Palmer, F.H., Wright, A., 1991. Polyurethanes as insulating systems for high temperature marine pipelines. In: Proceedings Volume, BHR Group Ltd et al Pipe Protect Conf., Cannes, France, September 23–25, 1991, pp. 169–187.

Purinton Jr., R.J., Mitchell, S., 1987. Practical applications for gelled fluid pigging. Pipe Line Gas Ind. 66 (3), 55–56.

Reynhout, M.J., Kind, C.E., Klomp, U.C., 1993. A method for preventing or retarding the formation of hydrates. EP Patent 526 929, February 10, 1993.

Rimmer, D.P., Gregoli, A.A., Hamshar, J.A., Yildirim, E., 1992. Pipeline emulsion transportation for heavy oils. In: Schramm, L.L. (Ed.), Emulsions: Fundamentals and Applications in the

Petroleum Industry, Volume 231 of ACS Advances in Chemistry Series. American Chemical Society, Washington, DC, pp. 295–312.

Ritter, W., Herold, C.P., 1990. New aqueous emulsion copolymerizates for improving flow properties of crude oils. WO Patent 9 002 766, March 22, 1990.

Ritter, W., Meyer, C., Zoellner, W., Herold, C.P., von Tapavicza, S., 1989a. Use of selected acrylic and/or methacrylic acid ester copolymers as flow enhancers in paraffin-rich crude oil and crude oil fraction (ii). EP Patent 332 002, September 13, 1989.

Ritter, W., Pietsch, O., Zoellner, W., Herold, C.P., von Tapavicza, S., 1989b. Use of selected acrylic and/or methacrylic acid ester copolymer versions as flow enhancers in paraffin-rich crude oil and crude oil fractions (i). EP Patent 332 000, September 13, 1989.

Rivas, H., Acevedo, S., Gutierrez, X., 1994. Emulsion of viscous hydrocarbon in aqueous buffer solution and method for preparing same. GB Patent 2 274 254, assigned to Intevep, July 20, 1994.

Rodriguez, D., Quintero, L., Terrer, M.T., Jimenez, G.E., Silva, F., Salazar, P.J., 1990. Hydrocarbon dispersions in water. GB Patent 2 231 284, November 14, 1990.

Rose, G.D., Tetot, A.S., Doty, P.A., 1987. Process for reversible thickening of a liquid. GB Patent 2 191 716, December 23, 1987.

Sartori, G., Savage, D.W., Dalrymple, D.C., Ballinger, B.H., Blum, S.C., Wales, W.E., 2001. Esterification of acidic crudes. US Patent 6 251 305, assigned to Exxon Research & Eng. Co., June 26, 2001.

Schriver, G.W., Patil, A.O., Martella, D.J., Lewtas, K., 1995. Substituted fullerenes as flow improvers. US Patent 5 454 961, assigned to Exxon Research & Eng. Co., October 3, 1995.

Sharov, A.G., Terteryan, R.A., Burova, L.I., Shulgaitser, L.A., 1989. Effect of a copolymer inhibitor of paraffin deposits on oils of various fields. Neft Khoz (9), 55–58.

Sloan Jr., E.D., 1994. Method for controlling clathrate hydrates in fluid systems. WO Patent 9 412 761, assigned to Colorado School Mines, June 09, 1994.

Sunil Kumar, M.N., 1989. Review on polymeric and copolymeric pour point depressants for waxy crude oils and studies on bombay high crude oil. Quart. J. Tech. Pap. (Inst. Petrol.) 15, 47–71.

Wirtz, H., von Halasz, S.P., Feustel, M., Balzer, J., 1994. Copolymers, their mixtures with polymers of esters of methacrylic acid and their use in improving the flowability of crude oil at a low temperature. EP Patent 376 138, assigned to Hoechst AG, January 19, 1994.

Wu, Y., 1990. Chemical problems and costs involved in downstream gas systems. In: Proceedings Volume, NACE Int. Corrosion Forum (Corrosion 90), Las Vegas, April 23–27, 1990.

Chapter 12

Drag Reducers

This chapter deals almost exclusively with drag reduction in pipelines for liquid transportation. Pipeline flow improvers, or drag-reducing agents (DRAs), have been utilized in the petroleum industry for many years (Almond, 1989). They are important in oil drilling applications and the maintenance of pumping equipment in pipelines.

The first application of drag reducers was the use of guar in oil well fracturing, which is now a routine practice. One of the first large-scale pipeline applications was to increase the throughput of crude oil on the Trans-Alaskan pipeline in 1979 through the successful use of oil-soluble polymers.

Since then, DRA use has increased in refined products pipelines to offset power costs. The DRA cost incurred to move an additional barrel of product through a pipeline system can be less than $0.05/bbl. This has been made possible by the improved performance of commercially available DRAs and a nearly unchanging price structure.

In the subsea production of oil and gas, production piping presents a significant bottleneck because of the difficulty and expense associated with the installation of subsea piping. The resulting production decrease can have severe economic ramifications because the hydrocarbon production system cannot be run at full capacity (Milligan et al., 2008).

This bottlenecking could be alleviated by either increasing the diameter of the flow lines, increasing the number of flow lines, or reducing the amount of friction loss, thereby allowing more flow through the same diameter lines. The first two options are obviously very expensive, hence reducing friction losses is highly desirable (Milligan et al., 2008).

OPERATING COSTS

Pipeline operators can decrease operating costs by using a drag-reducing flow improver to eliminate the need for underutilized intermediate or booster pump stations (Goudy, 1991; Muth and Kolby, 1985). Product lines operating below

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their capacity, or those that only use boosters intermittently, can also realize cost savings.

The overall benefits are likely to be most significant in 6–8 in. lines operating between 67% and 92% of their rated throughput capacity. Using computer modeling techniques, engineers have demonstrated potential power savings of up to 22% (from lower demand charges and reduced energy use) for systems using booster stations for 85% of the operating time. When stations operate only 70% of the time, total energy cost savings can approach 35%, depending on the diameter of the line and electricity costs.

MECHANISM OF DRAG REDUCTION

A review of drag-reducing polymers is given in the literature (Al-Sarkhi, 2010; Oh-Kil and Ling-Siu, 1996). It has been suggested that drag reduction occurs by the interaction between elastic macromolecules and macrostructures in turbulent flow. In turbulent pipe flow, the region near the wall, which is composed of a viscous sublayer and a buffer layer, plays a major role in drag reduction.

The most serious problem in the effectiveness of drag reducers is the chain degradation of polymers by shear strains under conditions of turbulent flow. Ultra-high molecular weight polymers are more sensitive to shear-induced degradation (Gampert and Wagner, 1985), polymers with linear-chain structures are more vulnerable than branched polymers (Chang and Meng, 1987), and natural gums with semirigid structures (Deshmukh et al., 1985).

The mechanism of shear degradation is thought to be associated with chain elongation. Chain degradation is often observed when the shear rate is increased to a critical point, after which drag reduction decreases sharply.

The friction drag and heat-transfer-reduction phenomena associated with turbulent flows of so-called drag-reducing fluids are not well understood (Kostic, 1994). It is believed that elastic fluid properties are strongly related to these phenomena. However, not all drag-reducing fluids are viscoelastic, nor are all viscoelastic fluids drag-reducing, suggesting that drag reduction and viscoelasticity are probably phenomena that co-occur only incidentally.

It is argued that turbulence suppression, i.e., flow laminarization, is a determining factor in drag reduction, but the fluid elasticity is not, because of the flow-induced anisotropic fluid structure and associated properties. It may, however, be a major cause of laminar heat transfer augmentation.

Damping of Transmission of Eddies

Drag reduction can occur if the transmission of eddies is damped by the viscoelastic properties of fluids. The transfer process of an isolated eddy in viscoelastic Maxwell fluids was studied, and expressions describing such phenomena were obtained (Li, 1991). The results of the study showed that eddy transmission was damped significantly with an increase of the viscoelastic properties of the fluids.

Viscoelastic Fluid Thread

In the extensive literature on polymer drag reduction, it has occasionally been reported that a continuous thread of a high-concentration polymer solution, injected into the axis of a pipe, produces a drag reduction effect on the water flow in the pipe (Hoyt and Sellin, 1988). The thread seems to persist through the length of the pipe and little, if any, diffusion of polymer to the walls of the pipe is apparent.

A polyacrylamide (PAM) polymer was injected as a 0.5% solution from an axially placed nozzle at the bellmouth entrance. The experiments showed that the central thread provided drag reduction that was almost equivalent to premixed solutions of the same total polymer concentration flowing in the pipe. Overall concentrations of 1–20 ppm were used.

The effects were additive: 2 ppm overall thread concentration plus 2 ppm of premixed polymer gave drag reductions equivalent to 4 ppm of either type. Reynolds numbers of up to 300,000 were investigated. In other experiments, a number of different polymer fluids were injected on the centerline of a water pipe flow facility (Hoyt and Sellin, 1991). Two distinct flow regions were identified:

- Reynolds numbers above 25,000, at which centerline injection acted as a rather efficient mixing device for water-soluble polymer and no drag reduction, resulted from materials insoluble in water.
- Reynolds numbers from 10,000 to 25,000, at which strong evidence exists that under certain conditions, a viscoelastic fluid thread can interact with turbulence eddies and reduce the overall flow friction in the pipe.

Polymer Degradation in Turbulent Flow

Drag reduction in turbulent flow is of great potential benefit to many industrial processes, including the long distance transportation of liquids, oil well operations, and transportation of suspensions and slurries, but it is complicated by the problem of polymer degradation.

A capillary rheometer was used to investigate the effect of various parameters on polymer degradation in turbulent flow (Moussa and Tiu, 1994). These parameters included polymer concentration, contraction ratio, pipe length, pipe diameter, number of passes, solvent weight, and molecular weight of polymer. A commercial organic drag reducer, two grades of PAM, and a high molecular weight polyisobutylene were used.

In turbulent flow, the polymer degraded more in a poor solvent at low Reynolds numbers, whereas an opposite effect was observed at high Reynolds numbers. The critical Reynolds number, Re_c or critical apparent shear extensional rate, V/d, was found to increase with polymer concentration and molecular weight, as represented by the dimensionless concentration $c(\eta)$.

Polysaccharide guar gum is used as a turbulent drag reducer in aqueous systems. It reduces the friction drag tremendously in turbulent flow even in small amounts. A study on the mechanical degradation of guar gum has been presented, in which the effectiveness of drag reduction was measured as a function of time using a rotating disk apparatus.

Two different degradation models of a single-relaxation process and a stretched-exponential model were examined. The stretched-exponential model seemed to fit the experimental data better (Hong et al., 2010).

Drag Reduction in Two-phase Flow

The drag-reducing properties of a PAM were tested in two-phase air/water flow, using a horizontal pipe of 31 mm diameter (Saether et al., 1989). The properties of the polymer were tested in single-phase water flow, and the results were found to comply with the reduction in pressure drop found by other workers. Positive effects in two-phase flow were found to depend on the Reynolds number of the liquid flow.

The drag reduction in stratified flow was found to be small or negative. In slug flow, the drag reduction seems to occur in the liquid slug, not in the layer below the bubble. The flow regime seems to be unaffected by the polymer. It has been established that in multiphase flow, drag reducers also act as corrosion inhibitors because they smooth the flow profile near the walls (Kang et al., 1998).

Drag Reduction in Gas Flow

For storage or pipeline transportation of natural gas at pressures over 5.5 MPa (800 psi), it is advantageous to add ammonia to the natural gas, but the ammonia should not create a liquid phase at the temperature and pressure used. A gaseous mixture of ammonia and natural gas can be compressed or pumped using less energy than would be needed for an equivalent volume of natural gas alone. When more than 4% by volume of ammonia is present, pumping through pipelines is also aided by the refrigerant effect of the ammonia, which reduces the temperature of the gas being transported (Morris and Perry, 2001).

Microfibrils

Friction loss in liquids can be reduced by adding a predetermined amount of selected organo-polymeric microfibrils to a liquid (Shinomura, 1988). These microfibrils are insoluble but highly dispersible in the liquid.

An organo-polymeric microfibril is a solid, organic polymer in the form of microfibrils, which have an average diameter in the range of 100–1000 Å, of an average length of 1–500 μ, and an aspect ratio (length/diameter) of 10–1,000,000. Polymeric materials to be processed into microfibrils should be insoluble but highly dispersible in a given liquid.

Drag-reducing Surfactant Solutions

The behavior of two types of drag-reducing surfactant solutions was studied under turbulent flow in pipes of different diameters (Bewersdorff and Ohlendorf, 1988). The surfactant systems contained rod-like micelles consisting of equimolar mixtures of *n*-tetradecyltrimethylammonium bromide, *n*-hexadecyltrimethylammonium bromide, and sodium salicylate.

The structure of the turbulence was studied using a laser-Doppler anemometer in a 50 mm pipe. In the regions of turbulent flow, both surfactant solutions exhibited characteristic flow regimes. In the regions of turbulent flow at low Reynolds numbers, velocity profiles similar to those observed for dilute polymer solutions were found, whereas at maximal drag reduction conditions, more S-shaped profiles that show deviations from a logarithmic profile occur.

Soapy Industrial Cleaner

Experiments have been conducted to investigate the effect of a soapy industrial cleaner on reducing the skin friction of a Jordanian crude oil flowing turbulently in pilot-scale pipes of different sizes. Experiments showed that a concentration of only 2 ppm of the additive injected into the crude oil line caused an appreciable amount of drag reduction (Mansour and Aldoss, 1988). The effects of additive concentration and pipe diameter on drag reduction were investigated.

Lyophobic Performance of the Lining Material

An experimental study was conducted on the characteristics of frictional drag for a lyophobic surface made of polytetrafluoroethylene (PTFE), with a working media of water and machine oil (Saether et al., 1989). The test results indicate that, depending on the lyophobic performance of the lining material, the pipes lined with PTFE have a better drag-reducing effect than conventional steel pipes.

A drag reduction of approximately 12% is achieved if the working medium is water or 6% with machine oil, respectively. In other words, PTFE has a higher lyophobic performance against water than against machine oil.

The theoretical analysis of the flow mechanism on the lyophobic surface shows that treatment can lower the surface energy level to such a degree that the attraction of the solid wall to liquid molecules becomes weaker than the liquid molecular absorption. This effect causes a gliding flow adjacent to the pipe wall, thus reducing the drag.

Interpolymer Complexes

It has been shown that hydrogen bonding-mediated interpolymer complexes can be powerful drag reducers. The drag reduction levels in such polymer systems are a factor of 2–6 greater than their nonassociating polymeric precursors. Their shear stability is also shown to be significantly enhanced (Malik and Mashelkar, 1995).

Hydrocarbon-soluble polymers containing small percentages of polar associating groups are used to determine the effects of polymer associations on solution drag reduction. Experimental data suggest that intrapolymer associations generally decrease the dilute solution drag reduction activities of single associating polymers with like polar groups (Kowalik et al., 1987).

Interpolymer complexes formed by a polymer with anionic groups and one with cationic groups can overcome this limitation and provide enhanced, dilute solution drag reduction activity as a result of favorable interpolymer associations, which build larger structures of higher apparent molecular weight. The latter associations may also increase the resistance of the polymers to degradation in turbulent flows.

DRAG-REDUCING CHEMICALS

Ultra-high Molecular Weight Polyethylene

The flow of liquid hydrocarbons can be enhanced by introducing a nonagglomerating suspension of ultra-high molecular weight polyethylene (UHMWPE) (Dindi et al., 1996; Smith et al., 1995) in water with small amounts of surfactant. The finely divided UHMWPE is prepared by polymerization and then cryogrinded below its glass transition temperature.

Copolymers of α-Olefins

Several copolymers of α-olefins are used as drag reducers. Suggested recipes are summarized in Table 12.1, and monomers are shown in Figure 12.1.

Linear, low density polyethylene is a copolymer of ethylene and α-olefins, obtained by copolymerization utilizing Ziegler-Natta or metallocene catalysts. Concentrates may be prepared by precipitating the polymer from a kerosene solution with isopropanol (Fairchild et al., 1997). The resulting slurry concentrate dissolves rapidly in flowing hydrocarbon streams.

By coating poly-α-olefins with a fatty acid wax as a partitioning agent, and dispersing it in a long chain alcohol, a nonagglomerating, nonaqueous suspension can be obtained (Johnston and Lee, 1998).

Latex Drag Reducers

Latex drag reducers comprise a polymer that is formed via an emulsion-polymerization reaction dispersed in a continuous phase. Subsequent modifications can be applied in order to increase the solubility of the polymer in hydrocarbons.

2-ethylhexyl methacrylate is polymerized by conventional emulsion polymerization techniques, details of which can be found elsewhere (Milligan et al., 2008). The emulsion polymerization reaction yields an initial latex composition, as a stable colloidal dispersion.

TABLE 12.1 Copolymers from α-Olefins and Others Used as Drag Reducers

Comonomer	References
Divinylbenzene/1-hexene, 1-octene, 1-decene, and 1-dodecene[a]	Aubanel and Bailly (1987), Brod et al. (1990), Eaton and Monahan (1999), and Gessell and Washecheck (1990)
Styrene/*N*-vinylpyridine (NVP)	Kowalik et al. (1986)
Ethene/α-olefins[b]	Hostetler et al. (1989)
Homo- or copolymers that α-olefins[c]	Rossi et al. (1993)
Polyisobutene[d]	Martischius et al. (1990)
Meth acrylic acid esters	Ritter et al. (1991a, 1989a, 1991b, 1989b, 1991c, 1995)
C_{12} to C_{18} acrylate or methacrylate/ionic monomer[e]	Malik et al. (1992) and Malik et al. (1996)
tert-Butylstyrene/alkyl acrylate, methacrylic acid	Naiman and Chang (1991)
Acrylamide-acrylate	Schulz et al. (1986, 1987)
Ultra-high molecular weight polyolefin	Mack (1986)
Styrene/methyl styrene sulfonate/NVP[f]	Peiffer et al. (1987)

a) Synthesis by a Ziegler-Natta process
b) Up to C_{30}, Ziegler-Natta
c) Molecular weight of up to 15,000 and an isotacticity of 75% or greater
d) Oil-soluble polymer
e) Reduce friction in the flow of a hydrocarbon fluid by a factor of 5 at concentrations as low as 1–25 ppm
f) Polyampholytes

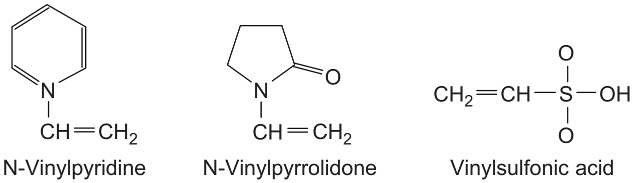

FIGURE 12.1 Vinyl monomers.

The dispersed phase is made up of up to 50% of colloidal particles of the high molecular weight polymer. The continuous phase is water and surfactant. The latex can be modified or formulated with additional surfactants and organic solvents to increase the viscosity. The drag reducer may be injected into the pipeline using conventional or umbilical delivery systems.

Polyether Compounds for Oil-based Well Drilling Fluids

A liquid oil, an emulsifier, and a friction modifier, which includes certain polyether compounds, can be added to a drilling fluid consisting of a water-in-oil emulsion formed from a brine (Malchow, 1997). The friction modifier serves to decrease the coefficient of friction of the well drilling fluid.

Decreasing the coefficient of friction lowers the force required to turn the drill bit in the hole. Gravitational forces increase the coefficient of friction in deviated, horizontal, and extended-reach wells.

Tylose

Tylose is not as effective in drag reduction as other substances described in the literature. Detailed mean velocity, normal Reynolds stress, and pressure drop measurements were performed with 0.4–0.6% aqueous solutions of tylose, a methylhydroxyl cellulose (molecular weight 6 kDalton), after a selection process from a set of low molecular weight fluids (Bewersdorff and Ohlendorf, 1988).

The measurements of the viscosity of these solutions showed shear thinning behavior, and the oscillatory and creep tests measured elastic components of the stress in the order of the minimal detectable values by the rheometer. These low molecular weight polymer solutions delay the transition from laminar to turbulent regimes and show drag reductions of approximately half those which occur with other low elasticity, shear thinning, high molecular, aqueous polymer solutions.

Microencapsulated Polymers

Highly concentrated DRAs may be prepared by microencapsulating a polymer or a monomer, which may be performed before, during, or after polymerization. If the encapsulation is done before or during polymerization, a catalyst must be present, but little or no solvent is required. The result is bulk polymerization within the microcapsule.

The inert capsule or shell may be removed before, during, or after the introduction of the microencapsulated drag reducer into a flowing liquid. No injection probes or other special equipment should be required to introduce the drag-reducing slurry into the liquid stream, nor is grinding (cryogenic or otherwise) of the polymer necessary to form a suitable DRA (Kommareddi and Rzeznik, 1999, 2000).

Aluminum Carboxylate

Aluminum-carboxylate-based DRAs are non-polymeric drag-reducing agents. These additives are not subject to shear degradation and do not cause undesirable changes in the emulsion or fluid quality of the fluid being treated, or undesirable foaming.

The compositions consists of an aluminum carboxylate and fatty acids. The aluminum carboxylates are selected from aluminum salts of fatty acids, including octoates, stearates, oleates, or naphthenates (Jovancicevic et al., 2007). The fatty acids are selected from long chain carboxylic acids. Aluminum salts of a combination of short and long chain carboxylic acids may provide an optimum balance between drag reduction and change in viscosity.

REFERENCES

Almond, N.E., 1989. Pipeline flow improvers. In: Proceedings Volume, API Pipeline Conference, Dallas, April 17–18, 1989, pp. 307–311.

Al-Sarkhi, A., 2010. Drag reduction with polymers in gas-liquid/liquid-liquid flows in pipes: a literature review. J. Nat. Gas Sci. Eng. 2 (1), 41–48.

Aubanel, M.L., Bailly, J.C., 1987. Amorphous high molecular weight copolymers of ethylene and alpha- olefins. EP Patent 243 127, October 28, 1987.

Bewersdorff, H.W., Ohlendorf, D., 1988. The behaviour of drag-reducing cationic surfactant solutions. Colloid Polym. Sci. 266 (10), 941–953.

Brod, M., Venables, P., Lota, G.S., 1990. Crude and heavy fuel flow improvers. AU Patent 603 180, assigned to Exxon Chemical Patents In, November 08, 1990.

Chang, H.F.D., Meng, J.S., 1987. Prediction of drag reduction from rheological properties of dilute polymer solutions. Physicochem. Hydrodyn. 9, 33.

Deshmukh, S.R., Chaturved, P.N., Singh, R.P., 1985. Novel biodegradable flocculants based on polysaccharides. J. Appl. Polym. Sci. 30, 4013–4420.

Dindi, A., Johnston, R.L., Lee, Y.N., Massouda, D.F., 1996. Slurry drag reducer. US Patent 5 539 044, assigned to Conoco Inc., July 23, 1996.

Eaton, G.B., Monahan, M.J., 1999. Composition of and process for forming polyalphaolefin drag reducing agents. US Patent 5 869 570, assigned to Energy & Environ. Int. Lc, February 09, 1999.

Fairchild, K., Tipton, R., Motier, J.F., Kommareddi, N.S., 1997. Low viscosity, high concentration drag reducing agent and method therefor. WO Patent 9 701 582, assigned to Baker Hughes Inc., January 16, 1997.

Gampert, B., Wagner, P., 1985. The Influence of Polymer Additives on Velocity and Temperature Fluid. Springer-Verlag, Berlin, Germany, p. 71.

Gessell, D.E., Washecheck, P.H., 1990. Composition and method for friction loss reduction. US Patent 4 952 738, assigned to Conoco Inc., August 28, 1990.

Goudy, C.F.L., 1991. How flow improvers can reduce liquid line operating costs. Pipe Line Gas Ind. 74 (6), 49–51.

Hong, C., Zhang, K., Choi, H., Yoon, S., 2010. Mechanical degradation of polysaccharide guar gum under turbulent flow. Ind. Eng. Chem. 16 (2), 178–180.

Hostetler, D.E., Kostelnik, R.J., Shanti In, Z.J., 1989. Polymerization process. US Patent 4 845 178, July 04, 1989.

Hoyt, J.W., Sellin, R.H.J., 1988. Drag reduction by centrally-injected polymer "threads". Rheol. Acta 27 (5), 518–522.

Hoyt, J.W., Sellin, R.H.J., 1991. Polymer "threads" and drag reduction. Rheol. Acta 30 (4), 307–315.

Johnston, R.L., Lee, Y.N., 1998. Nonaqueous drag reducing suspensions. WO Patent 9 816 586, assigned to Conoco Inc., April 23, 1998.

Jovancicevic, V., Campbell, S., Ramachandran, S., Hammonds, P., Weghorn, S.J., 2007. Aluminum carboxylate drag reducers for hydrocarbon emulsions. US Patent 7 288 506, assigned to Baker Hughes Incorporated (Houston, TX), October 30, 2007.

Kang, C., Jepson, W.P., Gopal, M., 1998. The effect of drag reducing agents on corrosion in multiphase flow. In: Proceedings Volume, NACE International Corrosion Conference (Corrosion 98), San Diego, March 22–27, 1998. Paper Number 98054, pp. 1–11.

Kommareddi, N.S., Rzeznik, L.J., 1999. Microencapsulated drag reducing agents. WO Patent 9 937 396, assigned to Baker Hughes Inc., July 29, 1999.

Kommareddi, N.S., Rzeznik, L.J., 2000. Microencapsulated drag reducing agents. US Patent 6 126 872, assigned to Baker Hughes Inc., October 03, 2000.

Kostic, M., 1994. On turbulent drag and heat transfer reduction phenomena and laminar heat transfer enhancement in non-circular duct flow of certain non-newtonian fluids. Int. J. Heat Mass Transfer 37, 133–147.

Kowalik, R.M., Duvdevani, I., Kitano, K., Schulz, D.N., 1986. Drag reduction agents for hydrocarbon solutions. US Patent 4 625 745, assigned to Exxon Research & Eng. Co., December 02, 1986.

Kowalik, R.M., Duvdevani, I., Lundberg, R.D., Schulz, D.N., Peiffer, D.G., Kitano, K., 1987. Enhanced drag reduction via interpolymer associations. J. Nonnewton. Fluid Mech. 24 (1), 1–10.

Li, Z., 1991. Effect of fluid viscoelasticity on isolated eddy transmission. J. Univ. Pet. China 15 (5), 33–38.

Mack, M.P., 1986. Improved use of flow improvers. EP Patent 196 350, October 08, 1986.

Malchow Jr., G.A., 1997. Friction modifier for oil-based (invert) well drilling fluids and methods of using the same. US Patent 5 593 953, assigned to Lubrizol Corp., January 14, 1997.

Malik, S., Mashelkar, R.A., 1995. Hydrogen bonding mediated shear stable clusters as drag reducers. Chem. Eng. Sci. 50 (1), 105–116.

Malik, S., Shintre, S.N., Mashelkar, R.A., 1992. Process for the preparation of a new polymer useful for drag reduction in hydrocarbon fluids in exceptionally dilute polymer solutions. US Patent 5 080 121, assigned to Council Sci & Ind. Researc, January 14, 1992.

Malik, S., Shintre, S.N., Mashelkar, R.A., 1996. A polymer useful for drag reduction in hydrocarbon fluids and its preparations. EP Patent 471 116, assigned to Council Sci & Ind. Researc, March 06, 1996.

Mansour, A.R., Aldoss, T., 1988. Drag reduction in pipes carrying crude oil using an industrial cleaner. SPE Unsolicited Pap. (17918-MS), pp. 1–12.

Martischius, F.D., Raab, B., Karau, D., 1990. Process for improving the drag reducing properties of high-molecular weight polymer solutions in crude oil or refined products (verfahren zur verbesserung der fliesswiderstandsvermindernden eigenschaften hochmolekularer polymerloesungen in rohoel oder raffinerieprodukten). EP Patent 397 002, assigned to BASF AG, November 14, 1990.

Milligan, S.N., Harris, W.F., Smith, K.W., Burden, T.L., Johnston, R.L., Anderson, V.S., 2008. Remote delivery of latex drag-reducing agent without introduction of immiscible low-viscosity flow facilitator. US Patent 7 361 628, assigned to ConocoPhillips Company (Houston, TX), April 22, 2008.

Morris, I., Perry, G., 2001. High pressure storage and transport of natural gas containing added C2 or C3, or ammonia, hydrogen fluoride or carbon monoxide. US Patent 6 217 626, assigned to Jl Energy Transport Inc., April 17, 2001.

Moussa, T., Tiu, C., 1994. Factors affecting polymer degradation in turbulent pipe flow. Chem. Eng. Sci. 49 (10), 1681–1692.

Muth, C.L., Kolby, S.M., 1985. Cost saving by use of flow improver. In: Proceedings Volume, 13th International Pipeline Technology Conference, Houston, February 5–7, 1985, pp. 353–357.

Naiman, M.I., Chang, J.C., 1991. Methods and compositions for reduction of drag in hydrocarbon fluids. US Patent 4 983 186, assigned to Petrolite Corp., January 08, 1991.

Oh-Kil, K., Ling-Siu, C., 1996. Drag reducing polymers. In: Joseph, C.S. (Ed.,) Concise Polymeric Materials Encyclopedia. CRC Press, Inc., Boca Raton, FL, pp. 395–397.

Peiffer, D.G., Kowalik, R.M., Lundberg, R.D., 1987. Drag reduction with novel hydrocarbon soluble polyampholytes. US Patent 4 640 945, February 03, 1987.

Ritter, W., Meyer, C., Zoellner, W., Herold, C.P., Tapavicza, S.V., 1991a. Copolymers of (meth)-acrylic acid esters as flow improvers in oils. US Patent 5 039 432, assigned to Henkel KG Auf Aktien, August 13, 1991.

Ritter, W., Meyer, C., Zoellner, W., Herold, C.P., von Tapavicza, S., 1989a. Use of selected acrylic and/or methacrylic acid ester copolymers as flow enhancers in paraffin-rich crude oil and crude oil fraction (ii) (verwendung ausgewaehlter copolymeren der acryl- und/oder methacrylsaeureester als fliessverbesserer in paraffinreichen erdoelen und erdoelfraktionen (ii)). EP Patent 332 002, September 13, 1989.

Ritter, W., Meyer, C., Zollner, W., Herold, C.P., von Tapavicza, S., 1991b. Copolymers of acrylic acid and/or methacrylic acid esters as flow improvers. AU Patent 611 265, assigned to Henkel KG Auf Aktien, June 06, 1991.

Ritter, W., Pietsch, O., Zoellner, W., Herold, C.P., von Tapavicza, S., 1989b. Use of selected acrylic and/or methacrylic acid ester copolymer versions as flow enhancers in paraffin-rich crude oil and crude oil fractions (i) (verwendung ausgewaehlter copolymertypen der acryl- und/oder methacrylsaeureester als fliessverbesserer in paraffinreichen erdoelen und erdoelfraktionen (i)). EP Patent 332 000, September 13, 1989.

Ritter, W., Pietsch, O., Zoellner, W., Herold, C.P., von Tapavicza, S., 1991c. Copolymers of acrylic and/or methacrylic acid esters as flow improvers. AU Patent 610 700, assigned to Henkel KG Auf Aktien, May 23, 1991.

Ritter, W., Pietsch, O., Zoellner, W., Herold, C.P., von Tapavicza, S., 1995. Copolymers of (meth) acrylic acid esters as flow improvers in petroleum oils. CA Patent 1 334 013, assigned to Henkel KG Auf Aktien, January 17, 1995.

Rossi, A., Chandler, J.E., Barbour, R., 1993. Polymers and additive compositions. WO Patent 9 319 106, assigned to Exxon Chemical Patents In, September 30, 1993.

Saether, G., Kubberud, K., Nuland, S., Lingelem, M., 1989. Drag reduction in two-phase flow. In: Proceedings Volume, 4th Bhra Multi-Phase Flow International Conference, Nice, Fr, June 19–21, 1989, pp. 171–184.

Schulz, D.N., Maurer, J.J., Bock, J., Kowalik, R.M., 1986. Process for the formation of novel acrylamide acrylate copolymers. CA Patent 1 213 606, November 04, 1986.

Schulz, D.N., Maurer, J.J., Bock, J., Kowalik, R.M., 1987. A process for the formation of novel acrylamide acrylate copolymers. EP Patent 116 779, January 14, 1987.

Shinomura, T., 1988. Method of reducing friction losses in flowing liquids. US Patent 4 751 937, June 21, 1988.

Smith, K.W., Haynes, L.V., Massouda, D.F., 1995. Solvent free oil soluble drag reducing polymer suspension. US Patent 5 449 732, assigned to Conoco Inc., September 12, 1995.

Chapter 13

Gas Hydrate Control

In petroleum technology, gas hydrates are undesirable compounds that may be formed during production of transportation of natural gas. Large accumulations of gas hydrates are, however, known in nature, and these are now considered as potential non-conventional energy sources.

Gas hydrates were first described by Davy in 1810 (Davy, 1811), based on chlorine, but hydrocarbon-based gas hydrates only became relevant more than 100 years later. The history and issues of gas hydrates has been reviewed in the literature (Barone and Chianese, 2009), and important milestones in the field of gas hydrates are summarized in Table 13.1. There are several monographs and review articles of both the physical and the physicochemical aspects of natural gas hydrates (Carroll, 2009; Sloan and Koh, 2008), as well as the geological aspects (Beauchamp, 2004; Max, 2003).

Gas hydrates are crystalline inclusion compounds of gas molecules in water, which form at low temperature and high pressures. The water molecules form cage structures around the appropriate gas molecules. The lattice structure formed from the water molecules is thermodynamically unstable and is always stabilized by the incorporation of gas molecules. Depending on pressure and gas composition, these ice-like compounds can exist above the freezing point of water, at up to 25°C. In the crude oil and natural gas industry, great significance attaches to the hydrates, which form from water and methane, ethane, propane, isobutane, *n*-butane, nitrogen, carbon dioxide, or hydrogen sulfide. They pose a great problem in modern natural gas extraction, especially in conditions where wet gas or multiphasic mixtures of water, gas, and alkane mixtures are subjected to low temperatures under high pressure. Because of their insolubility and crystalline structure, the formation of gas hydrates leads to the blockage of extraction equipment such as pipelines, valves, or production equipment in which wet gas or multiphase mixtures are transported over long distances; as occurs in colder regions or on the seabed (Dahlmann and Feustel, 2008a). Gas hydrate formation can also lead to problems in drilling operations.

Gas hydrate formation can be suppressed by using relatively large amounts of smaller alcohols such as methanol, glycol, or diethylene glycol. These

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TABLE 13.1 Important Milestones of Gas Hydrates (Sloan and Koh, 2008)

Year	Event
1810	First chlorine hydrate described (Davy, 1811)
1884	Study of phase diagrams (Roozeboom, 1884)
1936	Separation of rare gases by SO_2 hydrates (Makogon, 1994; Prytz and Nikitin, 1936)
1934	Studies on inhibition of gas hydrates (Hammerschmidt, 1934)
1942	Storage and transportation by gas hydrates (Benesh, 1942)
1959	Extensive crystallographic studies
1965	Discovery of gas hydrates in the Siberian permafrost
1974	Discovery of gas hydrates in Canada
1994	In situ sH hydrates in the Gulf of Mexico
1999	Hydrates as storage material for H_2 (Dyadin et al., 1999a,b)
2006	Indian National Gas Hydrate Program expedition

additives cause the thermodynamic limit of gas hydrate formation to shift to lower temperatures and higher pressures (thermodynamic inhibition), but they can cause serious safety problems (flash point and toxicity of the alcohols), logistic problems (large storage tanks, recycling of these solvents), and accordingly high costs, especially in offshore extraction.

Attempts are therefore being made to replace these inhibitors by using additives in amounts of $<2\%$ in temperature and pressure ranges in which gas hydrates can form. These additives either delay gas hydrate formation (kinetic inhibitors) or keep the gas hydrate agglomerates small and therefore pumpable, so that they can be transported through the pipeline. The inhibitors either prevent nucleation and the growth of the gas hydrate particles, or they modify the hydrate growth in such a way that relatively small hydrate particles result.

A great many compounds act as gas hydrate inhibitors. There are also a number of kinetic or agglomeration inhibitors. Polymers with a carbon backbone that contains both cyclic (pyrrolidone or caprolactam moieties) and acyclic amide structures in the side groups (Dahlmann and Feustel, 2008a) are particularly interesting in this respect.

NATURALLY OCCURRING GAS HYDRATES

The vast majority of gas hydrates occur naturally; the largest accumulations of natural gas on earth are in the form of gas hydrates, found mainly offshore in the outer continental margin sediment and also in the polar regions. The hydrocarbon gas composition and their isotope pattern indicates that these methane/water clathrates originate mainly from the microbial reduction of CO_2 in sedimentary organic matter. However, in the Gulf of Mexico and the Caspian Sea a thermogenically formed methane has been detected (Kvenvolden, 1995).

Large gas hydrate accumulations have been located in the terrestrial permafrost regions. These resources are considered as potential non-conventional energy sources in our planet. Here, gas hydrates may exist at subsurface depths ranging from about 130–2000 m (Mandal, 2007). Estimates of the amount of gas that exist in this type of accumulation differ by several orders of magnitude. Some authors estimate them in the range of some 10^{15} m^3 (Mandal, 2007; Milkov and Sassen, 2002) and others in the range of 10 Tt (Beauchamp, 2004; Kvenvolden and Lorenson, 2001). There is significant interest concerning their commercial use, although the matter should be assessed with considerable care (Bil, 2003).

PROBLEMS WITH GAS HYDRATES IN PETROLEUM TECHNOLOGY

The main problem with hydrate formation arises in pipelines that transport natural gas, because they are solids and deposit. The solid deposits reduce the effective diameter of the pipe and can therefore restrict or even clog the flow.

Experience indicates that large gas hydrate plugs in gas and oil pipelines form most actively during unforeseen long shut downs. In static conditions, three types of hydrate crystals can be formed (Makogon, 1996):

1. Surface-contact films and massive hydrates, which form by sorption of gas and water molecules onto the surfaces of growing crystals;
2. Bulk diffusional, whisker-like hydrate, which forms both in the volume of gas and in the bulk of liquid water, through sorption of molecules onto the growing crystal surface and by tunnel sorption of molecules at the base of the crystal; and
3. Gel-like soft crystals, which form in the bulk of liquid water at low concentrations of dissolved gas in water.

Under the appropriate pressure and temperature conditions there may be a simultaneous formation of some crystals and a decomposition of other crystals. The following precautions can be undertaken to prevent damage to the pipe (Klomp et al., 1997):

- Removal of free water,
- Maintaining elevated temperatures or reduced pressures, and
- Addition of melting point depressants.

The formation of condensates, hydrates, or ice may also occur in the course of decompression of natural gas stored in natural reservoirs, e.g., in salt caverns. The operation of oil and gas pipelines in the deep ocean is significantly complicated by the formation of gas hydrates (Mei et al., 1996).

Antifreeze agents, such as low molecular weight alcohols and glycols, must be added in substantial amounts to be effective, typically at levels of over 10% (Klomp et al., 1997), which is expensive. In addition, the recovery of these materials is complicated and expensive.

An attractive alternative to antifreeze agents is the use of crystal growth inhibitors (Klomp et al., 1997), which interfere with the kinetics of the growth of gas hydrate crystals. These issues will be discussed in detail below.

NATURE OF INCLUSION COMPOUNDS

Clathrates are crystalline addition compounds of at least two molecules, bound mainly by van der Waals forces. One compound, the host, makes up the structure. The other partner, the guest, is placed in the free spaces of the crystal lattice. If the free space is closed in every direction, then these compounds are considered clathrates in the closed sense. The structure of clathrates is illustrated in Figure 13.1.

Other types of inclusion compounds are channel inclusion compounds and layer inclusion compounds (Carroll, 2009; Makogon, 1981; Weber, 1987).

The size of the free space varies with the size and the shape of the molecule to be included. This fact is used in the separation of molecules. A relevant example in petroleum refinement is the separation of paraffins from other compounds by use of urea. In this case, a channel-like lattice is formed by urea with linear alkanes, e.g., *n*-octane embedded in the free space whereas branched alkanes, e.g., *i*-octane cannot be included.

Graphite is a host molecule with a layer-like structure. Various types of both organic and inorganic inclusion compounds, as well as stoichiometric and non-stoichiometric compounds, are known.

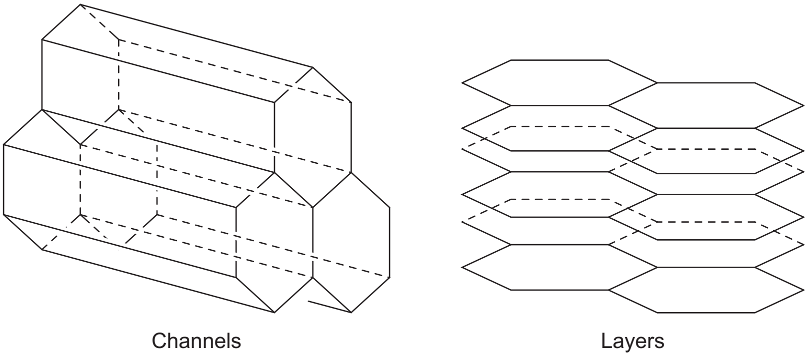

FIGURE 13.1 Structure of clathrates.

Gas Hydrates

Gas hydrates are a special form of clathrate where water is the host molecule. Hydrates have been classified by the arrangement of the water molecules in the crystal, i.e., after the crystal structure (Carroll, 2009). According to this classification, there are three types of gas hydrates; type I, type II, and type H. H refers to heavy.

Table 13.2 shows that the number of water molecules required to form the hydrate increases with the size of the guest molecule to be captured. Hydrates are classified into simple and mixed hydrates depending on whether one or more host or guest molecules are included.

Besides the main classes, several subclasses of gas hydrates haves been identified. Their crystallographic structures can be established by X-ray diffraction, whereas the microstructures can be assessed by cryo-stage field-emission scanning electron microscopy (Klapp et al., 2010). Early research into the structure of gas hydrates dates back to von Stackelberg (Stackelberg and Müller, 1951).

Type I Hydrates

The simplest type of hydrates is type I, which has a crystallographic unit cell containing 46 water molecules. There are two types of cages: small and large. The small cage has a the form of a pentagonal dodecahedron, i.e., a polyhedron, with 12 faces that are regular pentagons. Many structures of gas hydrated can be found in the literature (Carroll, 2009, p. 19).

The large cage has a tetradecahedron structure, which is a polyhedron with 14 faces: 12 of regular pentagons and 2 of regular hexagons.

In type I hydrates, the guest molecules CO_2 and CH_4 can enter both the small and the large cages, whereas larger molecules, e.g., ethane, may fill only the

TABLE 13.2 Composition of Gas Hydrates

Hydrate	Chemical Composition
Methane	$CH_4 \times 6\,H_2O$
Ethane	$C_2H_6 \times 8\,H_2O$
Propane	$C_3H_8 \times 17\,H_2O$
Isobutane	$C_4H_{10} \times 17\,H_2O$
Nitrogen	$N_2 \times 6\,H_2O$
Carbon dioxide	$CO_2 \times 6\,H_2O$
Hydrogen sulfide	$H_2S \times 6\,H_2O$

large cages. The cages are not filled in a regular way, therefore, these hydrates are non-stoichiometric compounds.

Type II Hydrates

Type II gas hydrates have larger crystallographic unit cells containing 136 water molecules. The small cage is built as a pentagonal dodecahedron, like the type I hydrates, but the large cage consists of a hexakaidodecahedron. This polyhedron has a total of 16 faces, with 12 being regular pentagons and 4 being regular hexagons.

O_2 and N_2 are guest molecules for type II hydrates. As in type I hydrates small molecules can fill both the small and the large cages, whereas larger guest molecules can fill only the large cages.

Type H Hydrates

In 1987 a new type of hydrate was discovered. Higher molecular weight compounds, such as benzene, cyclopentane, methylcyclopentane, cyclohexane, methylcyclohexane, isopentane, and 2,3-dimethylbutane may form gas hydrates of type H. Recent studies show that in certain circumstances, the effect of the heavy hydrate formers cannot be ignored and, in some cases, they significantly reduce the hydrate-free zone (Tohidi et al., 1996).

Structure H formation requires the presence of two different types of guest molecules: a smaller component, such as methane or hydrogen sulfide, and a large molecule, such as *i*-pentane or heavier hydrocarbons, which may occur naturally in petroleum. No aromatic molecules act as guests for this hydrate structure (Thomas and Behar, 1994). Structure H-hydrates are somewhat more stable than methane hydrates at higher temperatures.

A variety of systems have been investigated with respect to stability-covering systems of methane-2-methylbutane-water, methane-2,2-dimethylbutane-water, methane-*tert*-butyl methyl ether-water, and methane-adamantane-water (Huetz and Englezos, 1995; Makogon et al., 1996). A substantial inhibiting effect is observed in the presence of NaCl. Adamantane and related products in the formation of gas hydrates are shown in Figure 13.2.

Thermodynamic data suggest that H-hydrate structures may form in gas and oil reservoirs and industrial installations. Hydrates formed with methane and adamantane have been found in situ in Mobile Bay in the Gulf of Mexico

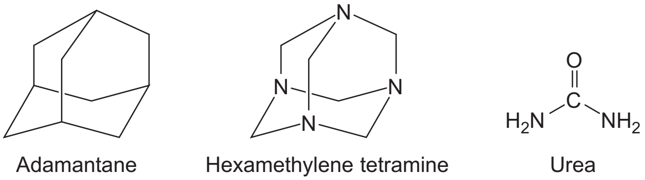

FIGURE 13.2 Hydrate guests.

(Mehta and Sloan, 1993). Since H-hydrates are now recognized as a potential problem in the petroleum industry, the existing hydrate prediction programs should be questioned and the hydrate phase itself should be measured, in contrast to previous experimental practices (Mehta and Sloan, 1996).

CONDITIONS FOR FORMATION

Water Content

The water content of a natural gas is a crucial parameter for the formation of gas hydrates, at least in transporting systems, since clearly, a water-free gas will not be able to form gas hydrates. Natural gas contains water in the range of 8000–10,000 ppm by volume, and specifications for pipelining restrict the water content to 120–160 ppm so drying the gas is essential. The reasons for this limitation are not only the risk of hydrate formation, but also potential corrosion problems.

The water content is most conveniently measured via the dew point, but electrical and optical methods are also available. The dew point is connected most directly to hydrate formation, because it is believed that condensate formation is essential to the formation of hydrates.

Decomposition

Clathrates and, in particular, gas hydrates can be decomposed very easily by dissolving or melting the crystal lattice of the host molecule.

Stability Diagram

Hydrates are stable below a certain temperature and above a certain pressure. A p–T stability diagram is shown in Figure 13.3.

The curve is significantly shifted to lower pressures for gases containing compounds with higher molecular weight. For gas mixtures without hydrogen sulfide, the gas may serve as parameter to estimate the conditions under which hydrate will be stable. Similar p–T diagrams to that for methane are given with the relative density of the gas in tables and figures in the literature.

Clausius-Clapeyron Equation

In some regions, the equilibrium pressure of coexistence of a gas hydrate with the corresponding gaseous state follows a Clausius-Clapeyron relation:

$$\ln p = A + \frac{B}{T} \tag{13.1}$$

Figure 13.4 shows the same data as plotted in Figure 13.3, but recalculated as the logarithm of the pressure and the reciprocal of the absolute temperature.

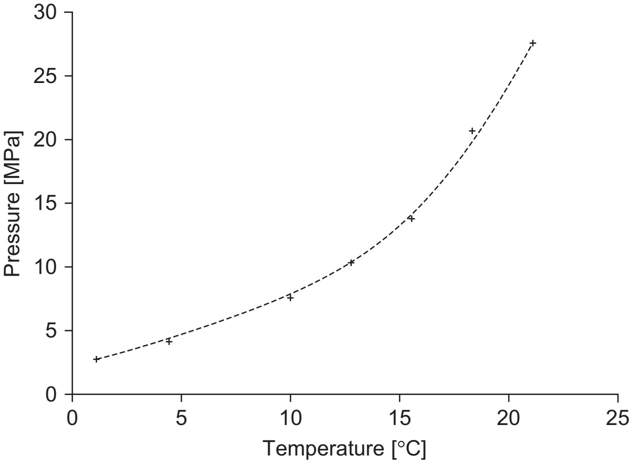

FIGURE 13.3 *p–T* Stability diagram of methane hydrate.

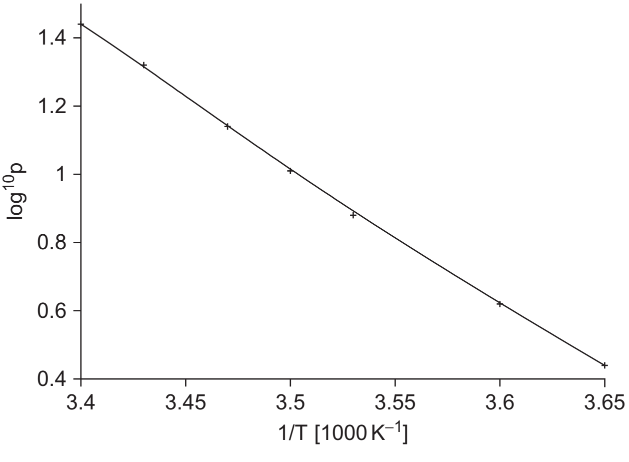

FIGURE 13.4 Clausius-Clapeyron linearized plot.

At elevated temperatures the relationship changes into:

$$\ln p = A + BT + CT^2 \tag{13.2}$$

The parameters A, B, and C depend on the particular nature of the gas. Katz developed a simple method for gas mixtures that takes the composition of the gas into account (Katz, 1959; Lee and Katz, 1991), and a graphic method is available that permits the estimation of hydrate-forming temperatures for natural gas containing up to 50% hydrogen sulfide (Baillie and Wichert, 1987).

Hammerschmidt Equation

Methanol has already been identified as a simple and cost-effective method hydrate inhibitor by Hammerschmidt (1934, 1939). The Hammerschmidt equation was the first to predict the freezing point depression, but is not directly related to the colligative properties:

$$\Delta T = \frac{1300}{M} \frac{I}{100 - I} \tag{13.3}$$

Here, ΔT is the freezing point depression in °C, I the amount of inhibitor added in weight percent, and M is the molecular weight of the inhibitor in $\mathrm{g\,mol^{-1}}$. For example, for 25% methanol, the freezing point depression is calculated as 13.5°C.

Eq. 13.3 is based on more than 100 experimental determinations of the freezing point depression (Sloan and Koh, 2008, p. 203), but proved to be not very accurate and does not take into account the dependence of the gas pressure on the freezing point depression. For this reason, various modifications and other methods for prediction of freezing point depression, have appeared (Nielsen and Bucklin, 1983) that are dealt with elsewhere (Sloan and Koh, 2008, p. 203).

On the other hand, attempts have been made to produce a theoretical basis for the Hammerschmidt equation (Nielsen and Bucklin, 1983; Pieroen, 1955). If certain assumptions are made, e.g., if the inhibitor is not soluble, the Hammerschmidt equation can be reduced to well-known expressions obtained from thermodynamics.

Other methods are for calculating the necessary amount of inhibitor, preferably methanol, include the K-chart method, and the CSMGem method (Bullin and Bullin, 2004; GPSA, 2004; Sloan and Koh, 2008). The latter is software that has been developed by the Colorado School of Mines (CSM) for the prediction of hydrate equilibria (Pratt and Sloan, 1995; Sloan, 2009).

FORMATION AND PROPERTIES OF GAS HYDRATES

Hydrate formation is believed to occur in two steps: a nucleation step followed by a growth reaction of the nucleus. Experimental nucleation results are difficult to reproduce, so stochastic models would be useful for investigating the mechanism of formation. Hydrate nucleation is an intrinsically stochastic process that involves the formation and growth of gas-water clusters to critical-sized, stable hydrate nuclei. The growth process involves the growth of stable hydrate nuclei into solid hydrates (Baillie and Wichert, 1987).

Two-Step Mechanism of Formation

The addition of surfactants in small quantities has a substantial effect on the kinetic characteristics of hydrate formation without changing the equilibrium parameters, because they reduce the surface tension at the liquid-gas interface considerably. Concentrations of surfactant that increase the induction period of hydrate formation of propane hydrates also increase the subsequent growth rate of the hydrate phase (Kutergin et al., 1992). The effect of stirring on the kinetics of formation of hydrate formation does not seem to be pronounced (Christiansen et al., 1994).

This contrasts with other results, which found that the induction time is strongly dependent on the stirring rate and the driving force (Skovborg et al., 1993). Experiments conducted at the same stirring rate and with a high driving force seem to show that the induction time varies exponentially with the size of the driving force. Surface effects are reported on the nucleation. For example, diatomaceous earth and synthetic amorphous silica were found to nucleate hydrate formation (Sloan and Christiansen, 1995).

Nucleation Particle Sizes

The nucleation and growth of gas hydrate crystals has been investigated by optical methods at different pressures and temperatures. The particle sizes measured during gas hydrate nucleation ranged from 2–80 nm (Nerheim et al., 1992, 1994). The nucleation process is nondeterministic, because of a probabilistic element within the nucleation mechanism (Parent and Bishnoi, 1996).

Clustering Before Nucleation

A controversy exists regarding the early stages of formation of gas hydrates. The mechanism proposed by Sloan and Fleyfel for the kinetics of hydrate formation consists of (Christiansen and Sloan, 1993; Fleyfel et al., 1993; Sloan and Fleyfel, 1991):

1. The formation of clusters of hydrogen-bonded water molecules around different sizes of apolar molecules and
2. The joining of these clusters to create a hydrate nucleus.

The hypothesis was extended to nucleation of hydrates from liquid water. An alternative hypothesis was proposed by Rodger (Rodger et al., 1995). The main difference between these two sets of theories is that Rodger's hypothesis relates the initial formation process to the surface of the water, whereas the theory of Sloan and coworkers considers clusters to be related to soluted hydrate formers in liquid water as the primary start for joining, agglomeration, and crystal growth. The theories of Sloan and coworkers have been discussed and related to elements of the hypothesis proposed by Rodger (Kvamme, 1993).

Experimental Methods

One of the major goals of research is to find additives that can inhibit hydrate crystallization. This goal is not restricted to gas hydrates, but applies to all scales that could be formed. Inhibitors of crystallization may be effective generally for a variety of mineral scales or, in some cases, may be selected to act on a narrower range.

Such generality and specificity of action may be understood in terms of stereospecific and nonspecific mechanisms of scale inhibition. New techniques for comparing the effectiveness and activity of hydrate inhibitors and laboratory results on various chemicals have been described.

Modern experimental methods are used to obtain information about interactions between potential crystallization inhibitors and the substrates themselves. By combining atomic force microscopy, scanning electron microscopy, and optical microscopy, both stereospecific and nonspecific interactions of inhibitors with various crystal species (e.g., calcite, calcium oxalate monohydrate, and ice) have been examined. The crystals were chosen as representatives of strong ionic, hydrated ionic, and hydrogen-bonded lattices. Both stereospecific and nonspecific interactions were observed in each case (Sikes and Wierzbicki, 1996). The strongest interactions of the adsorbate with the crystal surfaces were elucidated at the angstrom level with good agreement being observed between experiment and theory. Such a definition of the weaker interactions requires more work, and in fact may be beyond the scope of current methodology, but reasonable models of each of the interactions have been proposed.

Modeling the Formation of Gas Hydrates

Several packages are available to predict hydrate formation conditions with respect to pressure, temperature, and some special inhibitors. The models are based on thermodynamic considerations rather than on kinetic arguments. An algorithm has been developed to predict the formation of hydrates in systems containing oil or gas in equilibrium with water on the basis of purely thermodynamic correlations (Avlonitis et al., 1989). For a specified temperature and feed composition, the program computes the equilibrium pressure at the hydrate point. The authors report that the predictions are satisfactory for gas-water hydrate forming mixtures, but not for oil-water systems.

A practical model for the effect of alcohol and salinity on gas hydrate formation has been implemented as a stand-alone computer program, that either accesses the model via a spreadsheet or uses the model as an object code. A critical comparison of the various packages available has been given in the literature (Daubert, 1992), which evaluated four methods of hydrate prediction, namely, GPA/CSM, EQUI–PHASE, GPA/AQUA*SIM, and API/HYDRATE.

TEST PROCEDURES FOR INHIBITORS

In the literature, several test procedures have been described for assessing the performance of newly synthesized additives for the inhibition of gas hydrates. The procedures can be roughly subdivided into procedures that simulate real flow conditions and those that screen under performance to simplified test conditions. Unfortunately, these procedures are not really comparable, so only the results of series of specific tests can be compared safely.

Screening Method

Screening experiments have been shown to be much simpler than the simulation of field flow conditions (Klomp et al., 1997). In such procedures, a mixture of tetrahydrofuran and water is used to simulate a wet gas, because this material can form hydrate crystals in the same temperature range as a wet gas, but crystal formation takes place at atmospheric pressure. For example, a hydrate with a melting point of 4.3°C at atmospheric pressure containing 19% water is observed for tetrahydrofuran.

The effect of various additives on the growth of a single hydrate crystal has been studied as follows by adding the 0.5% of additive to a mixture of 18.9% tetrahydrofuran in water with 3% of NaCl. The solution is kept in a glass vessel at atmospheric pressure, and immersed in a thermostat at the freezing point of water. When the system reaches thermal equilibrium, a small subcooled ice crystal of ca. 0.1 g is introduced into the solution. After 3 h, the weight of the crystals is measured and their morphology inspected.

High Pressure Sapphire Cell

The performance of the hydrate inhibitor polymers can be estimated by using a high pressure sapphire cell (Kelland et al., 2006; Klug and Kelland, 2002) mounted in a thermostat at subambient temperature. The apparatus consists of a sapphire tube enclosed in a holder between two stainless steel end pieces. Inside the cell is a magnetic stirrer whose speed is measured by using a stroboscope.

The cell contains two temperature sensors for the measurement of the temperature in both the gas phase and in the water bath. The pressure is measured by a pressure transducer through the inlet tubing connection in the top end piece of the cell.

The tests are performed using synthetic sea water and synthetic natural gas. The additive to be tested is dissolved in the synthetic sea water, and the system is pressurized with synthetic gas. The gas consumed by hydrate formation is measured, as well as the torque necessary to keep the stirring speed at a constant value. Since no further gas is delivered during hydrate formation, the experiments are not conducted under isobaric conditions.

Circulating Loop

A rather complicated experimental setup is needed to simulate field flow conditions. A stainless steel pipe loop and a gear pump, coupled with a mixing tank for the additive under investigation is used to circulate a mixture of water and liquid hydrocarbons through the loop.

The pipe loop is divided into several sections, each being equipped with a thermometer and a differential pressure meter. The pressure meter allows the pressure drop over each individual section to be monitored, which is indicative for the formation of gas hydrates.

The formation of hydrate is triggered by cooling a certain section of the loop down to −15°C. This cold spot is switched-off immediately when the first hydrates are monitored. A standard test procedure is used, including programmed cooling, stopping the circulation temporarily, etc. The test procedure is given in detail in the literature (Klomp and Reijnhart, 1999).

INHIBITION OF GAS HYDRATE FORMATION

Both thermodynamic and kinetic factors affect the inhibition of hydrate deposits.

Drying

Hydrate formation can be prevented by drying a gas to such an extent that no condensate can be formed. This method is preferred, but inhibition of hydrate formation from the liquid phase can be achieved.

Thermodynamic Inhibition with Additives

The hydrate formation temperature can be reduced by the addition of antifreeze agents such as methanol, glycols (Petersen et al., 1991), or brines, as already mentioned. The depression of the freezing point is given by a generalized Hammerschmidt equation:

$$\Delta T = K \frac{I}{100 - I} \tag{13.4}$$

where K is a specific parameter dependent on the nature of the additive and I is the amount of antifreeze in percent with respect to water. Note that in the case of volatile additives, the additive will be partially present in the water phase, and partially in the gas phase.

Brines have inherently corrosive properties and therefore are not suitable for use. Ethylene glycol is preferred because of its low cost and low solubility in hydrocarbons. The cryoscopic depression of some substances is shown in Table 13.3. Some combination of alcohols and carboxylic acid salts may provide a synergistic cryoscopic depression effect (Lugo et al., 2010).

Kinetic Inhibition

As mentioned previously, alcohol is the classic additive to prevent hydrate formation. Traditional hydrate inhibitors such as methanol and glycols have been in use for many years, but the demand for cheaper methods of inhibition is great. Therefore the development of alternative, cost-effective, and environmentally acceptable hydrate inhibitors is a technological challenge for the oil and gas industry (Kelland et al., 1995).

TABLE 13.3 Cryoscopic Depression of the Freezing Point (Lugo et al., 2010)

Substance	Depression/[K]
Sodium lactate	9.8
Sodium acetate	12.5
Sodium formate	11.8
Glycerol	5.6
Monoethylene glycol	7.8
Methanol	14.8
Sodium chloride	16.6

Nucleation Inhibitors

Crystals formation can be subdivided into two stages: the formation of precursors, i.e., nuclei and the growth of these nuclei as they develop into crystals. Nucleation inhibitors act on the precursor stage.

Polyethylene Oxide

An aqueous solution of polyethylene oxide can be introduced into a petroleum fluid either by using mechanical equipment or by utilizing it in treating fluid. Experimental data indicate that these positively charged polymers interfere with the nucleation of hydrates, increase the induction time of gas hydrate nucleation, suppress the memory effect, and act as antifreeze agents, thereby controlling the formation of hydrates (Kannan and Punase, 2009).

Crystal Growth Inhibitors

Certain alkylated ammonium, phosphonium, or sulfonium compounds are effective, in relatively low concentrations, in interfering with the growth of gas hydrate crystals (Klomp et al., 1995). Gas hydrate or ice formation is further inhibited in lines by adding amino acids or amino alcohols (Duncum et al., 1994).

Crystallization kinetics in the presence of polypolyvinylpyrrolidone and tyrosine have been examined by time-resolved experiments (Koh et al., 1996). An influence is evident on the particle size distribution of the hydrate (Pic et al., 2001).

Certain alkylated ammonium or phosphonium compounds are very effective as crystal growth inhibitors at comparatively low concentrations (Klomp et al., 1997), so they can be very useful for inhibiting the plugging of conduits by gas hydrates containing low boiling hydrocarbons and water. They are also biodegradable. Compounds containing an ester linkage are preferred, as the ester linkage imparts biodegradability.

Several alkylated ammonium or phosphonium compounds have been tested with respect to their ability to inhibit crystal growth. In Table 13.4, selected results from a large series of experiments using the screening method are reproduced. These results show that the additives resulting in crystals having a weight of less than 3.0 g and exhibiting a crumbled sheet (CS) or a rounded edges (RE) appearance are particularly effective.

TABLE 13.4 Seeded Crystal Formation in Water/Tetrahydrofuran Mixtures the Presence of Crystal Growth Inhibitors (Klomp et al., 1997)

Crystal Growth Inhibitor	Weight/[g]	Shape
No additive	13.2	RP
Tetrapentylammonium bromide	<0.1	CS
Tripentylbutylammonium bromide	<0.1	CS
Triisopentybutylammonium bromide	<0.1	CS
Tripentyldecylammonium bromide	<0.1	CS
Triisopentylammoniumsulfate	0.1	RE
Tetrabutylphosphoniumchloride	0.1	RE
Tributyldecylammonium bromide	0.4	RE
1,10-Ditribentylammoniumdecamethylene dibromide	0.1	CS
Tributyldecylammonium bromide	0.4	RE
Tributyldodecylammonium bromide	0.5	RE
Tributylisopentylammonium bromide	0.6	RE
Dibutyldecylammonium sulfate	0.6	RE
Tripentylammoniumsulfate	0.8	RP
Tributylpentylammonium bromide	0.9	RP
Tributyl tetradecylammonium bromide	1.1	RE
Tetrabutylammonium bromide	1.1	RE
1,6-Ditributylammoniumhexamethylene dibromide	1.1	RE
Tetrabutylammonium chloride	1.2	RE
Tributylhexadecylphosphoniumbromide	1.7	CS
Tetrabutylammonium-toluene-4-sulfonate	1.9	RE

TABLE 13.4 Seeded Crystal Formation in Water/Tetrahydrofuran Mixtures the Presence of Crystal Growth Inhibitors (Klomp et al., 1997)–Cont'd

Crystal Growth Inhibitor	Weight/[g]	Shape
1,2-Ditripentylammoniumdi-methylene dibromide	2.1	RE
Tributylammoniumsulfate	2.2	RP
Trihexylbutylammonium bromide	2.3	RP
Dibutypentylethanolammonium bromide	2.4	RP
Tributylheptylammonium bromide	2.6	RP
Tetraethylammonium bromide	12.1	RP
Dodecyltrimethylammonium bromide	12.3	RP
2-Dimethyl amino ethyl-triphenyl phosphoniumbromide	13.9	RP
Ethyltriphenylphosphoniumbromide	14.0	RP
Trisobutylammonium sulfate	15.6	RP
Ethylhexadecyldimethyl ammonium bromide	15.9	RP
Octadecyltrimethylammonium bromide	17.4	RP

RP Regular pyramids
CS Crumbled sheets
RE Rounded edges

Vinyl Polymers

Vinyl monomers used as gas hydrate inhibitors are summarized in Table 13.5. Copolymers made from *N*-vinylcaprolactam and 5–15% diethylaminoethyl acrylate or diethylaminoethyl methacrylate considerably prolong the induction time of the formation of gas hydrates (Thieu et al., 2002).

They are synthesized by radical copolymerization using di-*tert*-butyl peroxide as initiator. The copolymer is dissolved in 2-butoxyethanol. For testing, a synthetic gas mixture is used whose composition is given in Table 13.6.

Bimodal Distributions

A polymer is sometimes pictured as a bowl of spaghetti. Sometimes the individual strands are all approximately the same length, while at other times, they may have a wide variety of different lengths.

Bimodal polymers would be characterized as bowls of spaghetti wherein the individual strands of spaghetti primarily have two lengths, with a significant difference between the two (Colle et al., 2009).

While certain polymers are known as effective inhibitors for gas hydrate formation, it is surprising that inhibitor polymers with bimodal molecular weight distributions have a substantially improved performance as kinetic hydrate

TABLE 13.5 Vinyl Monomers for Gas Hydrate Inhibitors

Monomer	References
N-Isopropyl methacrylamide	Colle et al. (2009)
N-Vinylcaprolactam	Colle et al. (2009) and Thieu et al. (2002)
Diethylaminoethyl acrylate	Thieu et al. (2002)
Diethylaminoethyl methacrylate	Thieu et al. (2002)
Acrylamide	
Methacrylamide	
N-Vinylpyrrolidone	

TABLE 13.6 Synthetic Gas Mixture for Testing Hydrate Formation (Thieu et al., 2002)

Component	Amount/[mol-%]
n-Pentane	0.19
Isopentane	0.20
Isobutane	0.62
n-Butane	1.12
Propane	4.63
Carbon Dioxide	1.36
Ethane	10.84
Nitrogen	1.75
Methane	79.29

inhibitors relative to the same polymers with a narrow molecular weight range. Therefore, polymers or blends with a bimodal distribution of the molecular weight are preferred (Colle et al., 2009).

A polymeric material with a bimodal molecular weight distribution can be produced either during the polymerization process itself or after polymerization. This can be achieved during the polymerization reaction by the (Colle et al., 2009):

- Choice of polymerization catalyst,
- Staged initiator addition,
- Use of emulsifiers,

- Control of reaction viscosity,
- Presence of preformed polymer, and
- Choice of solvent.

The conditions for the production of a bimodal distribution must be optimized for a particular polymer. Alternatively, a bimodal molecular weight distribution can be obtained after the polymerization reaction. Most simply, two grades of the same polymer with different molecular weight are blended.

Poly-*N*-vinyl-2-pyrrolidone

The use of polymers or copolymers with a linear backbone, such as poly-*N*-vinyl-2-pyrrolidone for inhibiting the formation, growth, and the agglomeration of gas hydrates, has been described (Anselme et al., 1993).

The use of compounds referred to as quats has also been described (Klomp et al., 1997). These quat type compounds contain quaternary ammonium groups. Preferred quats comprise two long chains, with 8–50 carbon atoms, which may also contain ester groups or branched structures (Klomp, 2005).

Functionalization

Copolymers of ethylene and maleic anhydride (MA) have the anhydride moiety in their backbone, which is reactive toward amines and alcohols. The modification with amines is shown in Figure 13.5.

When opening the anhydride ring with an amine, a pending hydroxy group is formed. This hydroxy group can be reacted further, for example, it can be neutralized. Several compounds have been synthesized and evaluated for their activity in hydrate control. The effectiveness of these compounds is shown in Table 13.7.

Dendrimers

Dendrimeric polymers are basically highly branched molecules, consisting of a core and a number of branching generations and some end groups. In Figure 13.6, the structure of a dendrimer of succinic anhydride and diisoproanolamine is shown.

For example, diisoproanolamine bears one amino functionality and two hydroxyl functionalities. Dendrimers from diisoproanolamine will be classified as dendrimers of the AB_2 type.

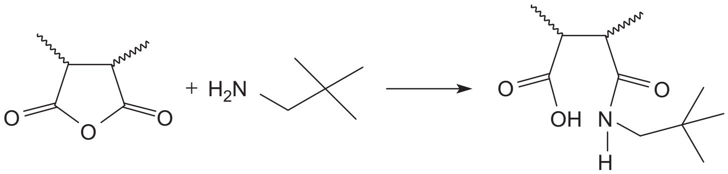

FIGURE 13.5 Modification of copolymers from ethylene and MA (Klug and Kelland, 2003).

TABLE 13.7 Crystal Growth Inhibitors (Klug and Kelland, 2003)

Polymer	Amine Group	$t_i{}^a$/[min]	St-1^b/[min]
EM	*n*-Propylamine	137	37
EM	*i*-Butylamine	885	183
EM	*i*-Propylamine	115	15
EM	*n*-Butylamine	190	37
EM	*i*-Pentylamine	21	27
MVM	*i*-Butylamine	48	43
MVM	*i*-Butylamine + Ethanolamine 4:1	>1212	
MVM	Dimethyl aminopropylamine	795	192

EM: Ethylene/MA
MVM: Methyl vinyl ether/MA
a) Induction time
b) Crystal growth delay time
3.5% Sodium chloride solution mixed with tetrahydrofuran in a ratio of 4:1, 0.5% functionalized polymer added

A concise introduction to dendrimers, including highly appealing chemical drawings, can be found in the literature (Dykes, 2001). A branching moiety consists of structural units, which are bound radially to the core or to the structural units of a previous generation and which extend outwards. The structural units have at least two reactive monofunctional groups along with one monofunctional group and one multifunctional group. The degree of branching of a particular generation is defined as the ratio between the number of branchings present and the maximum number of branchings possible in a completely branched dendrimer.

Dendrimeric compounds may have defects in the branching structure, may also be branched asymmetrically, or have an incomplete degree of branching in which case the dendrimeric compound contains both functional groups and functional end groups.

Dendrimers have been claimed to be low dose, hydrate inhibitors (Rivers et al., 2009), and some types are commercially available. Among them, hyperbranched polyester amides have been found to be suitable as hydrate formation inhibitors (Klomp, 2005).

These compounds are synthesized by the condensation of cyclic anhydrides with di- or trialkanolamines. Examples for monomers for hyperbranched polyester amides are shown in Table 13.8.

Their effectiveness was demonstrated as follows. A standard solution was prepared containing 78.7% water, 18.4% tetrahydrofuran, and 2.9% sodium chloride. Varying amounts of dendritic compounds were added to 70 g of this solution. The solution was maintained at 0°C, and after 30 min the amount of

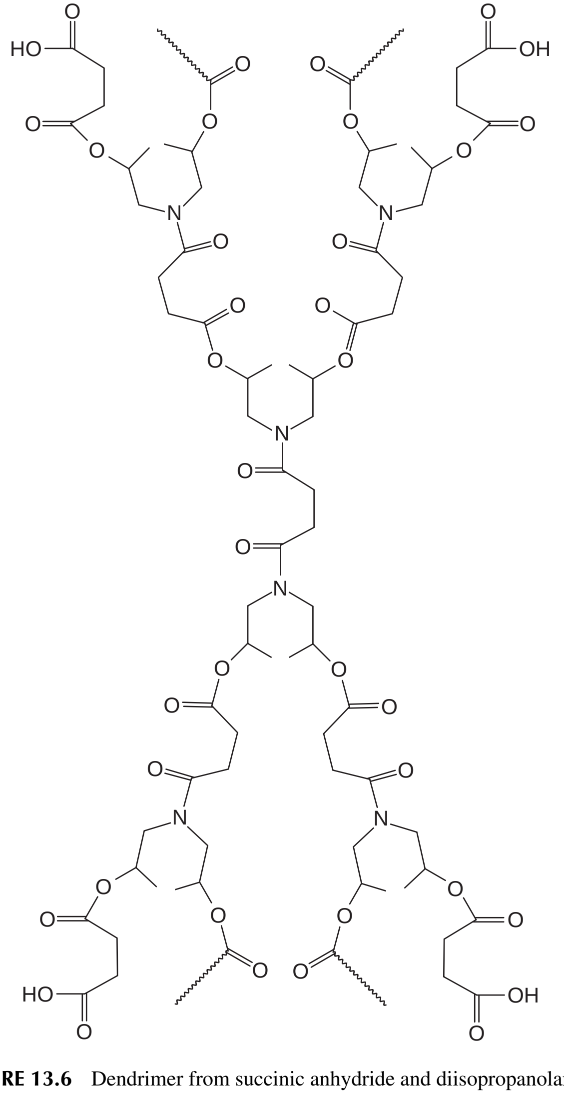

FIGURE 13.6 Dendrimer from succinic anhydride and diisopropanolamine.

TABLE 13.8 Monomers for Hyperbranched Polyester amides

Tradename	Anhydride	Alkanolamine
HYBRANE® S1200	Succinic anhydride	Diisopropanolamine
HYBRANE® HA1300	Hexahydrophthalic anhydride	Diisopropanolamine and *N*,*N*-bis-(3-dimethyl aminopropyl)amine

hydrate crystals that had formed was determined (Klomp, 2005). The results are given in Table 13.9.

The promising results that were obtained with tetrahydrofuran water solutions were confirmed under more realistic conditions with a more complicated experimental setup (Klomp, 2005).

Polyether Amines

A series of polyether amines are available under the tradename Jeffamine® from Huntsman. There are monoamines that contain a single amino end group, as well as diamines with amino groups on both ends of the polyether. The ether moieties are formed from the ring opening reaction of ethylene oxide (EO) or propylene oxide (PO) (Garibay-Vasquez, 2007).

The Jeffamine® D series are end-capped diamines, with the polyether made from EO or PO moieties. The trailing number refers to the molecular weight given in Dalton. In addition, there are products made from both EO and PO. The basic structure of a polyether amine is shown in Figure 13.7.

Quaternized polyether amines are effective as gas hydrate inhibitors (Pakulski, 2000, 2001). These compounds are also useful in preventing the growth of gas hydrates that are already formed.

Preparation 13–1: Quaternary salt products can be prepared from polyether amines and alkyl bromides. The polyether amine is warmed up to 75°C under stirring, and the alkyl bromide is added dropwise to the amine during a period of 1.5 h.

During the bromide addition, the temperature of the reaction mixture is allowed to increase to 90°C. After complete bromide addition, the reaction mixture is stirred for an additional 2 h at 90°C. The reaction products are mostly viscous amber liquids. ■

TABLE 13.9 Effect of Dendritic Compounds on Hydrate Formation (Klomp, 2005)

Additive	Amount Added/[%]	Amount Hydrate/[g]
–	0	8.7
HYBRANE® S1200	0.5	5.1
HYBRANE® S1200	1.0	3.3
HYBRANE® HA1300	0.5	0.1

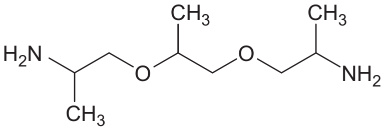

FIGURE 13.7 Polyether diamine with three propylene oxide units.

TABLE 13.10 Freeze Times of Quaternized Polyether Amines (Pakulski, 2000)

		Freeze Time at °C/[h]				
Amine Type	**Amount/[%]**	**−9**	**−10**	**−11**	**−12**	**−15**
No Additive	–	2	1.5	0.1		
Bu_4NBr	0.5		4.5	2.5		
Bu_4NBr	1.0	39	7	4	1	
$Bu_3C_{16}H_{31}NBr$	0.5		>24		10	
$Bu_3C_{14}H_{29}PCl$	0.5		>24		12	0.1
Jeffamine® D-230	0.5	>24	13.3		0.5	
Jeffamine® D-230 $C_{16}Br$	0.5				>24	11
Jeffamine® D-230 $C_{12}Br$	0.5					>24

Quaternized polyether amines have been tested for their effectiveness at subambient temperatures in a flow apparatus. The times after which the flow stopped due to extensive hydrate formation were noted and noted as the freeze time. The results are shown in Table 13.10.

The data show that the salts of polyether ammonium compounds are better than simple ammonium and phosphonium quaternary compounds, or starting amines by themselves for inhibiting gas hydrate formation.

These compounds also display a synergistic effect when applied with a polymeric kinetic hydrate inhibitor such as polyvinylcaprolactam. For example, a mixture of only 0.05% polyvinylcaprolactam and 0.05% Jeffamine® D-230 $C_{12}Br$ exhibits a freeze time of 27 h at −14°C.

Amines

Several amines have been synthesized and tested as gas hydrate inhibitors (Meier et al., 2008). Certain quaternary alkylammonium compounds have not only corrosion-inhibiting but also biostatic properties. However, their strong to toxicity algae and only moderate biodegradability restrict their use to ecologically insensitive fields of application, for example, onshore (Dahlmann and Feustel, 2008b).

N,*N*′-Dimethyl-*N*,*N*′-dilauryl ethylene diamine can be prepared from lauronitrile and *N*,*N*′-dimethylethylene diamine under hydrogen pressure. This compound is then the starting point for quaternization and formation of the respective hydroxide and the oxide. Several analogous compounds have been prepared according to this procedure (Klomp et al., 1997).

In addition to their activity as gas hydrate inhibitors, some of the compounds described in the literature (Klomp et al., 1997) may exhibit increased biodegradation and lower aquatic toxicity compared to conventional inhibitors.

In the same way, alkylaminoalkyl esters, which can be obtained via alkenylsuccinic anhydrides, show enhanced biodegradability and are also active as corrosion inhibitors (Dahlmann and Feustel, 2008c). Some of these compounds are summarized in Table 13.11.

Polyimine Adducts

Adducts of polyamides, amines, glycols, and formaldehyde are suitable gas hydrate inhibitors (Rivers and Crosby, 2007). The adducts can be prepared as follows (Rivers and Crosby, 2007):

Preparation 13–2: 6.67 g of caprolactam is dissolved in a solution of 2.54 g of polyethyleneimine with a molecular weight of 600 Dalton in 56 g of methanol. To this solution 4.79 g of 37% aqueous formaldehyde is added. It is then sealed in a bottle and kept at 65°C for 20 h to give a clear, light amber solution of the gas hydrate inhibitor. ■

Antifreeze Proteins

Plants and poikilothermic animals, such as insects and cold-water fish are known to protect themselves from freezing, both by antifreezes such as glycols and by special peptides and glycopeptides that act as antifreeze proteins and glycoproteins that act by interfering with the crystal growth of ice (Klomp et al., 1997). Glycopeptides composed of alanine, threonine, galactose, and *N*-acetylgalactosamine are present in animals in the Antarctic region. In other northern fishes, peptides containing alanine, aspartate, glutamate, threonine, and serine have been found (DeVries, 1982).

Microbes show an extraordinary variety of adaptations to extreme conditions. Thermophiles are organisms that survive at temperatures near the boiling

TABLE 13.11 Alkylaminoalkyl Succinic Esters (Dahlmann and Feustel, 2008c)

Ester Compound
N,*N*-Dibutylamino-*N*-ethyl tetrapropylenesuccinate
N,*N*-Dibutylamino-*N*-ethyl pentapropylenesuccinate
N,*N*-Dibutylamino-*N*-ethyl polyisobutenylsuccinate
Bis[*N*,*N*-dibutylamino-*N*-ethyl]tetrapropylenesuccinate
Bis[*N*,*N*-dibutylamino-*N*-ethyl]pentapropylenesuccinate
Bis[*N*,*N*-dibutylamino-*N*-ethyl]polyisobutenylsuccinate

point of water, and psychrophiles are bacteria that tolerate extraodrinarily low temperatures. To survive temperatures below the freezing point of ordinary water, these microbes protect themselves against growing ice crystals, which could damage cell membranes. They produce cryoprotectants that lower nucleation temperatures for ice. These cryoprotectants include ice nucleation proteins (Walker et al., 2008). The growth of ice crystals can be inhibited even in the presence of small amounts of such substances. The homogeneous nucleation and crystallization rates are sensitive to low concentrations.

The antifreeze activity of glycoproteins results from the sorption of the protein on the active growth sites of ice crystals (Franks et al., 1987). As the proteins are adsorbed, they change the curvature of the surface, thus making the nucleation and growth of ice crystals very difficult (Walker et al., 2008). In contrast, ice-nucleating proteins prevent extensive supercooling and allow the formation of ice close to the freezing temperature. Antifreeze proteins exhibit three kinds of activities (Wang, 2000):

1. They can maintain the supercooled state of body fluids by inhibiting the usual growth of ice,
2. They have the capacity to inhibit recrystallization, and
3. They may serve as plasma membrane protectors at low temperatures.

Antifreeze proteins have been classified into several basic types summarized in Table 13.12 (Tokunaga et al., 2008).

The effect of type I fish antifreeze protein from the winter flounder, *Pleuronectes americanus* (Walbaum), on the formation of tetrahydrofuran clathrate hydrate has been investigated. The antifreeze protein acts by changing the clathrate hydrate crystal morphology from octahedral to plate-shaped. The protein seems to be more effective than polyvinylpyrrolidone. In addition, the experiments suggest propane-hydrate growth could be also inhibited (Zeng et al., 2003).

Surface adsorption has been proposed as the mechanism involved. After the protein molecules attach to the surface of ice, the growth of ice crystals becomes unfavorable in the area between the adsorbed protein molecules because they

TABLE 13.12 Types of Antifreeze Proteins

Type	Features
I	Single, long, amphipathic α-helix
II	Cysteine-rich globular proteins with disulfide moieties
III	Similar overall hydrophobicity to type I proteins
IV	α-Helical proteins rich in glutamate and glutamine
V	Great thermal hysteresis value

cause an increase in curvature of the surface. This curvature subsequently inhibits further growth of the ice crystals (Zeng et al., 2005).

Lower alcohols, glycols, and inorganic salts are melting point depressants, i.e., antifreezes that can be used to prevent the formation of hydrates. However, at the high degrees of subcooling experienced in deep waters, they need to be added in substantial amounts, up to quantities equal to the amount of produced water, to be effective (Klomp et al., 1997).

Not only antifreeze proteins themselves, but also active fragments derived from them, as well as mimetics of antifreeze proteins have been proposed for gas hydrate inhibition. Suitable proteins or fragments contain a P-helix or 3-helices, a P-roll, a glycoprotein, or a globular structure. Such antifreeze proteins may be derived from animals, plants, fungi, protists, or bacteria (Walker et al., 2003). Special examples of antifreeze proteins are summarized in Table 13.13.

Deoxyribonucleic acids (DNAs) encoding antifreeze proteins of *Tenebrio molitor* have been isolated and found to encode 7–13 kDalton, cystine-rich proteins, composed largely of 12 amino acid repeat units (Graham et al., 1997, 1999). DNA of *Choristoneura fumiferana* encoding antifreeze proteins of 9–12 kDalton have also been cloned (Doucet et al., 2002).

Threonines match the ice lattice in antifreeze protein/ice models. In some antifreeze proteins, threonines are substituted by valine or isoleucine, which are amino acids with methyl groups and similar spatial volumes to threonine. It is believed that nonpolar interactions could be important for the inhibition of ice growth (Walker et al., 2003). Insect antifreeze proteins exhibit higher activity than fish antifreeze proteins by 1–2 orders of magnitude. Unfortunately, despite their remarkable performance, their production and use in oil field applications has been considered to be uneconomical (Klomp et al., 1997).

TABLE 13.13 Antifreeze Proteins (Walker et al., 2003)

Origin	Reference
Insects	
Mealworm beetle (*T. molitor*)	Graham et al. (1999)
Spruce budworm (*C. fumiferana*)	Walker et al. (1999)
Milkweed bug (*Oncopeltus fasciatus*)	Patterson et al. (1981)
Dendroides canadensis	Duman (1997)
Plants	
Rye grass (*Lolium perenne*)	Kuiper et al. (2001)
Bittersweet nightshade (*Solanum dulcamara*)	Worrall et al. (1998)
Winter rye (*Secala cereale*)	Worrall et al. (1998)
Carrot (*Daucus carota*)	Byass et al. (2000)

Agglomeration Inhibitors

Compounds that inhibit the formation and agglomeration of hydrate crystals (Klomp et al., 1995, 1997; Klomp and Reijnhart, 1999), such as ammonium, phosphonium, or sulfonium alkylated compounds, including quaternary compounds can be used.

Further, to reduce the tendency of hydrates to agglomerate, the addition of a condensation product from poly(alkenylsuccinic acid) and a polyethyleneglycolmonoether is successful (Durand et al., 1994). The product is non-ionic and has amphiphilic properties. In general, a concentration between 0.1% and 5%, based on the water present, is sufficient to prevent agglomeration. The following copolymers, as well as several other polymers (e.g., copolymers from acrylamides, acrylates, methacrylamides, methacrylates, *N*-vinyl heterocyclics, vinyl ethers, and *N*-vinyl amides), are useful for inhibiting the formation of clathrate hydrates in fluids (Angel and Negele, 1999; Angel et al., 2001; Colle, 2001; Costello et al., 1998; Klug et al., 1998; Klug and Kelland, 1998; Talley and Mitchell, 1999):

- Acrylamide-maleimide,
- *N*-Vinyl amide-maleimide,
- Vinyl lactam-maleimide,
- Alkenyl cyclic imino ether-maleimide, and
- Acryloylamide-maleimide.

Modified amino acids such as *N*-acyl-dehydroalanine polymers and copolymers with *N*-vinyl-*N*-methyl acetamide seem to be particularly effective (Colle, 2001).

Dispersing hydrates into a condensate phase by anti-agglomerants is another alternative to kinetic or thermodynamic inhibitors for preventing hydrate-plug formation in a gas production pipeline (Frostman and Przybylinski, 2001; Huo et al., 2001). Several commercial dispersants were successful in laboratory experiments. At low water concentrations, dodecyl-2-(2-caprolactamyl) ethanamide was shown to be superior (Huo et al., 2001).

Anti-agglomerants have been used in several field applications in deep-water systems, both in subsea wells and dry tree wells, under both flowing and shut-in conditions (Frostman and Przybylinski, 2001). Potential advantages of the anti-agglomerants over methanol include smaller umbilicals, smaller pumps, smaller storage facilities, and less frequent supply trips.

Gas Hydrate Inhibitors with Corrosion Inhibition

Gas hydrate inhibitors are commonly added with corrosion inhibitors but often, incompatibility between the two means additional work for the user in preparing the formulation.

Di-*N*-alkoxylated and carbonylated ammonium salts are excellent gas hydrate inhibitors, and their corrosion inhibiting action is so good that no additional corrosion inhibitors need be added (Dahlmann and Feustel, 2007). The basic structure of this type of compound is shown in Figure 13.8.

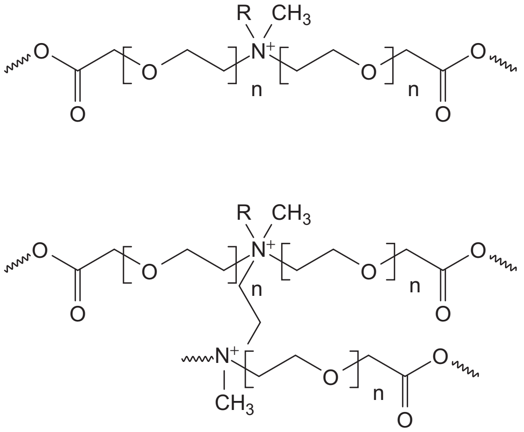

FIGURE 13.8 Di-*N*-alkoxylated and carbonylated ammonium salts (schematically) (Dahlmann and Feustel, 2007).

They can be prepared by the reaction of alkoxylated alkyl amines or alkylaminoalkylenamines with monochlorocarboxylic acids to give the corresponding ether carboxylic acids, which is then esterified with an alcohol. Alternatively, the bisalkoxylated monoalkyl amines or alkylaminoalkylenamines can be reacted directly with carboxylic acids, anhydrides, or acid chlorides. Finally, a quaternization is performed. The synthesis, exemplified with isobutylamine, is shown in Figure 13.9.

The alkoxylated alkyl amines consist of 2–35 units of EO. Actually, the chain consists of oligo-ethers. The basic alkyl amines are summarized in Table 13.14. In addition, the alcohols used for esterification are given, if appropriate.

Examples for the synthesis of a wide variety of these type of compounds are presented in detail elsewhere (Dahlmann and Feustel, 2007). The compounds are dissolved in alcoholic solvents, such as methanol, ethanol, propanol, butanol, or oxyethylated monoalcohols such as butylglycol, isobutylglycol, butyldiglycol, and polyglycols, for use as gas hydrate inhibitors.

Recyclable Antifreeze Agents

It would be economically and ecologically advantageous if the antifreeze agents could be recycled, so a special process that includes the recycling of antifreeze additives has been developed. This process consists of (Rojey et al., 1999):

1. Adding a dispersive additive in a hydrocarbon solution to the fluid to be transported, so as to form an emulsion;
2. Transporting the liquid and gaseous hydrocarbons in the presence of water and the hydrates;

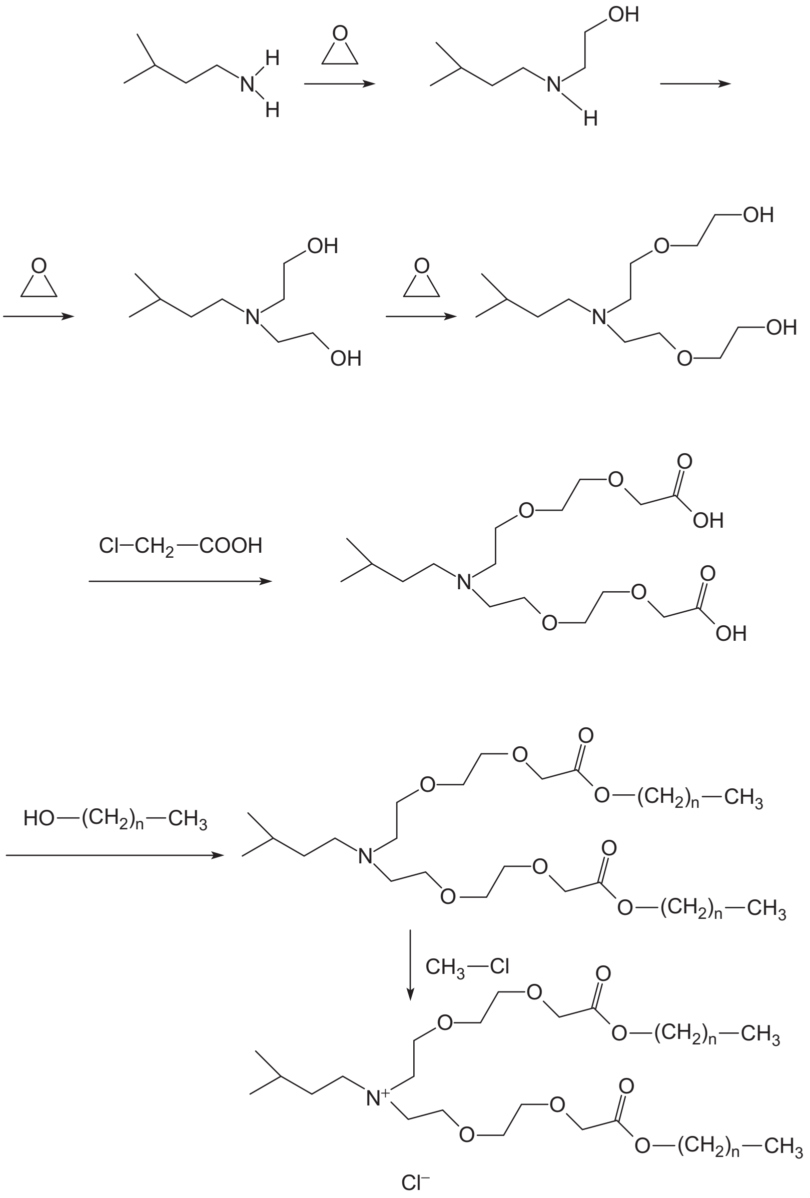

FIGURE 13.9 Synthesis steps of quaternized alkoxylated amines with end-capped acids or esters.

3. Separating the gas phase, the hydrocarbon liquid in excess, and a liquid hydrocarbon phase comprising the hydrates and the dispersing additive; and
4. Separating the liquid hydrocarbon phase comprising the hydrates and the dispersing additives.

TABLE 13.14 Alkyl Amines for Oxethylation (Dahlmann and Feustel, 2007)

Amine	EO units	Alcohol
n-Butylamine	2–10	–
n-Butylamine	10	Dodecanol
Isobutylamine	6–30	–
Isobutylamine	2–6	2-Ethylhexanol
Isobutylamine	10	Dodecanol
Cyclopentylamine	2–6	–
Cyclohexylamine	2	–
Cyclohexylamine	2–6	2-Ethylhexanol
Cyclohexylamine	2–6	2-Ethylhexanol
Caprylamine	6	2-Ethylhexanol
Caprylamine	6–10	–
Laurylpropylenediamine	10	2-Ethylhexanol
Tallow fat propylenediamine	10–35	–
Tallow fat propylenediamine	10–30	2-Ethylhexanol

The hydrates are then left behind in a water-in-oil emulsion, while the additives remain dissolved in the oil phase. Finally, the water-in-oil emulsion is broken to yield an aqueous phase and a liquid hydrocarbon phase that contains the additives. This hydrocarbon phase can be reused.

As hydrate inhibitor, oxalkylated amides from fatty acids are used (Sugier et al., 1990).

Also, carboxylic acid hydroxycarbylamide, substituted or non-substituted, such as an aliphatic or cyclic hydroxycarbylamide or a carboxylic acid monoethanolamide or diethanolamide containing preferably 3–36 carbon atoms are used as hydrate inhibitors.

The synthesis of these hydroxycarbylamides can be done with fatty acids, esters of these fatty acids, and vegetable or animal oils or fats, by reacting these compounds with hydroxycarbylamines such as diethanol amine or monoethanolamine. What is referred to as *hydroxycarbyl* is a hydrocarbyl radical substituted by at least one hydroxy group. The additive can be used together with a conventional thermodynamic inhibitor such as methanol or the glycols.

HYDRATE INHIBITORS FOR DRILLING FLUIDS

Low density gas hydrate-suppressive drilling fluids have been developed for deep water applications. These fluids are glycol-based (Halliday et al., 1998a,b).

REFERENCES

Angel, M., Negele, A., 1999. Utilization of vinyl formamide homopolymers or copolymers for inhibiting gas hydrates (verwendung von homo- oder copolymerisaten des vinylformamids zur inhibierung von gashydraten). WO Patent 9 964 717, assigned to BASF AG, December 16, 1999.

Angel, M., Neubecker, K., Sanner, A., 2001. Grafted polymers as gas hydrate inhibitors [pfropf-polymerisate als gashydratinhibitoren]. WO Patent 0 109 271, assigned to BASF AG, February 08, 2001.

Anselme, M.J., Reijnhout, M.J., Muijs, H.M., Klomp, U.C., 1993. A method for inhibiting gas hydrate formation. WO Patent 9 325 798, assigned to Shell Canada Ltd. and Shell Int. Research, December 23, 1993.

Avlonitis, D., Danesh, A., Todd, A.C., Baxter, T., 1989. The formation of hydrates in oil-water systems. In: Proceedings Volume, 4th Bhra Multi-Phase Flow International Conference, Nice, Fr, June 19–21, 1989, pp. 15–34.

Baillie, C., Wichert, E., 1987. Chart gives hydrate formation temperature for natural gas. Oil Gas J. 85 (14), 37–39.

Barone, G., Chianese, E., 2009. Hydrates of natural gases and small molecules: structures, properties, and exploitation perspectives. Chem Sus Chem 2 (11), 992–1008.

Beauchamp, B., 2004. Natural gas hydrates: myths, facts and issues. C. R. Geosci. 336 (9), 751–765.

Benesh, M.E., 1942. The use of gas hydrates in improving the load factor of gas supply systems. US Patent 2 270 016, assigned to Chicago By Products Corp., January 13, 1942.

Bil, K.J., 2003. Economic perspective of methane from hydrate. In: Max, M.D. (Ed.), Natural Gas Hydrate in Oceanic and Permafrost Environments, chap. 26. Kluwer Academic Publishers, Dordrecht, pp. 349–360.

Bullin, K.A., Bullin, J.A., 2004. Optimizing methanol usage for hydrate inhibition in a gas gathering system. In: 83rd Annual GPA Convention, no. P2004.23. Gas Processors Association, New Orleans, LA, pp. 1–10.

Byass, L.J., Darling, D.F., Doucet, C.J., Fenn, R.A., Lillford, P.J., McArthur, A.J., et al., 2000. Frozen food product. US Patent 6 096 867, assigned to Good Humor-Breyers Ice Cream, Division of Conopco, Inc. (Green Bay, WI), August 1, 2000.

Carroll, J.J., 2009. Natural Gas Hydrates: A Guide for Engineers, second ed. Gulf Professional Publishing, Burlington.

Christiansen, R.L., Bansal, V., Sloan Jr., E.D., 1994. Avoiding hydrates in the petroleum industry: kinetics of formation. In: Proceedings Volume, SPE & Tulsa University of Centen Petrol. Engineering Symposium, Tulsa, August 29–31, 1994, pp. 383–393.

Christiansen, R.L., Sloan Jr., E.D., 1993. Mechanics and kinetics of hydrate formation. In: Proceedings Volume, New York Acad Sci et al Natur Gas Hydrates International Conference, New Paltz, NY, June 20–24, 1993, pp. 283–305.

Colle, K.S., 2001. Method for inhibiting hydrate formation. US Patent 6 222 083, assigned to Exxonmobil Upstream Res. C, April 24, 2001.

Colle, K.S., Talley, L.D., Longo, J.M., 2009. Method for inhibiting hydrate formation. US Patent 7 585 816, assigned to ExxonMobil Upstream Research Company (Houston, TX), September 8, 2009.

Costello, C.A., Berluche, E., Oelfke, R.H., Talley, L.D., 1998. Maleimide copolymers and method for inhibiting hydrate formation. US Patent 5 744 665, assigned to Exxon Production Res. Co., April 28, 1998.

Dahlmann, U., Feustel, M., 2007. Additives for inhibiting the formation of gas hydrates. US Patent 7 183 240, assigned to Clariant Produkte (Deutschland) GmbH (Sulzbach, DE), February 27, 2007.

Dahlmann, U., Feustel, M., 2008a. Corrosion and gas hydrate inhibitors having improved water solubility and increased biodegradability. US Patent 7 341 617, assigned to Clariant Produkte (Deutschland) GmbH (Sulzbach, DE), March 11, 2008.

Dahlmann, U., Feustel, M., 2008b. Corrosion and gas hydrate inhibitors having improved water solubility and increased biodegradability. US Patent 7 323 609, assigned to Clariant Produkte (Deutschland) GmbH (Sulzbach, DE), January 29, 2008.

Dahlmann, U., Feustel, M., 2008c. Corrosion and gas hydrate inhibitors having improved water solubility and increased biodegradability. US Patent 7 435 845, assigned to Clariant Produkte (Deutschland) GmbH (Sulzbach, DE), October 14, 2008.

Daubert, T.E., 1992. Evaluation of four methods for predicting hydrate equilibria. GPA Res. Rep. RR-134, Pennsylvania State University (July 1992).

Davy, H., 1811. On a combination of oxymuriatic gas and oxygene gas. Phil. Trans. R. Soc. Lond. 101, 155–162, [electronic:] http://rstl.royalsocietypublishing.org/content/101/155.full.pdf+html.doi:doi:10.1098/rstl.1811.0008.

DeVries, A.L., 1982. Biological antifreeze agents in coldwater fishes. Comp. Biochem. Physiol. A: Physiol. 73 (4), 627–640.

Doucet, D., Tyshenko, M.G., Davies, P.L., Walker, V.K., 2002. A family of expressed antifreeze protein genes from the moth, Choristoneura fumiferana. Eur. J. Biochem. 269 (1), 38–46.

Duman, J.G., 1997. Nucleic acid sequences encoding dendroides antifreeze proteins. US Patent 5 627 051, assigned to University of Notre Dame du Lac (Notre Dame, IN), May 6, 1997.

Duncum, S.N., Edwards, A.R., Lucy, A.R., Osborne, C.G., 1994. Method for inhibiting solids formation and blends for use therein. WO Patent 9 424 413, assigned to BP Chemicals Ltd. and BP Exploration Oper. Co. Ltd., October 27, 1994.

Durand, J.P., Baley, A.S., Gateau, P., Sugier, A., 1994. Process to reduce the tendency of hydrates to agglomerate in production effluents (methode pour reduire la tendance a l'agglomeration des hydrates dans des effluents de production). EP Patent 582 507, assigned to Inst. Francais Du Petrole, February 09, 1994.

Dyadin, Y., Larionov, A., Aladko, E., Manakov, A., Zhurko, F., Mikina, T., et al., 1999a. Clathrate formation in water-noble gas (hydrogen) systems at high pressures. J. Struct. Chem. 40 (5), 790–795.

Dyadin, Y.A., Larionov, E.G., Manakov, A.Y., Zhurko, F.V., Aladko, E.Y., Mikina, T.V., et al., 1999b. Clathrate hydrates of hydrogen and neon. Mendeleev Commun. (5), 209–210.

Dykes, G.M., 2001. Dendrimers: a review of their appeal and applications. J. Chem. Technol. Biotechnol. 76 (9), 903–918.

Fleyfel, F., Song, K.Y., Kook, A., Martin, R., Kobayashi, R., 1993. ^{13}C NMR of hydrate precursors in metastable regions. In: Proceedings Volume, New York Acad Sci et al. Natur Gas Hydrates International Conference, New Paltz, NY, June 20–24, 1993, pp. 212–224.

Franks, F., Darlington, J., Schenz, T., Mathias, S.F., Slade, L., Levine, H., 1987. Antifreeze activity of antarctic fish glycoprotein and a synthetic polymer. Nature 325 (6100), 146–147.

Frostman, L.M., Przybylinski, J.L., 2001. Successful applications of anti-agglomerant hydrate inhibitors. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, Houston, TX, February 13–16, 2001, pp. 1–10.

Garibay-Vasquez, A., 2007. Jeffamine® polyetheramines, Technical Information 0507. Huntsman Corporation, The Woodlands, TX 77380, http://www.huntsman.com/performance_products/Media/JEFFAMINE_Polyetheramines.pdf.

GPSA, 2004. GPSA Engineering Data Book, twelfth ed. Gas Processors Suppliers Association & Gas Processors Association, Tulsa, OK.

Graham, L.A., Liou, Y.C., Walker, V.K., Davies, P.L., 1997. Hyperactive antifreeze protein from beetles. Nature 388, 727–728.

Graham, L.A., Liou, Y.-C., Walker, V.K., Davies, P.L., 1999. Tenebrio antifreeze proteins. WO Patent 9 900 493, assigned to Univ. Kingston, Graham Laurie A, Liou Yih Cherng, Walker Virginia K, and Davies Peter L, January 07, 1999.

Halliday, W., Clapper, D.K., Smalling, M., 1998a. New gas hydrate inhibitors for deepwater drilling fluids. In: Proceedings Volume, IADC/SPE Drilling Conference, Dallas, March 3–6, 1998, pp. 201–209.

Halliday, W.S., Clapper, D.K., Smalling, M.R., Bland, R.G., 1998b. Glycol derivatives and blends thereof as gas hydrate inhibitors in water base drilling, drill-in, and completion fluids. WO Patent 9 840 446, assigned to Baker Hughes Inc., September 17, 1998.

Hammerschmidt, E.G., 1934. Formation of gas hydrates in natural gas transmission lines. Ind. Eng. Chem. 26 (8), 851–855. doi:10.1021/ie50296a010.

Hammerschmidt, E.G., 1939. Gas hydrate formations: A Further Study on Their Prevention and Elimination from Natural *Gas* Pipe Lines. *Gas* 15 (5), 30–35.

Huetz, U., Englezos, P., 1995. Measurement of structure H hydrate phase equilibrium and the effect of electrolytes. Fluid Phase Equilib. 117 (1–2), 178–185.

Huo, Z., Freer, E., Lamar, M., Knauss, D.M., Sloan Jr., E.D., Sannigrahi, B., 2001. Hydrate plug prevention by anti-agglomeration. Chem. Eng. Sci. 56 (17), 4979–4991.

Kannan, K., Punase, A., 2009. Low-dosage, high-efficiency, and environment-friendly inhibitors: a new horizon in gas hydrates mitigation in production systems. In: SPE International Symposium on Oilfield Chemistry, 20–22 April 2009, no. 120905-MS, SPE, Society of Petroleum Engineers, The Woodlands. Texas, pp. 1–8.

Katz, D.L., 1959. Handbook of Natural Gas Engineering, McGraw-Hill Series in Chemical Engineering. McGraw-Hill, New York.

Kelland, M.A., Svartaas, T.M., Dybvik, L., 1995. Studies on new gas hydrate inhibitors. In: Proceedings Volume, SPE Offshore Europe Conference, Aberdeen, Scot, September 5–8, 1995, pp. 531–539.

Kelland, M.A., Svartaas, T.M., Øvsthus, J., Tomita, T., Chosa, J.-I., 2006. Studies on some zwitterionic surfactant gas hydrate anti-agglomerants. Chem. Eng. Sci. 61 (12), 4048–4059.

Klapp, S.A., Bohrmann, G., Kuhs, W.F., Mangir Murshed, M., Pape, T., Klein, H., et al., 2010. Microstructures of structure I and II gas hydrates from the Gulf of Mexico. Mar. Pet. Geol. 27 (1), 116–125.

Klomp, U.C., 2005. Method for inhibiting the plugging of conduits by gas hydrates. US Patent 6 905 605, assigned to Shell Oil Company (Houston, TX), June 14, 2005.

Klomp, U.C., Kruka, V.R., Reijnhart, R., Weisenborn, A.J., 1995. Method for inhibiting the plugging of conduits by gas hydrates. US Patent 5 460 728, assigned to Shell Oil Co., October 24 1995.

Klomp, U.C., Kruka, V.R., Reijnhart, R., Weisenborn, A.J., 1997. Method for inhibiting the plugging of conduits by gas hydrates. US Patent 5 648 575, assigned to Shell Oil Company (Houston, TX), July 15, 1997.

Klomp, U.C., Reijnhart, R., 1999. Method for inhibiting the plugging of conduits by gas hydrates. US Patent 5 879 561, assigned to Shell Oil Company (Houston, TX), March 9, 1999.

Klug, P., Feustel, M., Frenz, V., 1998. Additives to inhibit the formation of gas hydrate. WO Patent 9 822 557, assigned to Clariant GmbH, May 28, 1998.

Klug, P., Kelland, M., 1998. Additives for inhibiting formation of gas hydrates. WO Patent 9 823 843, assigned to Clariant GmbH and Rf Rogaland Research, June 04, 1998.

Klug, P., Kelland, M., 2002. Additives for inhibiting gas hydrate formation. US Patent 6 369 004, assigned to Clariant GmbH (Frankfurt, DE) and RF-Rogaland Research (Stavanger, NO), April 9, 2002.

Klug, P., Kelland, M., 2003. Additives for inhibiting gas hydrate formation. US Patent 6 544 932, assigned to Clariant GmbH (Frankfurt, DE) RF–Rogaland Research (Stavanger, NO), April 8, 2003.

Koh, C.A., Savidge, J.L., Tang, C.C., 1996. Time-resolved in-situ experiments on the crystallization of natural gas hydrates. J. Phys. Chem. 100 (16), 6412–6414.

Kuiper, M.J., Davies, P.L., Walker, V.K., 2001. A theoretical model of a plant antifreeze protein from lolium perenne. Biophys. J. 81 (6), 3560–3565.

Kutergin, O.B., Melnikov, V.P., Nesterov, A.N., 1992. Effect of surface-active agents on the mechanism and kinetics of hydrate formation of gases. Dokl. Akad. Nauk SSSR 323 (3), 549–553.

Kvamme, B., 1993. Mechanisms for initiation of hydrate from liquid water: liquid phase clustering, surface adsorbtion, or what? In: Proceedings Volume, New York Acad Sci et al Natur Gas Hydrates International Conference, New Paltz, NY, June 20–24, 1993, pp. 306–310.

Kvenvolden, K.A., 1995. A review of the geochemistry of methane in natural gas hydrate. Org. Geochem. 23 (11–12), 997–1008.

Kvenvolden, K.A., Lorenson, T.D., 2001. The global occurrence of natural gas hydrate. In: Paull, C.K., Dillon, W.P. (Eds.), Natural Gas Hydrates: Occurrence, Distribution, and Detection, vol. 124 of Geophysical monograph. American Geophysical Union, Washington, DC, pp. 3–18.

Lee, R.L., Katz, D.L.V., 1991. Natural Gas Engineering: Production and Storage, McGraw-Hill Chemical Engineering Series. McGraw-Hill Economics Dept, New York.

Lugo, R., Dalmazzone, C., Audibert, A., 2010. Method and thermodynamic inhibitors of gas hydrates in water-based fluids. US Patent 7 709 419, assigned to Institut Francais du Petrole (Rueil Malmaison Cedex, FR), May 4, 2010.

Makogon, Y.F., 1981. Hydrates of Natural Gas. Pennwell, Tulsa, OK.

Makogon, Y.F., 1994. Russia’s contribution to the study of gas hydrates. Ann. New York Acad. Sci. 715, 119–145. Issue: *Natural Gas Hydrates*.

Makogon, Y.F., 1996. Formation of hydrates in shut-down pipelines in offshore conditions. In: Proceedings Volume, vol. 4, 28th Annual SPE et al Offshore Technology Conference, Houston, May 6–9, 1996, pp. 749–756.

Makogon, T.Y., Mehta, A.P., Sloan Jr., E.D., 1996. Structure H and structure I hydrate equilibrium data for 2,2-dimethylbutane with methane and xenon. J. Chem. Eng. Data 41 (2), 315–318.

Mandal, B., 2007. Natural gas hydrates and their potentiality for future energy supply: a survey of literature. Altenergymag[electronic:] http://www.altenergymag.com/emagazine.php?issue_number=07.06.01&article=hydrate.

Max, M.D. (Ed.), 2003. Natural Gas Hydrate in Oceanic and Permafrost Environments. Kluwer Academic Publishers, Dordrecht.

Mehta, A.P., Sloan, E.D., 1993. Structure H hydrates: data and industrial potential. In: Proceedings Volume, 72nd Annual GPA Convention, San Antonio, March 15–17, 1993, pp. 67–75.

Mehta, A.P., Sloan, E.D., 1996. Structure H hydrates: implications for the petroleum industry. In: Proceedings Volume, Annual SPE Technology Conference, Denver, October 6–9, 1996, pp. 607–613.

Mei, D.H., Liao, J., Yang, J.T., Guo, T.M., 1996. Experimental and modeling studies on the hydrate formation of a methane + nitrogen gas mixture in the presence of aqueous electrolyte solutions. Ind. Eng. Chem. Res. 35 (11), 4342–4347.

Meier, I.K., Goddard, R.J., Ford, M.E., 2008. Amine-based gas hydrate inhibitors. US Patent 7 452 848, assigned to Air Products and Chemicals, Inc. (Allentown, PA), November 18, 2008.

Milkov, A.V., Sassen, R., 2002. Economic geology of offshore gas hydrate accumulations and provinces. Mar. Pet. Geol. 19 (1), 1–11.

Nerheim, A.R., Samuelson, E.K., Svartaas, T.M., 1992. Investigation of hydrate kinetics in the nucleation and early growth phase by laser light scattering. In: Proceedings Volume, vol. 1, 2nd Soc. Offshore Polar Eng. et al Offshore & Polar Engineering International Conference, San Francisco June 14–19, 1992, pp. 620–627.

Nerheim, A.R., Svartaas, T.M., Samuelsen, E.J., 1994. Laser light scattering studies of natural gas hydrates. In: Proceedings Volume, vol. 2, 69th Annual SPE Technology Conference, New Orleans, September 25–28, 1994, pp. 303–309.

Nielsen, R.B., Bucklin, R.W., 1983. Why not use methanol for hydrate control? Hydrocarbon Process. 62 (4), 71–78.

Pakulski, M.K., 2000. Quaternized polyether amines as gas hydrate inhibitors. US Patent 6 025 302, assigned to BJ Services Company (Houston, TX), February 15, 2000.

Pakulski, M.K., 2001. Method for controlling gas hydrates in fluid mixtures. US Patent 6 331 508, assigned to BJ Service Company, U.S.A. (Houston, TX), December 18, 2001.

Parent, J.S., Bishnoi, P.R., 1996. Investigations into the nucleation behaviour of methane gas hydrates. Chem. Eng. Commun. 144, 51–64.

Patterson, J.L., Kelly, T.J., Duman, J.G., 1981. Purification and composition of a thermal hysteresis producing protein from the milkweed bug, Oncopeltus fasciatus. J. Comp. Physiol. 142 (4), 539–542.

Petersen, H., Martens, J., Harms, W., Kramer, U., 1991. Process for avoiding the formation of condensates, hydrates or ice in the decompression of natural gas stored in salt caverns (verfahren zur vermeidung der bildung von kondensaten, hydraten oder eis bei der entspannung von in salzkavernen gespeichertem erdgas). DE Patent 3 927 905, assigned to Energieversor Weser Ems A, February 21, 1991.

Pic, J.S., Herri, J.M., Cournil, M., 2001. Experimental influence of kinetic inhibitors on methane hydrate particle size distribution during batch crystallization in water. Can. J. Chem. Eng. 79 (3), 374–383.

Pieroen, A.P., 1955. Gas hydrates-approximate relations between heat of formation, composition and equilibrium temperature lowering by inhibitors. Recueil Trav. Chim. 74, 995–1002.

Pratt, R.M., Sloan Jr., E.D., 1995. A computer-simulation and investigation of liquid-solid interfacial phenomena for ice and clathrate hydrates. Mol. Simul. 15 (4), 247.

Prytz, M., Nikitin, B.A., 1936. Das Radonhydrat. Z. Anorg. Allg. Chem. 227 (1), 81–93. doi:10.1002/zaac.19362270111.

Rivers, G.T., Crosby, D.L., 2007. Gas hydrate inhibitors. US Patent 7 164 051, assigned to Baker Hughes Incorporated (Houston, TX), January 16, 2007.

Rivers, G.T., Tian, J., Trenery, J.B., 2009. Kinetic gas hydrate inhibitors in completion fluids. US Patent 7 638 465, assigned to Baker Hughes Incorporated (Houston, TX), December 29, 2009.

Rodger, P.M., Forester, T.R., Smith, W., 1995. Simulations of the methane hydrate/methane gas interface near hydrate forming conditions. Fluid Phase Equilib. 116 (1–2), 326–332.

Rojey, A., Thomas, M., Delion, A.-S., Durand, J.-P., 1999. Process for recycling a dispersing additive used for the transportation of a condensate gas or of an oil with associated gas in the presence of hydrates. US Patent 5 877 361, assigned to Institute Francais du Petrole (Rueil Malmaison, FR), March 2, 1999.

Roozeboom, H.W.B., 1884. Recherches sur quelques hydrates de gaz. Recueil des travaux chimique des Pays-Bas et de la Belgique 3, 29–104. Available, eg. at Technical University of Vienna.

Sikes, C.S., Wierzbicki, A., 1996. Stereospecific and nonspecific inhibition of mineral scale and ice formation. In: Proceedings Volume, 51st Annual NACE International Corrosion Conference (Corrosion 96), Denver, March 24–29, 1996, pp. 1–16.

Skovborg, P., Ng, H.J., Rasmussen, P., Mohn, U., 1993. Measurement of induction times for the formation of methane and ethane gas hydrates. Chem. Eng. Sci. 48 (3), 445–453.

Sloan Jr., E.D., 2009. The colorado school of mines hydrate prediction program (CSMGem), [electronic:] http://hydrates.mines.edu/CHR/Software.html.

Sloan Jr., E.D., Christiansen, R.L., 1995. Prediction and inhibition of hydrate and wax formation: final report (January 1991–December 1993). Gas Res Inst Rep GRI-94/0404, Gas Res Inst (March 1995).

Sloan, E.D., Fleyfel, F., 1991. Hydrate dissociation enthalpy and guest size. Fluid Phase Equilib. 76, 123–140.

Sloan, E.D., Koh, C.A., 2008. Clathrate Hydrates of Natural Gases, third ed., vol. 119 of Chemical Industries Series. CRC Press, Boca Raton, FL.

Stackelberg, M., Müller, H., 1951. Zur struktur der gashydrate. Naturwissenschaften 38 (19), 456–456.

Sugier, A., Bourgmayer, P., Stern, R., 1990. Process for delaying the formation and/or reducing the agglomeration tendency of hydrates. US Patent 4 973 775, assigned to Institut Francais du Petrole (Rueil Malmaison, FR), November 27, 1990.

Talley, L.D., Mitchell, G.F., 1999. Application of proprietary kinetic hydrate inhibitors in gas flowlines. In: Proceedings Volume, vol. 3, 31st Annual SPE et al Offshore Technology Conference, Houston, May 3–6, 1999, pp. 681–689.

Thieu, V., Bakeev, K.N., Shih, J.S., 2002. Gas hydrate inhibitor. US Patent 6 359 047, assigned to ISP Investments Inc. (Wilmington, DE), March 19, 2002.

Thomas, M., Behar, E., 1994. Structure h hydrate equilibria of methane and intermediate hydrocarbon molecules. In: Proceedings Volume, 73rd Annual GPA Convention, New Orleans, March 7–9, 1994, pp. 100–107.

Tohidi, B., Danesh, A., Burgass, R.W., Todd, A.C., 1996. Effect of heavy hydrate formers on the hydrate free zone of real reservoir fluids. In: Proceedings Volume, SPE/Norwegian Petrol. Soc. Europe Prod. Oper. Conference, Stavanger, Norway, April 16–17, 1996, pp. 257–261.

Tokunaga, Y., Ferdows, M., Endou, H., Ota, M., Murakami, K., 2008. Continuous production of CO_2 hydrate slurry added antifreeze proteins. In: Proceedings of the 6th International Conference on Gas Hydrates, International Conference on Gas Hydrates. Vancouver, British Columbia, CA. http://hdl.handle.net/2429/2298

Walker, V.K., Davies, P.L., Rahavard, M., Tyshenko, M.G., 1999. Spruce budworm antifreeze proteins, genes and methods of using same. US Patent 6 008 016, assigned to Queen'S University at Kingston (Ontario, CA), December 28, 1999.

Walker, V.K., Ripmeester, J.A., Zeng, H., 2003. Antifreeze proteins for inhibition of clathrate hydrate formation and reformation. WO Patent 03 087 532, assigned to Univ. Kingston, Walker Virginia, Ripmeester John A, and Zeng Huang, October 23, 2003.

Walker, V.K., Wilson, S.L., Wu, Z., Miao, D.N., Zeng, H., Ripmeester, J.A., et al., 2008. Screening microbes for ice-associating proteins with potential application as green inhibitors for gas hydrates. In: Shah, V. (Ed.), Emerging Environmental Technologies, chap. 2. Springer Netherlands, Dordrecht, NL, pp. 29–41.

Wang, J.-H., 2000. A comprehensive evaluation of the effects and mechanisms of antifreeze proteins during low-temperature preservation. Cryobiology 41 (1), 1–9.

Weber, E. (Ed.), 1987. Molecular Inclusion and Molecular Recognition – Clathrates 1, vol. 140 of Topics in Current Chemistry. Springer Verlag, Berlin.

Worrall, D., Elias, L., Ashford, D., Smallwood, M., Sidebottom, C., Lillford, P., et al., 1998. A carrot leucine-rich-repeat protein that inhibits ice recrystallization. Science 282 (5386), 115–117. doi:10.1126/science.282.5386.115.

Zeng, H., Moudrakovski, I.L., Ripmeester, J.A., Walker, V.K., 2005. Effect of antifreeze protein on nucleation, growth and memory of gas hydrates. AIChE J 52 (9), 3304–3309.

Zeng, H., Wilson, L.D., Walker, V.K., Ripmeester, J.A., 2003. The inhibition of tetrahydrofuran clathrate-hydrate formation with antifreeze protein. Can. J. Phys. 81 (1–2), 17–24.

TRADENAMES

TABLE 13.15 Tradenames in References

Tradename Description	Supplier
Cellosolve® (Series) Solvents for gums, resins, cellulose esters (Rivers and Crosby, 2007)	Union Carbide Corp.
Ethyl CELLOSOLVE® 2-Ethoxyethanol (Rivers and Crosby, 2007)	Union Carbide Corp.
Gantrez® Methyl vinyl ether/maleic anhydride copolymer (Klug and Kelland, 2002, 2003)	ISP
NONIDET® P40 Octylphenolpoly(ethylenglycolether), non-ionic detergent (Walker et al., 1999)	Roche
Triton® X (Series) Poly(alkylene oxide), non-ionic surfactants (Walker et al., 1999)	Union Carbide Corp. (Rohm & Haas)

Chapter 14

Antifreeze Agents

An antifreeze is defined as an additive that, when added to a water-based fluid, will reduce the freezing point of the mixture (Stefl and George, 1996). Antifreezes are used in mechanical equipment that is environments below the freezing point of water to prevent the freezing of heat transfer fluids. They are also used in cementing jobs.

Hydrate control is not included in this chapter, but is discussed in Chapter 13, because of the relative importance and difference in chemical mechanism of these compounds. Many chemicals will result in a depression of the freezing point when added to water. Their practical application is restricted, however, because of some other unwanted effects, such as corrosion, destruction of rubber sealings in engine parts, or economic considerations.

THEORY OF ACTION

Freezing point depression follows the colligative laws of thermodynamics at low concentrations in water. The result can readily be explained by the theory of phase equilibria in thermodynamics.

In equilibrium, the chemical potential of coexisting phases must be equal. The assumption is that the solid phase must consist of one component, water, whereas the liquid phase will be a mixture of water and salt. So the chemical potential for water in the solid phase μ_s is the chemical potential of the pure substance. However, in the liquid phase the water is diluted with the salt, so the chemical potential of the water in liquid state must be corrected. x refers to the mole fraction of the solute, that is, salt or an organic substance. The equation is valid for small amounts of salt or additives in general:

$$\mu_s = \mu_l + RT \ln(1 - x). \tag{14.1}$$

It is best expressed in the following form:

$$\frac{\mu_s - \mu_l}{RT} = \ln(1 - x) \cong -x. \tag{14.2}$$

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The derivative with respect to temperature will give the dependence of equilibrium concentration on temperature itself:

$$\frac{d\dfrac{\mu_s-\mu_l}{RT}}{dT}=-\frac{dx}{dT}=\frac{\Delta H}{RT^2}. \tag{14.3}$$

ΔH is the heat of melting of water. Because this is always positive, an increase in solute concentration will result in a depression of the freezing point. For small freezing point depressions, the temperature on the right-hand side of the equation can be treated as a constant. It can also be seen that additives with low molecular weight will be more effective in depressing the freezing point than those with higher molecular weights. It is once again emphasized that the preceding equation is only valid for small amounts of additive. The concept of activity coefficient has to be introduced to explain the phase diagram over a broader range of concentrations.

ANTIFREEZE CHEMICALS

Some data concerning the activity of antifreeze chemicals are presented in Table 14.1, which shows that there are two different types of antifreeze chemicals, namely liquids that are miscible over the full concentration range and salts which are only soluble to a certain amount. As an example, ethylene glycol (EG) forms a eutectic point with water between 65% and 80% at around

TABLE 14.1 Antifreeze Chemicals

Component	Concentration in Water/[%]	Depression of Freezing Point/[°C]
Calcium chloride	32	−50.0
Ethanol	50	−38.0
Ethylene glycol	50	−36.0
Glycerol	50	−22.0
Methanol	50	−50.0
Potassium chloride	13	−6.5
Propylene glycol	50	−32.0
Sea water (6% salt)	–	−3.0
Sodium chloride	23	−21.0
Sucrose	42	−5.0
Urea	44	−18.0

TABLE 14.2 Depression of the Freezing Point in a Mixture of Ethylene Glycol–Water

Amount of Ethylene Glycol/[%]	Depression of Freezing Point/[°C]
10	−4
20	−9
30	−15
40	−24
50	−36

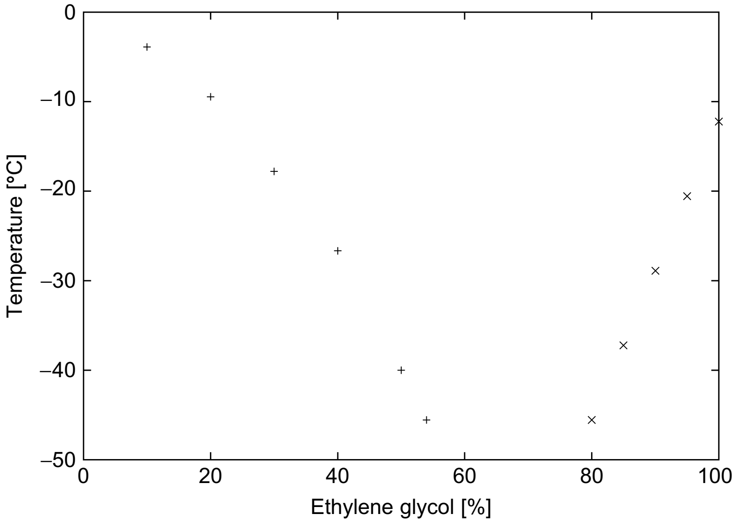

FIGURE 14.1 Phase diagram of the binary system for ethylene glycol–water.

−70°C, whereas pure EG will solidify at −14°C. So the equilibrium freezing points cannot be measured.

The freezing point depression of a mixture of EG and water is shown in Table 14.2, and the phase diagram of the binary EG–water system is plotted in Figure 14.1. Some organic antifreeze agents are depicted in Figure 14.2.

HEAT TRANSFER LIQUIDS

The classic antifreeze agents in heat transfer liquids are brine solutions and alcohols.

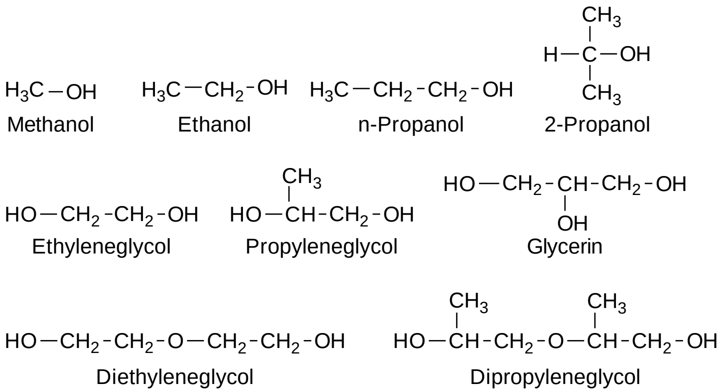

FIGURE 14.2 Organic antifreeze agents.

Brines

Of the commonly used antifreeze agents, brines are the most corrosive to metals, and exhibit scale deposition characteristics that are highly restrictive to heat transfer. Today brines (sea water) still find application in offshore uses because they are cheap.

Alcohols

Alcohols, such as methanol and ethanol, are readily available and are occasionally used despite their significant disadvantages, such as their low boiling points, which during summer months, mean that significant amounts can be lost due to evaporation. Such losses lead to a costly replacement of the additive. Alcohols also have low flash points, which may cause safety problems, and methanol is highly poisonous. The use of alcohols has therefore ceased almost completely in recent years.

Glycols

EG is not as active in depression of the freezing point as methanol, but it has a very low vapor pressure. Evaporation loss in a coolant system is due more to the evaporation of water than to that of EG. There is also no flammability problem, since 1:1 mixtures of EG and water do not exhibit a flash point. EG-based antifreeze formulations may contain small amounts of other glycols, such as diethylene glycol or triethylene glycol. Propylene-based glycols such as propylene glycol and propylene glycol ethers have limited use, especially in areas in which regulations about human toxicity apply. EG is the most effective freezing point depressant and heat transfer agent.

Properties of Glycol-based Antifreeze Formulations

Pour Point

The desired concentration of an antifreeze agent will be governed by several features. The freezing point of a mixture is the point at which the first ice crystal can be observed, but this is not necessarily the lowest temperature that can be used. In the case of heat transfer agents, the fluid will not function efficiently, but because the fluid will not freeze completely to a solid state it may still be operational. Pure water will expand about 9% by completely freezing, but the addition of antifreeze, such as EG, will significantly lower the amount of expansion, thus protecting the system from damage. The crystals that separate out are pure water, so the concentration of the antifreeze agent still in the solution will increase. This causes a further depression of the freezing point of the residual liquid. At higher glycol concentrations the fluid never solidifies completely, but becomes thick and taffy like. The point at which the fluid ceases to flow is referred to as the pour point, which is significantly lower than the freezing point. However, the use of such a system at the pour point will significantly increase the energy required for pumping. Furthermore, it is generally not recommended to regularly use systems beyond the freezing point of the mixture because of its decreased ability to transfer heat.

Corrosion

Alcohols may be corrosive to some aluminum alloys. In an aqueous mixture corrosion may still occur because of dissolved ions from residual salts. At high temperatures and in the presence of residual oxygen, glycols are oxidized slowly to the corresponding acids, which can corrode metals.

The inhibition of acid corrosion can be achieved by adding buffer systems that keep the pH constant and neutralize the acids. For example, a formulation of 100 kg EG with 400 g KH_2PO_4, 475 g Na_2HPO_4, and 4 l of water is used as an antifreeze agent, which can be diluted with water, approximately 50:50. This formulation will be highly anticorrosive. Also, borax can be used to protect metal surfaces from corrosion.

Besides pure chemical corrosion, solid corrosion products in the system will give rise to erosion, in which the particles moving with the fluid will impact the surfaces and can remove protective layers. Such corrosion effects are most pronounced in regions of high fluid-stream velocity.

The most common corrosion inhibitors, which may form protective films on the metal surfaces, are borates, molybdates, nitrates, nitrites, phosphates, silicates, amines, triazoles, and thiazioles, e.g., monoethanolamine, urotropin, thiodiglycol, and mercaptobenzothiazole. The addition of such inhibitors does not effectively protect against corrosion (Barannik et al., 1995). Some corrosion inhibitors are shown in Figure 14.3.

Dibasic salts of dicyclopentadiene dicarboxylic acid are claimed to be active as corrosion inhibitors (Darden and McEntire, 1986), and certain salts of fatty

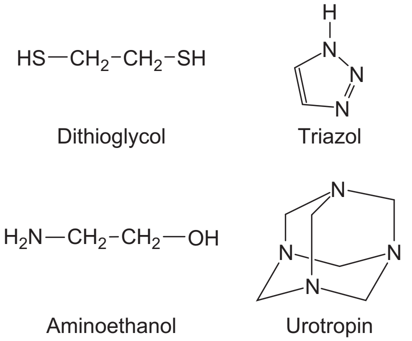

FIGURE 14.3 Corrosion inhibitors.

acids (metal soaps), together with benzotriazole, are claimed to give synergistic effects for corrosion in antifreeze agent formulations (Darden et al., 1987).

The choice of a corrosion inhibitor as an additive in antifreezing agents is also dependent on its mode of operation. For instance, cars are operated intermittently, so the corrosion inhibitors must also protect the system when it is idle, which can be acheived by film-forming silicates. This is especially true of aluminum parts, used in cars for weight reduction. However, silicones can react with EG to form crosslinked polymers, which may clog lines.

Engines used in the oil industry are usually heavy stationary diesels that run continuously. Aluminum is normally not used in this type of engine. Corrosion inhibitors for glycol systems based on silicate-forming films are not recommended in these cases, because of gel formation. Appropriate blends of corrosion inhibitors added to the glycol–water mixture have been developed (Hohlfeld, 1996).

Coolant formulations for engines used for natural gas transmission consist of phosphate for ferrous metal protection and a triazole for the protection of brass parts. Corrosion is discussed in detail in Chapter 6.

Foam Inhibitors

Although glycol–water formulations are not prone to foaming, the use of corrosion inhibitors and the presence of contaminants may enhance the tendency to form foams. For these reasons, antifoaming agents, such as silicones, polyglycols, or oils, are sometimes added.

Damage to Elastomers

Some elastomer sealings that are in contact with the antifreeze mixture may not be stable in such a medium because of their tendency to swell. The compatibility of EG with certain plastics is shown in Table 14.3.

TABLE 14.3 Compatibility of Ethylene Glycol with Some Elastomers

Material	25°C	80°C	160°C
Polyurethane	Good	Poor	Poor
Acrylonitrile-butadiene copolymer	Good	Poor	
Styrene-butadiene copolymer	Good	Fair	Poor
Ethylene-propylene-diene copolymer	Good	Good	Good
Natural rubber	Good	Poor	Poor
Silicone rubber polydimethylsiloxane	Good	Good	
Vinylidene fluoride-hexafluoropropene rubber	Good	Good	Poor

Toxicity and Environmental Aspects

Human and aquatic toxicity have been typically measured with fresh formulations. Spent fluids may contain various contaminants and degradation products that may change their effect.

Human Toxicity

The toxicity of antifreeze agents is due to EG. It is often believed that glycols are healthy to the skin, because the compounds are related to glycerol. This is completely wrong, because the degradation metabolism (i.e., catabolism) is completely different due to a difference in a single carbon atom.

EG is acutely toxic to humans and animals if ingested, and is classified as an animal teratogenic. Propylene glycol has not shown teratogenic effects, and its oral toxicity is lower, but it is more irritating to the skin than EG.

Aquatic Toxicity

The aquatic toxicity of antifreeze agents is not strictly due to the main component, but may be due to minor components in the formulation. Both EG and propylene glycol are believed to be essentially non-toxic to aquatic life.

Biodegradation

Laboratory tests of EG-containing formulations have shown a complete biooxidation within 20 days. The rate of biooxidation is constant over the full period. On the other hand, propylene glycol initially degrades more rapidly during the first 5 days of the test by 62%, then slowing to 79% conversion after 20 days. The mechanism of oxidation of EG is shown in Figure 14.4.

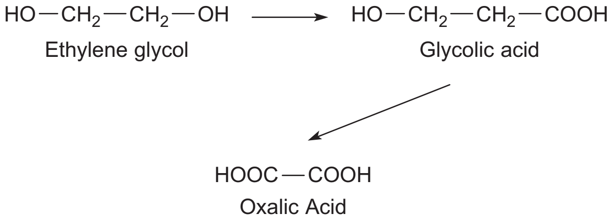

FIGURE 14.4 Oxidation of ethylene glycol to glycolic acid and oxalic acid.

Recycling

Recycling is achieved either by simply filtering or by redistillation. In the case of filtering, only deposits are removed. There is essentially no information concerning the activity of other additives as corrosion inhibitors. Redistillation is more effective because this process recovers the glycol in high quality, although it is more complicated and cost intensive than filtering. The refined glycol must be re-inhibited before use.

Spent antifreeze formulations can be purified before recycling. If the antifreeze agent is kept separate from waste oils, it can be easily treated and recycled into a new product.

SPECIAL USES

Hydraulic Cement Additives

Antifreezing agents for cement are mainly salts such as calcium chloride, magnesium chloride, sodium chloride, and soda. Calcium chloride is highly corrosive and very restricted in use. Some salts, especially potassium chloride, will affect the curing time of cement, and the latter chemical is in fact used to increase the pot life of cement. Likewise, alcohol-based freezing point depressants, such as EG, can be also included in the composition (Kunzi et al., 1993).

Pipeline Transportation of Aqueous Emulsions of Oil

Mixtures of aqueous emulsions of oil can be transported more effectively through pipelines if certain antifreeze formulations are added to the system. Stable oil-in-water emulsions for pipeline transmission are obtained by using 0.05–4% ethoxylated alkyl phenol as an emulsifier and freezing point depressant for water. Pipeline transmission at temperatures below the freezing point of water can then be performed (Gregoli and Olah, 1992).

Highly viscous petroleum oil containing 30–80% water can be transported through pipes more efficiently when a 1:1 mixture of washing liquid and antifreeze (i.e., EG with borax) is added to the oil in amounts of 0.002–0.2%.

In addition to the increased efficiency of transport, the corrosion of pipes is reduced (Ivashov et al., 1993).

Low Temperature Drilling Fluids

Antifreeze agents are occasionally added to a drilling fluid to reduce its freezing point (Hale, 1989; Hale et al., 1989). Such a water-based drilling fluid is composed of water, clay or polymer, and a polymeric glycerol.

More recently, antifreeze agents, such as polyvinylpyrrolidone, quaternary ammonium salts, or antifreeze fish proteins have been proposed for low temperature drilling (Grainger et al., 2006).

REFERENCES

Barannik, V.P., Kubyshkina, E.K., Lezina, N.M., 1995. Corrosion and thermophysical properties of lithium chloride-based coolant. Zashch Korrozii Okhrana Okruzhayushchej Sredy (8–9), 12–14.

Darden, J.W., McEntire, E.E., 1986. Dicyclopentadiene dicarboxylic acid salts as corrosion inhibitors. EP Patent 200 850, assigned to Texaco Development Corp., November 12, 1986.

Darden, J.W., Triebel, C.A., van Neste, W.A., Maes, J.P., 1987. Monobasic-dibasic acid/salt antifreeze corrosion inhibitor. EP Patent 229 440, assigned to Texaco Development Corp. and Texaco Development NV SA, July 22, 1987.

Grainger, N., Herzhaft, B., White, M., Audibert Hayet, A., 2006. Well drilling method and drilling fluid. US Patent 7 055 628, assigned to Institut Francais du Petrole (Rueil Malmaison Cedex, FR) and Imperial Chemical Industries Plc. (London, GB), June 6, 2006.

Gregoli, A.A., Olah, A.M., 1992. Low-temperature pipeline emulsion transportation enhancement. US Patent 5 156 652, assigned to Canadian Occident Petrol. Ltd., October 20, 1992.

Hale, A.H., 1989. Water base drilling fluid. GB Patent 2 216 573, assigned to Shell Internat. Res. Mij BV, October 11, 1989.

Hale, A.H., Blytas, G.C., Dewan, A.K.R., 1989. Water base drilling fluid. GB Patent 2 216 574, assigned to Shell Internat. Res. Mij BV, October 11, 1989.

Hohlfeld, R., 1996. Longer life for glyco-based stationary engine coolants. Pipeline Gas J. 223 (7), 55–57.

Ivashov, V.I. Shafiev, R.U., Azizkhanov, T., Azizov, K.K., Usmanova, M.A., 1993. Transporting highly viscous, water-laden oil through pipe – comprises addition to oil of 1:1 mixture of washing liquid and prescribed antifreeze (rus). SU Patent 1 827 499, assigned to Central Asia Nonferr Meta, July 15, 1993.

Kunzi, R.A., Vinson, E.F., Totten, P.L., Brake, B.G., 1993. Low temperature well cementing compositions and methods. CA Patent 2 088 897, August 06, 1993.

Stefl, B.A., George, K.L., 1996. Antifreezes and deicing fluids. In: Kroschwitz, J.I. (Ed.), Kirk-Othmer, Encyclopedia of Chemical Technology, vol. 3. John Wiley and Sons, New York, pp. 347–366.

Chapter 15

Odorization

The hazards of odorless combustible gases were probably first realized by miners. The idea of the odorization of combustible gases results from Julius Quaglio in 1880, who was engaged in researching various aspects of water gas (Quaglio, 1880). The gas produced at that time already contained impurities that created the typical odor of gas, but later it was obtained in such a purity that dangers emerged in handling it. Some aspects concerning the history of this issue are given in the literature (Usher, 1999). The primary objective of gas odorization is safety. It allows natural gas in air to be detected before it reaches combustible levels and hence acts as a warning. Naturally, odorization is a part of risk management for pipelines of natural gas (Muhlbauer, 2004).

Certain federal pipeline safety regulations, including those of the national fire protection association (US), require that combustible gases in pipelines be detectable at one-fifth of the lower explosive limit by a person with a normal sense of smell, either by the natural odor of the gas or by means of artificial odorization (Fant, 1993). Therefore proper odorization and odorants are integral parts of safety (Henderson, 1993; Toth, 1989).

Odorization is a primary concern for any gas transmission company (Henderson, 1993; Oudman, 1993). Accurate injection of the odorant, proper monitoring techniques, and complete record maintenance are important factors in developing and sustaining a successful odorization program.

A review has been presented concerning most aspects of odorization. Important points to consider are which pipelines require odorization, the detectable limits of gas odor, odorants and odorizing considerations, and the monitoring of the pipeline system to ensure that the odorization program is meeting regulatory requirements (Fant, 1993).

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GENERAL ASPECTS

Limits of Explosion

The approximate lower explosion limits of certain gases in air are shown in Table 15.1. There is also an explosion upper limit, which is dependent on the oxygen content – of course a constant for ordinary air. However, the limits of explosion are dependent on the total pressure (Holtappels et al., 2001).

There are mathematical models in order to calculate the limits of explosion (Askar et al., 2008), for example, the Software GasEq® and some additional software has been used to calculate the flammability limits of mixtures with, e.g., ethylene oxide, air, and inert gases at temperatures between 20°C and 100°C and pressures between 0.4 bar and 1.0 bar.

GasEq® is a Microsoft Windows-based program with a Microsoft Excel interface. The program can be used to calculate the equilibrium of combustion. It is intended primarily for gas phase calculations, although there is some limited facility for condensed phases, such as soot (Morley, 2005).

Desirable Properties of Odorants

An ideal odorant should have the following physical and functional properties (Kato, 2007):

- Low perceptual threshold,
- Preferably distinguishable from the smells of daily life and able to function as a warning smell,
- Low boiling point (essential for hydrogen gas),
- Low corrosivity,
- Little or no olfactory fatigue, and
- Low toxicity.

Odorants should allow leaks to be detected without any external equipment, so the end user need not worry about maintaining any measuring equipment. In this way equipment failures will not cause leaks to go undetected. Consequently, odorants allow the detection of leaks in places where it may be difficult to position detectors, and they can be used in small concentrations because of the sensitivity of the human olfactory system (Kopasz, 2007).

TABLE 15.1 Lower Explosion Limits

Gas	[%]
Methane	4.4
Natural gas	3.9
Hydrogen	4
Liquid petroleum gas	1.9

Furthermore, a fuel-gas odorant should be easily distinguishable from smells encountered in daily life, i.e., those smells that are experienced in daily life situations and are not perceived as a foreign or unusual odor.

By contrast, a warning smell is in general an unpleasant smell that is perceived as an odor that indicates an unusual situation, clearly distinguishable from the smells in daily life. In this way, the smell acts as a warning signal (Kato, 2007).

MEASUREMENT AND ODOR MONITORING

The methods of odor monitoring are reviewed by Klusmann (1993) and by Wetteman and Wilson (1993).

In the early days of the coal mining industry, open flames were take taken into the mine. When the candle started burning irregularly, a possible danger of a near explosion could be realized. However, often this technique indicated a danger too late. A significant step forward was the invention of the safety lamp in 1815 by Sir Humphry Davy. The presence of combustible gases could be still detected, but the explosive reaction only happened inside the wired cage of the safety lamp.

Another method of monitoring utilized the extraordinary sensitivity of canary birds to methane. These birds were taken by the miners into the mines, admittedly involuntary, in small cages. The canary stopped singing in the presence of even small amounts of coal gas, and died at higher levels that were still harmless to the human body (Kopasz, 2007).

The addition of odorants to liquid petroleum gas and natural gas gives an improved level of safety, but their use suffers from certain limitations and disadvantages. Firstly, for an odor to be detected, a human being must be present in the vicinity of the leak. Secondly, not every individual is able to detect the odors at the same mandatory level. Most dangerous is that some individuals are not able detect the odor at all.

The sensitivity of an individual may be affected by a seasonal illness, such as influenza or a cold. Also, the exposure to other odors lowers one's overall sensitivity and during sleep the olfactory response decreases.

Olfactoric Response

Odorants are chemicals that stimulate the olfactoric sense. The human olfactory system is much less sensitive than that of animals, such as dogs, which are notorious for their sense of smell. Nevertheless, a human being can still detect certain odorants in concentrations in the air in the parts per trillion (ppt) range.

There are several definitions that are relevant to quantifying the odor. The threshold odor concentration is the absolute perception threshold at which a substance can be barely identified, however faint the impression. The odor recognition threshold is the concentration at which a representative odor for a certain substance can be detected (Patnaik, 2007).

There is a difference between the minimum detectable concentration and the minimum identifiable concentration. The former is defined as the lowest concentration at which 50% of the human population is able *to smell something*. This concentration is sometimes known as the perceptual threshold or odor recognition threshold.

In contrast, the recognition threshold is the minimum concentration at which a certain, predefined percentage of people can identify the substance coarsely. At the detection and recognition thresholds there will still be a large number of individuals who do not detect or recognize the odor. Data indicate that, as a rule of the thumb, the recognition threshold is roughly a factor of 10 higher than the detection threshold (Kopasz, 2007).

Perceptual Threshold and Olfactoric Intensity

The perceptual threshold of an odorant is the minimum concentration of the odorant in the air, expressed in ppm, etc., at which a human being can easily notice the smell of the odorant. In general, the values refer to ratios by volume and not by weight, as is usual in gas analysis.

This threshold value can be determined by panelists, who assess the olfactory intensity of a test substance in an odorless chamber. The air in the chamber is stirred until the concentration of the test substance becomes constant and is then left to stand. The olfactory intensity is assessed, for instance, on a scale of 0 to 5 for smell pollution. The olfactoric response of human males and females between the ages of 16 and 82 years were tested with various odorants, including *tert*-butylmercaptan, thiophene, ethylmercaptan, dimethyl sulfide, isopropylmercaptan, and mixtures of these odorants. The perceptual and recognition thresholds of selected chemicals are summarized in Table 15.2.

The goal was to establish the warning levels below the explosion limit in the event of a gas leak (Ripley et al., 1990). The study suggests that ethylmercaptan is the most suitable odorant. Trained dogs can detect odorizing agents in concentrations as small as 10–18 ppb (Bissell et al., 1993; Quaife and Moynihan, 1990; Quaife et al., 1992a).

Odor Index

The odor index (OI) is the ratio of the vapor pressure to the odor recognition threshold (Patnaik, 2007, p. 13).

$$OI = \frac{\text{vapor pressure [ppm]}}{\text{recognition threshold [ppm]}} \tag{15.1}$$

Thus, the odor index is a dimensionless number, and a value less than 1 means that the substance has a vapor pressure that is too small for the substance to be detected.

Olfactory Power

There is another definition of the intensity of a certain smell called, the olfactory power (Flynn and Sprague, 2009), which is defined as the negative decadic

TABLE 15.2 Perceptual and Recognition Thresholds of Chemicals (Verschueren, 2009)

Perceptual thresholds (Kato, 2007)	**Concentration**
p-Cresol	51.3 ppt
5-Ethylidene-2-norbornene	4 ppb
Methylmercaptan	1.6 ppb
γ-Undecalactone	22.8 ppt
3-Hydroxy-4-methyl-5-ethyl-2(5H)-furanone	7.4 ppt
trans-2-*trans*-4-Decadienal	87 ppt
Recognition thresholds (Patnaik, 2007, pp. 14)	**Concentration**
Ethane	1500 ppm
Propane	11,000 ppm
Butane	5000 ppm
Pentane	900 ppm
Octane	200 ppm
Methanol	6-000 ppm
Ethanol	6-000 ppm
Octanol	2 ppb
Geosmin	5 ppt
Diethylether	300 ppb
Ethyl acrylate	2 ppb
Hydrogen sulfide	1 ppm
Methylmercaptan	35 ppb
Ethylmercaptan	2 ppb
Butylmercaptan	0.8 ppb
Ethyl sulfide	4 ppb

logarithm of the detection threshold. Olfactory power tables are given in Table 15.3.

Physiological Methods

An example of a specific method for determining the perceptual threshold is as follows. A test odorant in a dish is left in an odorless chamber for a given period of time. The air in the chamber is agitated until the concentration of the

TABLE 15.3 Functionality and Odor Potency of Low Molecular Weight Compounds (Flynn and Sprague, 2009)

Functionality	Compound	Olfactory Power
Hydrocarbons	Ethane	2.00
	Propane	2.57
	Butane	3.69
Halides	Chloromethane	4.99
	Ethylchloride	5.39
Alcohols	Methanol	3.85
	Ethanol	4.54
	1-Propanol	5.62
Esters	Methyl formate	4.03
	Methyl acetate	5.21
Ketones	Acetone	4.84
Aldehydes	Formaldehyde	6.06
	Acetaldehyde	6.73
Amines	Methylamine	7.73
	Dimethylamine	7.09
	Ethylamine	6.49
	Diethylamine	6.73
	Propylamine	7.96
Thiols	Methylmercaptan	8.98
	Ethylmercaptan	8.97
	Isobutylmercaptan	8.95
	tert-Butylmercaptan	9.48
Sulfides	Dimethyl sulfide	8.65
	Methylethyl sulfide	8.42
	Diethyl sulfide	8.41
Selenides	Diethylselenide	9.13
Selenols	Ethylselenol	10.74

test substance becomes constant, and then it is left standing for 1 min. Panelists then enter the chamber and assess the olfactory intensity on a scale of 0 to 5. This procedure is then repeated for different concentrations of the test odorant. A perceptual threshold is then obtained by determining the concentration of the odorant that corresponds to the olfactory intensity of 2, at which the smell can easily be identified as described below. The olfactory intensity is assessed on a scale of 0 to 5 (Kato, 2007):

0: Odorless,
1: Slight smell, but not identified,
2: Easily noticed and can be identified,
3: Obvious smell,
4: Strong smell, and
5: Intolerably strong smell.

Triangle Odor Bag Method

The measurement of the odor threshold by the triangle odor bag method has been described in detail (Nagata, 2003). The data were collected over a comparatively long period of time, i.e., from 1976 to 1988, and 223 substances were tested in total for this study.

It was found that isoamylmercaptan exhibited the lowest threshold, of 0.77 ppt, and propane exhibited the highest threshold of 1500 ppm. The distribution of the thresholds of the substances investigated follows a Gaussian normal distribution. As expected from common sense, sulfur compounds, apart from sulfur dioxide and carbon disulfide, exhibit a comparatively low threshold.

There is a relationship between the molecular weight of the substance and its odor threshold, and there is a great difference in threshold between isomers. The thresholds may differ by up to four powers of ten. Extensive listings of the odor thresholds measured in this study have been presented (Nagata, 2003).

For comparison, Table 15.4 presents selected odor thresholds measured by the triangle odor bag method. Observe that these values differ appreciably from those given in Table 15.2. This may be caused by the different methods used in the acquisition, but considerable variation was discovered when tests were repeated on the same substance.

Standardized Methods

Sensory thresholds have been established in order to determine the potential of substances at low concentrations to impart odor, taste, haptic, etc., to some form of matter (ASTM E 0679-04, 2009).

Procedures for referencing the odor intensities of materials have been standardized, and the so-called *ASTM Odor Intensity Referencing Scale* has been developed (ASTM E 544-99(2004), 2009). This scale is a geometric progression scale. Reference odorant vapors are evaluated by a panel of at least eight independent judges, who compare the odor intensity of the sample to the odor intensities of a series of concentrations of *n*-butanol, the reference odorant.

TABLE 15.4 Odor Thresholds Measured by the Triangle Odor Bag Method (Nagata, 2003)

Substance	Concentration
Propane	1500 ppm
Butane	1200 ppm
Pentane	1.4 ppm
Octane	1.7 ppm
Methanol	33 ppm
Ethanol	0.52 ppm
Octanol	2.7 ppb
Methylmercaptan	70 ppt
Ethylmercaptan	8.7 ppt
n-Propylmercaptan	13 ppt
Isopropylmercaptan	6 ppt
n-Butylmercaptan	2.8 ppt
Isobutylmercaptan	6.8 ppt
Butylmercaptan	30 ppt
tert-Butylmercaptan	29 ppt
n-Amylmercaptan	0.78 ppt
Isoamylmercaptan	0.77 ppt
n-Hexylmercaptan	15 ppt

Two methods are used to create the smell. In the dynamic scale method, a dynamic-dilution apparatus is used, equipped with a series of sniffing ports from which constant concentrations of 1-butanol emerge at constant volumetric flow rates in air. In the static-scale method, a series of Erlenmeyer flasks containing known concentrations of *n*-butanol dissolved in water is used.

Chemical and Physical Methods

Chromatographic and Spectroscopic Methods

The concentration of odorants in gases can be measured by their absorbance in the ultraviolet region (Shimokawatoko et al., 1998a,b). The absorbance of odorized gas is much higher than that of untreated gas.

An integrated natural gas pipeline leak detector based on near-infrared diode laser absorption spectroscopy, wavelength modulation spectroscopy, and harmonic detection has been used (Gao et al., 2006). Direct absorption spectroscopy has the drawback of low sensitivity.

It is difficult to detect a small flux pipeline leak of natural gas, so the second harmonic signal is used in a modulated wave. The method directly accesses the absorbance by methane, so the presence of an odorant is immaterial.

Gas chromatography with an electrochemical detector is also suitable (Wallace et al., 1991) for the analysis of mercaptans. Portable equipment for the measurement and analysis of odorants in gas distribution networks is available.

The analysis and characterization of odorants plays an important role in the food industry and in the perfume and oil and gas industries. Remarkably the sensitivity of an analytical instrument, such as a mass spectrometer and the sensitivity of the human nose do not correlate at all. Substances with an intense smell may cause only a small mass spectrometric peak and vice versa.

Colorimetric Methods

The classical analysis of traces of gases is by colorimetric methods, originally invented by the Dräger company in Lübeck, Germany. An indicator is placed inside a thin glass tube that is sealed at both ends by melting the glass. In the test procedure, the sealed ends of the glass tube are broken and a known amount of gas is sucked through. The indicator will react with any impurity and change color. The distance up the tube that changes color is proportional to the concentration of impurity present. On the tube itself, a scale is printed so that the concentration of the respective impurity can be read out directly in ppm, provided the correct volume of gas has been sucked through.

Electronic Nose

The term *electronic nose* was created around the late 1980s (Gardner and Bartlett, 1994). It is based on a chemical sensor (Junichi et al., 2006), a device that converts chemical information into an analytically useful signal.

Chemical sensors are important for a variety of industrial and environmental applications, including the detection of hazardous chemicals, quality control in the food, perfume, and beverage industries, and medical applications (McGill et al., 2009). These types of sensors include a sorbent layer deposited on the active area of a signal transducer.

Some chemical sensors have been described that are potentially suitable for the detection of natural gas (Ameer and Adeloju, 2005; Munoz et al., 2009). For example, conducting polypyrrol films have been found useful for the detection of methane, since the sensitivity of the film is dependent on the CH_4 concentration and the pressure.

Nanocomposites based on iron oxide and polypyrrol have been used for sensing various gases (Suri et al., 2002), and could potentially be used for the sensing of methane in oil fields, natural gas pipelines and joints, and waste water treatment plants (Ameer and Adeloju, 2005).

Commercial metal-oxide-based gas sensors that are specifically sensitive to methane are available. They are recommended as sensors for domestic gas alarms for the detection of methane (TGS 842, 2008). Suitable sensor systems have also been described for the detection of water traces in natural gas (May, 2009), which operate by the change in the electric capacitance in the presence of water vapor.

ADDITIVES FOR ODORIZATION

Sulfur Compounds

Certain organic sulfur compounds are used for odorization because of their inherent penetrating smell. Skunk repellents contain sulfur compounds such as *trans*-2-butene-1-thiol and 3-methyl-1-butanethiol. Ethylmercaptan, because of its extremely low odor threshold, is the main compound used as an odorant in natural gas and liquid propane for leak detection, although tetrahydrothiophene is also often used. Common odorization reagents are summarized in Table 15.5 and Figures 15.1 and 15.2.

tert-Butylmercaptan is very common in single component odorant, with good soil penetration and a high resistance to oxidation. Its high freezing point means that it needs to be used in mixtures with other components.

TABLE 15.5 Sulfur-based Additives for Odorization

Additive	References
Ethylmercaptan or mixture of ethyl-, propyl-, and butylmercaptans dimethyl disulfide, diethyl disulfide, and methyl ethyl disulfide[a]	Arkema Inc. (2008); Fakhriev et al. (1993, 1994); Ismagilov et al. (1995), and Mazelli (1977)
Diethyl sulfide and ethyl propyl sulfide	McClure (1958)
Cyclohexylmercaptan	Oister (1970)
Dimethyl sulfide	Quaife et al. (1992b)
Tetrahydrothiophene, thiophenemercaptans with additional pyridine and picoline	Yashchenko et al. (1997)
Mixture of ethyl-, propyl-, butyl-, and amylmercaptan	Fakhriev et al. (1995), and Yoshida et al. (1984)
2-Methoxy-3-isobutyl pyrazine and 4-methyl-4-mercapto-2-pentanone	Yoshida et al. (1984)

a) From wastes

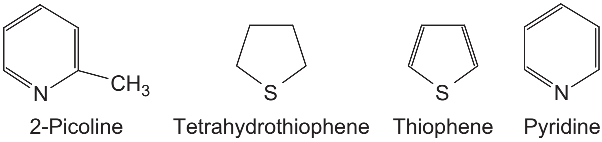


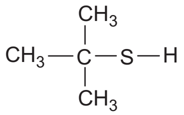
FIGURE 15.1 Cyclic odorants.

CH_3-CH_2-SH

Ethylmercaptan

$CH_3-CH_2-CH_2-CH_2-SH$

n-Butylmercaptan



$CH_3-C(CH_3)_2-S-H$

tert-Butylmercaptan

$CH_3-CH_2-S-CH_2-CH_3$

Diethylsulfide

$CH_3-CH_2-S-CH_2-CH_2-CH_3$

Ethylpropylsulfide

FIGURE 15.2 Mercaptans and sulfides.

Isopropylmercaptan has a strong odor and a good resistance to oxidation. It is usually blended with *tert*-butylmercaptan to depress the freezing point of the latter compound (Usher, 1999).

Alkyl sulfides are resistant to oxidation, but they do not have as strong an odor as the mercaptans, so they are not used as stand-alone odorants. They are usually added to lower the freezing point of mercaptans. The commonly used odorant blends fall into one of the following main categories (Usher, 1999):

1. Mercaptan blends,
2. Mercaptan–alkyl sulfide blends, and
3. Tetrahydrothiophene–mercaptan blends.

Thermodynamic Properties of Odorants

The effectiveness of an odorant depends on its partition coefficients and solubility. Vapor-liquid equilibria data for sulfur compounds in liquefied natural gas are available (Guilbot et al., 1997; Kedzierski, 1996).

Structure Property Relationships

The power of the odor depends on certain properties of the respective molecule. A number of structure-odor relationships for odor intensity and quality have been established (Chastrette, 1997) using statistical methods.

Other Compounds

Sulfur-containing compounds are widely known as odorants used for fuel gases, but they usually generate sulfur dioxide when the fuel gases are burned. Also, if the fuel gases are used in fuel cells, a desulfurizer must be installed to remove odorant components that would cause catalyst poisoning (Kato, 2007).

Attempts have been undertaken to provide sulfur-free gas odorizing compositions, including the use of alkyl acrylates, vinyl or alkyl ethers, *n*-valeric acid, ethyl acrylate, cyclohexene, and norbornene derivatives (Mansfeld et al., 2006). These odorants have certain disadvantages, however. For example, acrylic ester odorants are chemically unstable. The content of cyclohexene or ethylidene norbornene must be larger than those of mercaptans (Kato, 2007). On the other hand, nitrogen-containing odorants may cause the enhanced formation of nitrogen oxides, which are toxic and react with sunlight to form ozone.

Among the alcohols that are suitable as odorants, geosmin is a preferred compound. Geosmin actually means *earth smell*. It is a naturally occuring organic compound produced by microorganisms. The human nose is extremely sensitive to geosmin. Its structured name is 2,6-dimethylbicyclo [4.4.0]decan-1-ol. The structures of geosmin and other sulfur-free odorants are shown in Figure 15.3.

trans-2-*trans*-4-Decadienal also has a low perceptual threshold (Kato, 2007). Mixtures of acrylates and pyrazines have been proposed as sulfur-free odorants (Mansfeld et al., 2006). The odorizing compositions may contain antioxidants, e.g., butylhydroxyanisole, ionol, i.e., *tert*-butyl hydroxytoluene,

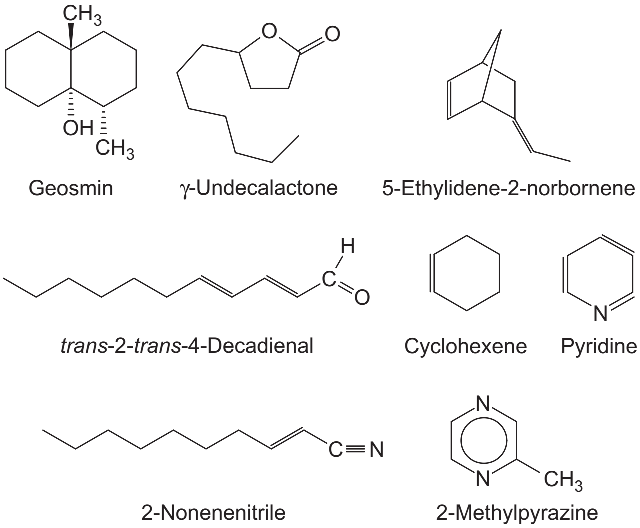
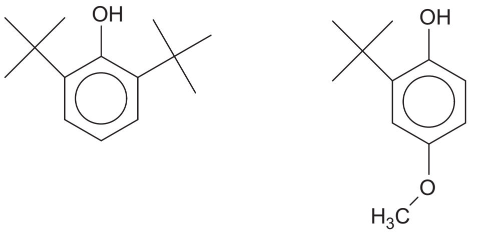
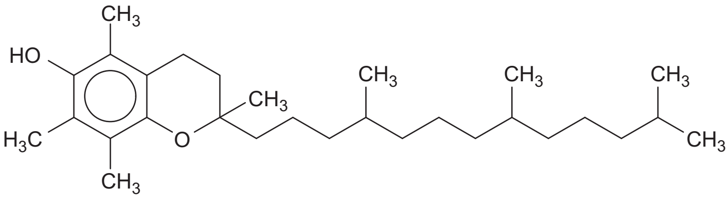


FIGURE 15.3 Sulfur-free odorants.



tert-Butylhydroxytoluene Butylhydroxyanisole



α-Tocopherol

FIGURE 15.4 Antioxidants.

TABLE 15.6 Sulfur-Free Additives for Odorization

Additive	References
trans-2-*trans*-4-Decadienal	Kato (2007)
Geosmin	Kato (2007)
Cyclohexene	Mansfeld et al. (2006)
n-Valeric acid	Mansfeld et al. (2006)
Ethyl acrylate	Charles (2008), and Mansfeld et al. (2006)
1-Methoxy-buten-3-yne	Müller and Short (2008)
Methyl ethyl pyrazine	Müller and Short (2008)

hydroquinone monomethyl ether, and α-tocopherol to protect against undesired oxidation. Examples are shown in Figure 15.4.

Sulfur-free odorants are shown in Table 15.6. Commercial sulfur-free odorants (or compositions with a reduced sulfur content) include a mixture of ethyl acrylate and methyl acrylate (Gasodor S Free™) and a mixture of ethyl acrylate and tetrahydrothiophen (Spotleak Z) (Heimlich et al., 2008).

Sulfur-free odorants can be smelled readily, but the odor rather resembles garlic. Human common sense does not associate this type of smell with combustible gas, because people are accustomed to the mercaptan smell.

Some cities have changed their odorant in the natural gas pipelines to sulfur-free odorants, with reports of success (Wagner, 2005), but others have returned to the conventional sulfur-based odorants.

The behavior of Gasodor S Free™ during reforming of methane that has been odorized with just this odorant has been tested with respect to the application of methane in fuel gas systems. It has been verified that odorization with Gasodor S Free would not have a negative impact on its subsequent use in fuel gas systems (Hennings and Reimert, 2007).

INDUSTRIAL SYNTHESIS OF ODORANTS

The chemistry of thiols has been reviewed by Roberts (1997). Ethylmercaptan is readily formed by the reaction of ethyl bromide with hydrogen sulfide. Mercaptans can also be produced by the reaction of hydrogen sulfide and an olefin in the presence of a catalyst. Ethylmercaptan can be prepared by reaction of pure ethylene and hydrogen sulfide without the need for separation because it is the only mercaptan product. The basic reactions are

$$CH_3-CH_2-Br+H_2S \rightarrow CH_3-CH_2-SH+HBr \qquad (15.2)$$

and

$$CH_2=CH_2+H_2S \rightarrow CH_3-CH_2-SH. \qquad (15.3)$$

However, where the reactants are a mixture of more than one olefin, such as ethylene and propylene, the reaction is likely to produce both ethylmercaptan and propylmercaptan resulting in separation difficulty, because these mercaptans cannot be easily separated by distillation, extraction, filtration, or membrane diffusion. However, the selective production of ethylmercaptan from a fuel gas mixture can be achieved by special catalysts, i.e., oxides of cobalt and molybdenum (Sattich, 1994).

Mercaptans and sulfides can be selectively produced from alcohols by an electrophilic substitution reaction with hydrogen sulfide, in the presence of a catalyst blend. The alcohols can include primary and secondary alcohols (Hasenberg and Refvik, 2008).

$$R-OH+H_2S \rightarrow R-SH+H_2O \qquad (15.4)$$

In addition, mercaptans are formed by the reaction of sulfides with hydrogen sulfide:

$$R-S-R+H_2S \rightarrow 2R-SH \qquad (15.5)$$

USES AND PROPERTIES

Odorant Injection Techniques

Odorants are typically provided in liquid form, and are added to the gas where the distribution gas is taken from a main gas pipeline and transferred to a distribution pipeline. In such circumstances, the gas pressure may be stepped down through a regulator to a lower pressure. The odorants added to natural gas are extremely concentrated. Odorants such as *tert*-butylmercaptan and other blends are mildly corrosive and are also very noxious.

If a leak of odorant were to occur at an injection site, people in the surrounding area would assume that a gas leak had occurred with areas being evacuated and commerce being interrupted. However, if such mistakes become commonplace, people in the surrounding area will become desensitized to potential gas leaks and will fail to report them.

Three techniques are commonly used for odorizing incidents natural gas in a main distribution pipeline. A liquid odorant can be injected directly into the pipeline by a high-pressure injection pump, which pumps the odorant from a liquid storage tank into a small pipe that empties directly into the main gas pipeline. Because the odorant is extremely volatile, drops injected into the pipeline immediately disperse and spread throughout the gas in the pipeline. In this way, the drops of liquid odorant are dispersed in gaseous form within a few seconds (Marshall and Zeck, 2001).

The flow of gas in the pipeline is typically metered, so that liquid odorant can be injected periodically. For example, a few drops of odorant will suffice for a 30 m^3 flow of natural gas. When the gas flow meter indicates that such an amount of natural gas has flowed through the pipe, another aliquot of liquid odorant is injected into the pipeline. This process is then repeated, even though the injection is performed periodically, the odorant diffusion within the gas provides adequate levels of odorant throughout the pipeline, assuming the time between injections is not too great.

Another odorization technique involves bypassing a small amount of natural gas at a slightly higher pressure than that of the main distribution pipeline through a tank containing a liquid odorant. This bypass gas absorbs relatively high concentrations of odorant while it is in the tank, and then returns to the main pipeline. The odorant, now volatilized, diffuses throughout the pipeline in much the same manner as described in the previous method (Arnold, 2000).

A third method for odorizing natural gas is to inject the odorant into the pipeline at a controlled rate. The system includes an odorant storage tank containing the odorant to be injected. A pressurized source of inert gas, such as nitrogen, maintains the tank at a desired positive pressure above that of the natural gas pipeline. An injection conduit communicates the odorant storage tank with the pipeline. A photooptic metering means, located within the injection conduit, meters the odorant to be injected into the pipeline (Zeck, 2006).

In an improved version of this method, the chemical is metered on a drop wise basis, with individual drops being counted as they pass through a measuring unit into the injection conduit and hence the pipeline. The measuring unit includes ultrasonic transmitters and receivers, which act as either proximity sensors or by measuring the transit time, to provide a measurement of the flow rate of the odorant on either a drop basis or in a steady state flow condition. Alternatively, liquid drops may land on the diaphragm of a piezoelectric sensor and thereby generate sound waves. These are then transmitted to an associated crystal, which generates a proportional electric charge resulting in a voltage difference between the two electrodes. The resulting voltage spikes can be counted and measured (Zeck, 2008).

Leak Detection

Leaks in pipelines can be detected by means of a test fluid. The test fluid, a mixture of dimethyl sulfide in solvent, is injected into a pipeline. It will escape through any leak, and the odorant is released from the closed compartments (Quaife et al., 1991, 1993).

Fuel Cells

With the advent of hydrogen-based fuels cells, the odorization of hydrogen has become an issue (Kopasz, 2007). Here another problem emerges, since common odorants may have a negative impact on the performance of the fuel cells, since commercial odorants act as poisons for the catalysts used in hydrogen-based fuel cells, most specifically for proton exchange membrane fuel cells. Chemical compounds based on mixtures of acrylic acid and nitrogen compounds have been adopted to achieve sulfur-free odorization of the gas (Puri, 2007).

In the use of natural gas and other petroleum gases to generate hydrogen for fuel cell applications, sulfur-free natural or petroleum gases are needed, or else a desulfurization step must be incorporated in the reforming process, which adds further cost to hydrogen generation.

Fuel cells are sulfur intolerant due to sulfur poisoning of the noble metal catalysts used. If sulfur-containing odorants are used, it would be necessary to remove sulfur-containing materials, like mercaptan odorants, from the feed gas using materials like zinc oxide. However, some sulfur-containing materials, like thiophenes, cannot be removed by zinc oxide and may require a specific hydrodesulfurization process, using hydrogen gas, to remove sulfur.

A further complexity for hydrogen fuel comes from the nature of the hydrogen flame propagation. When gases burn in air, their flames propagate upward with greater ease than they propagate downward. This is primarily due to the natural upward convection of hot burnt gases. For petroleum gases, propane and methane, the upward and downward propagating lean limits of combustion are approximately the same.

However, for hydrogen, since they differ by a factor of 2.5, the amount of odorant needed for leak detection in hydrogen could be > 2.5 times that needed for methane or propane. The higher quantity of the odorant needed for hydrogen odor detection further complicates the sulfur poisoning problems for hydrogen gas used in fuel cells (Puri, 2007).

Odor-fading

One specific problem of odorization is odor-fading. The gas may be satisfactorily odorized at the source, but if it no longer has the necessary odor impact and intensity by the time it reaches the customer, escaping gas can remain undetected and result in a serious fire or explosion hazard. Basically three causes of fading may arise (Usher, 1999):

1. Oxidation, the formation of disulfides in the presence of iron oxide and traces of oxygen;
2. New pipe materials may cause adsorption or absorption of the odorant on to the surface of a plastic pipe; and
3. Gas quality problems may cause masking, or reaction of odorant components with impurities in the gas stream.

The presence of rust and air within a pipeline may act as a catalyst for the oxidation of mercaptans, resulting in compounds that do not smell at all. On the other hand, sulfide components are much more resistant to oxidation.

Dry gas is the easiest to odorize and does not cause odor-fade. Condensed liquids in the pipeline may absorb components of the odorant. Odor masking may also occur because of the odor imparted by any impurities present in the gas.

Odor-fading from odorized liquefied petroleum gas stored in carbon steel containers can occur by catalytic effects of the containers. To postpone this effect, the respective steel surfaces can be deactivated by treating them with a deactivating agent (Nevers, 1990) before exposure to the liquefied petroleum gas.

Examples of such deactivating agents are benzotriazole, tolyl triazole, mercaptobenzothiazole, benzothiazyl disulfide, or mixtures of these compounds (Nevers, 1987). It has been suggested that a mathematical model and adequate software should be developed to predict odorant fade (Altpeter, 1997).

Environmental Problems

If natural gas for storage in natural reservoirs is odorized with sulfur compounds, then a possible environmental impact can result. Some of the odorant is lost in the formation (Sasnanand, 1993). If the loss occurs in a reservoir adjacent to an aquifer, it could contaminate the water and cause environmental problems. When gas is drawn off, water is also often injected into the reservoir. A case was described in which the respective water had a strong characteristic odor (Girod et al., 1996). A stripping column has been recommended to overcome this problem.

Contaminated ground water can be decontaminated by reaction with iron (Huang and Lee, 1997). This technique was proposed to remedy ground water that was contaminated with ethylmercaptan in situ. Studies suggest chemical reactions with iron rather than an irreversible surface adsorption. Gas odorizers can be removed by extraction, similar to the usual glycol dehydration and desulfurization process (Jullian et al., 1997; Rojey et al., 1998).

Another cleaning process for the removal of tetrahydrothiophene uses an advanced oxidation technique, consisting of water treatment by UV radiation in combination with a dose of hydrogen peroxide (Panneman et al., 1997). It is possible to keep the concentrations of odorant and condensate in the effluent below 0.1 ppb.

REFERENCES

Altpeter Jr., L.L., 1997. Research recommended to develop odorant-fade model. Pipe Line Gas Ind. 80 (2), 39–40.

Ameer, Q., Adeloju, S.B., 2005. Polypyrrole-based electronic noses for environmental and industrial analysis. Sens. Actuators B 106 (2), 541–552.

Arkema Gas Odorants, 2008. Arkema Inc., Philadelphia, PA. http://arkema-inc.com/literature/pdf/802.pdf (accessed 29.05.08).

Arnold, J.F., 2000. System and method for odorizing natural gas. US Patent 6 142 162, assigned to Odoreyes Technology, Inc., Birmingham, AL, November 7, 2000.

ASTM E 0679-04, 2009. Practice for determination of odor and taste thresholds by a forced-choice ascending concentration series method of limits, ASTM Standard, Book of Standards, vol. 15.08. ASTM International, West Conshohocken, PA.

ASTM E 544-99(2004), 2009. Standard practices for referencing suprathreshold odor intensity, ASTM Standard, Book of Standards, vol. 15.08. ASTM International, West Conshohocken, PA.

Askar, E., Schröder, V., Acikalin, A., Steinbach, J., 2008. Calculation of flammability limits of gas phases with ethylene oxide in sterilisers. Biomed. Eng. 53 (6), 265–269.

Bissell, J., Acker, D., Quaife, L.R., 1993. Pipeline leak-location technique utilizing a novel test fluid and trained dogs. In: Proceedings Volume, no. 9, 5th Pipe Line Ind. & Pipes Pipelines Int. Pipeline Pigging & Integrity Monit Int. Conf., Houston, February 1–4, 1993.

Charles, P., 2008. Gas odorant. US Patent Application 20080295404, assigned to Arkema France, Colombes, December 4, 2008.

Chastrette, M., 1997. Trends in structure-odor relationship. SAR QSAR Environ. Res. 6 (3), 215–254.

Fakhriev, A.M., Ismagilov, F.R., Latypova, M.M., 1995. Odorant for natural gas. RU Patent 2 041 243, assigned to Bashkirskoe Sp Kt B Kontserna, August 9, 1995.

Fakhriev, A.M., Latypova, M.M., Ismagilov, F.R., Navalikhin, P.G., 1993. Odorisation of liquefied hydrocarbon gases – using waste from oxidising demercaptanisation of light hydrocarbon material. RU Patent 2 000 313, September 7, 1993.

Fakhriev, A.M., Latypova, M.M., Nasteka, V.I., Berdnikov, A.I., Klimov, V.Y., 1994. Odorising agent for compressed hydrocarbon gas – contains ethyl-mercaptan or mixed mercaptans, and additionally waste from process of oxidising de-mercaptanisation of light hydrocarbons. RU Patent 2 009 178, assigned to Hydro Carbon Raw Mat. Res. and Orenburg Gas Process Wks, March 15, 1994.

Fant, E.E., 1993. Odorization – a regulatory perspective. In: Wilson, G.G., Attair, A.A. (Eds.), Odorization, vol. 3. Institute of Gas Technology, Chicago, IL, pp. 109–118.

Flynn, P.J., Sprague, M., 2009. Hydrogen odorants and odorant selection method. US Patent Application 20090179177, assigned to Enersol, Inc. N.A., L.P. Fairfax VA, July 16, 2009.

Gao, X., Fan, H., Huang, T., Wang, X., Bao, J., Li, X., et al., 2006. Natural gas pipeline leak detector based on NIR diode laser absorption spectroscopy. Spectrochim. Acta Part A 65 (1), 133–138.

Gardner, J.W., Bartlett, P.N., 1994. A brief history of electronic noses. Sens. Actuators B 18 (1–3), 210–211.

Girod, J.F., Leclerc, J.P., Muhr, H., Paternotte, G., Corriou, J.P., 1996. Removing a small quantity of THT (tetrahydrothiophene) from gas storage groundwater through air stripping and gas-phase carbon adsorption. Environ. Progr. 15 (4), 277–282.

Guilbot, P., Valtz, A., Richon, D., 1997. Partition coefficients at infinite dilution for different sulfur compounds in various solvents. In: Proceedings Volume, 76th Annu. Gpa Conv, San Antonio, March 10–12, 1997, pp. 33–39.

Hasenberg, D.M., Refvik, M.D., 2008. Process and catalyst for synthesis of mercaptans and sulfides from alcohols. US Patent 7 399 893, assigned to Chevron Phillips Chemical Company LP, The Woodlands, TX, July 15, 2008.

Heimlich, F., Niebialek, S., Schulz, C., 2008. Odorization with spotleak Z. Gas und Wasserfach Gas Erdgas 149 (3), 165.

Henderson, D.F., 1993. Large volume odorization, installation, operation, and maintenance. In: Wilson, G.G., Attair, A.A. (Eds.), Odorization, vol. 3. Institute of Gas Technology, Chicago, IL, pp. 239–249.

Hennings, U., Reimert, R., 2007. Behaviour of sulfur-free odorants in natural gas fed PEM fuel cell systems. Fuel Cells 7 (1), 63–69.

Holtappels, K., Brinkmann, C., Dietlen, S., Schröder, V., Stickling, J., Schönbucher, A., 2001. Messung und Simulation des Inertgaseinflusses auf Explosionsgrenzen bei erhöhten Anfangsdrücken. Chem. Ing. Tech. 73 (3), 270–274.

Huang, F., Lee, R., 1997. Degradation of ethyl mercaptan in the presence of zero-valence iron. In: Proceedings Volume, 4th US DOE, Tulsa Univ, et al Petrol. Environ. Conf., San Antonio, September 9–12, 1997.

Ismagilov, F.R., Kazantsev, A.V., Akhunov, R.R., Rygalov, V.A., Navalikhin, P.G., Andrianov, V.V., et al., 1995. Odorant for liquefied hydrocarbon gases and method for its production. RU Patent 2 051 168, assigned to Bashkirskoe Sp Kt B Kontserna, December 27, 1995.

Jullian, S., Thomas, M., Rojey, A., 1997. Process for the complete treatment of natural gas on a production site. EP Patent 0 781 832, assigned to Inst. Francais Du Petrole, May 2, 1997.

Junichi, K., Masayuki, O., Hisamitsu, A., Motoo, K., 2006. Electronic nose. J. Jpn. Assoc. Odor Env. 37 (3), 172–178 (in Japanese).

Kato, Y., 2007. Odorant for fuel gas. US Patent 7 182 796, assigned to Soda Aromatic Co., Ltd. (JP), February 27, 2007.

Kedzierski, S., 1996. The solubility of odorants in natural gas (rozpuszczalnosc preparatow nawaniajacych w gazie ziemnym). Nafta Gaz (Pol) 52 (8), 357–360.

Klusmann, E.B., 1993. Odor monitoring at southern california gas company. In: Wilson, G.G., Attair, A.A. (Eds.), Odorization, vol. 3. Institute of Gas Technology, Chicago, IL, Southern California Gas C., pp. 407–423.

Kopasz, J.P., 2007. Fuel cells and odorants for hydrogen. Int. J. Hydrogen Energy 32 (13), 2527–2531.

Mansfeld, G., Rohde, U., Henke, F., Kaesler, H., 2006. Gas odorization method. US Patent 7 108 803, assigned to Symrise GmbH & Co. KG (DE), September 19, 2006.

Marshall, S.E., Zeck, M.V., 2001. Chemical injection system. US Patent 6 208 913, assigned to YZ Systems, Inc., Conroe, TX, March 27, 2001.

May, R.D., 2009. System and method for detecting water vapor within natural gas. US Patent 7 504 631, assigned to SpectraSensors, Inc., Rancho Cucamonga, CA, March 17, 2009.

Mazelli, J.R., 1977. Method of odorizing liquid natural gas. US Patent 4 025 315, assigned to San Diego Gas & Electric Co. (San Diego, CA) Dual Fuel Systems, Inc. (Los Angeles, CA), May 24, 1977.

McClure, J.S., 1958. Warning agent and process for the odorization of a hydrocarbon fuel gas therewith. US Patent 2 823 104, assigned to California Research Corp., February 11, 1958.

McGill, R.A., Voiculescu, I., Fedder, G.K., 2009. Microelectro-mechanical chemical sensor. US Patent 7 556 775, assigned to The United States of America as represented by the Secretary of the Navy (Washington, DC), July 7, 2009.

Morley, C., 2005. GasEq: A chemical equilibrium program for windows. http://www.gaseq.co.uk (accessed 27.04.11).

Muhlbauer, W.K., 2004. Distribution systems. In: Pipeline Risk Management Manual, third ed. Gulf Professional Publishing, Burlington, pp. 223–242 (Ch. 11).

Müller, U., Short, J.N., 2008. Gas odorant. US Patent Application 20080256847, October 23, 2008.

Munoz, B.C., Pierce, K.J., Galloway, C.P., 2009. Sensors with improved properties. US Patent 7 501 091, assigned to Smiths Detection Inc., Pasadena, CA, March 10, 2009.

Nagata, Y., 2003. Measurement of odor threshold by triangle odor bag method. In: International Symposium on Odor Measurement, Asian Network on Odor Measurement and Control. Japan Association on Odor Environment, Tokyo, JP, pp. 118–127, http://www.env.go.jp/en/air/odor/measure/02_3_2.pdf.

Nevers, A.D., 1987. Odor-fading prevention from organosulfur-odorized liquefied petroleum gas. US Patent 4 701 303, October 20, 1987.

Nevers, A.D., 1990. Odor-fading prevention from organosulfur-odorized liquefied petroleum gas. CA Patent 1 274 692, assigned to Atochem North America Inc., October 2, 1990.

Oister, W.H., 1970. Odorized gas. US Patent 3 545 949, assigned to Pennwalt Corp., December 8, 1970.

Oudman, P., 1993. Odorization and odorant monitoring practices at canadian western natural gas company limited. In: Wilson, G.G. (Ed.), Odorization, vol. 3. Institute of Gas Technology, Chicago, IL, Southern California Gas C., pp. 389–405.

Panneman, H.J., Pot-Gerritsen, R.C., Kuiper-Van Loo, E.M., Pastoor, H., Janssen- Van Rosmalen, R., 1997. UV (ultraviolet)-oxidation process for water treatment at gas plant sites. In: Proceedings Volume, Pt. B, 20th Int. Gas Union World Gas Conf., Copenhagen, Denmark, June 10–13, 1997, pp. 269, 271–285.

Patnaik, P., 2007. A Comprehensive Guide to the Hazardous Properties of Chemical Substances, third ed. John Wiley & Sons, New York.

Puri, P.S., 2007. Leak site odorization for gas leak detection. US Patent 7 229 831, assigned to Air Products and Chemicals, Inc., Allentown, PA, June 12, 2007.

Quaife, L.R., Moynihan, K.J., 1990. A new pipeline leak-locating technique utilizing a novel odourized test-fluid (patent pending) and trained domestic dogs. In: Proceedings Volume, 1st US Environ. Protect Agency et al Oil & Gas Explor & Prod. Waste Manage Pract Int. Symp., New Orleans, September 10–13, 1990, pp. 647–657.

Quaife, L.R., Moynihan, K.J., Larson, D.A., 1992a. A new pipeline leak-location technique utilizing a novel (patented) test-fluid and trained domestic dogs. In: Proceedings Volume, 71st Annu. Gpa Conv., Anaheim, California, March 16–18, 1992, pp. 154–161.

Quaife, L.R., Szarka, J., Moynihan, K.J., Moir, M.E., 1991. Test-fluid composition and method for detecting leaks in pipelines and associated facilities. US Patent 5 049 312, assigned to Exxon Production Research Co., September 17, 1991.

Quaife, L.R., Szarka, J., Moynihan, K.J., Moir, M.E., 1992b. Test-fluid composition and method for detecting leaks in pipelines and associated facilities. US Patent 5 167 867, assigned to Exxon Production Research Company, December 1, 1992.

Quaife, L.R., Szarka, J., Moynihan, K.J., Moir, M.E., 1993. Test-fluid composition and method for detecting leaks in pipelines and associated facilities. CA Patent 2 052 242, February 14, 1993.

Quaglio, J., 1880. Wassergas als Brennstoff der Zukunft: Strong's Patent zur Bereitung von Heizgas in Verwendung mit Lowe's Verfahren für Leuchtgas, Bericht 252123468. Bergmann, Wiesbaden.

Ripley, D.L., Goetzinger, J.W., Whisman, M.L., 1990. Human response research evaluation of alternate odorants for LP-gas. GPA Res. Rep. RR-129.

Roberts, J.S., 1977. Thiols. In: Kroschwitz, J.I. (Ed.), Kirk-Othmer Encyclopedia of Chemical Technology, fourth ed., vol. 24. John Wiley & Sons, New York, p. 19.

Rojey, A., Thomas, M., Jullian, S., 1998. Process for treatment of natural gas at a storage site. US Patent 5 803 953, assigned to Inst. Francais Du Petrole, September 8, 1998.

Sasnanand, S., 1993. Adsorption of tetrahydrothiophene in porous media: an experimental approach. Ph.D. thesis, New Mex Inst Mining Techn, Socorro, New Mexico.

Sattich, W.E., 1994. Selective production of ethyl mercaptan. US Patent 5 352 838, assigned to Phillips Petroleum Company, Bartlesville, OK, October 4, 1994.

Shimokawatoko, T., Sumida, K., Ueda, H., 1998a. Method and apparatus for measuring odorant concentration and oderant adding system. US Patent 5 844 124, assigned to Osaka Gas Co. Ltd., December 1, 1998.

Shimokawatoko, T., Sumida, K., Ueda, H., 1998b. Method and apparatus for measuring odorant concentration and odorant adding system. EP Patent 836 091, assigned to Osaka Gas Co. Ltd., April 15, 1998.

Suri, K., Annapoorni, S., Sarkar, A.K., Tandon, R.P., 2002. Gas and humidity sensors based on iron oxide-polypyrrole nanocomposites. Sens. Actuators B 81 (2–3), 277–282.

Toth, J.M., 1989. Natural gas odorization and its techniques. In: Proceedings Volume, 49th Annu. Appalachian Gas Meas Short Course, Coraopolis, Penn, August 15–18, 1989, pp. 170–174.

TGS 842 – for the detection of methane, 2008. Tech. rep., Figaro USA, Inc., Arlington Heights, IL 60005. http://www.figarosensor.com/products/842pdf.pdf (accessed 17.01.08).

Usher, M.J., 1999. Odor fade – possible causes and remedies. In: Proceedings Volume, no. 285. CGA Gas Measurement School, Canadian Gas Association, Ontario, CA.

Verschueren, K., 2009. Handbook of Environmental Data on Organic Chemicals, fifth ed. Wiley & Sons, Hoboken, NJ.

Wagner, T., 2005. Erfahrungsbericht zur regionalen Zentralodorierung mit schwefelfreiem Odoriermittel. Gas und Wasserfach Gas Erdgas 146 (10), 560–563.

Wallace, J.R., Stetter, J.R., Nacson, S., Findlay Jr., M.W., 1991. Odorant analyzer system. EP Patent 0 445 927, assigned to Gas Res. Inst., September 11, 1991.

Wetteman, A.J., Wilson, J.R., 1993. Operation of large volume odorizers. In: Odorization, vol. 3. Institute of Gas Technology, Chicago, IL, pp. 251–255.

Yashchenko, V.L., Vakulin, V.I., Berdnikov, A.I., Grunvald, V.R., Nikolaev, V.V., Klimov, V.Y., et al., 1997. Odorant for natural gas. RU Patent 2 076 137, assigned to Aktsionernoe Obshchestvo Zakry, March 27, 1997.

Yoshida, T., Katz, I., Warren, C.B., Wiener, C., 1984. Odorization of combustible hydrocarbon gases. US Patent 4 487 613, assigned to International Flavors & Fragrances Inc., New York, NY, December 11, 1984.

Zeck, M., 2006. Optical odorization system. US Patent 7 056 360, June 6, 2006.

Zeck, M., 2008. Ultrasonic and sonic odorization systems. US Patent 7 389 786, June 24, 2008.

TRADENAMES

TABLE 15.7 Tradenames in References

Tradename Description	Supplier
Black Pearls® Carbon black (Munoz et al., 2009)	Cabot Corp.

Chapter 16

Enhanced Oil Recovery

Approximately 60–70% of oil reserves cannot be recovered by conventional methods (Al-Khafaji, 1999), and so enhanced oil recovery methods become increasingly important with respect to the limited worldwide resources of crude oil. The estimated worldwide production from enhanced oil recovery and heavy oil projects at the beginning of 1996 was approximately 2.2 million barrels per day (bpd) compared to 1.9 million bpd at the beginning of 1994 (Moritis, 1996). This is approximately 3.6% of the world's oil production. Some production data by enhanced oil recovery (EOR) are summarized in Table 16.1.

Enhanced oil recovery processes include chemical and gas floods, steam, combustion, and electric heating. Gas floods, including immiscible and miscible processes, are usually defined by injected fluids used (carbon dioxide, flue gas, nitrogen, or hydrocarbon). Steam projects involve cyclic steam (huff and puff) or steam drive. Combustion technologies can be subdivided into those that autoignite and those that require a heat source at injectors (Duncan, 1994).

Chemical floods are identified by the specific chemical that is injected. The most commonly used are polymers, surfactants, and alkalis, but chemicals are often combined. For example, polymer slugs usually follow surfactant or alkaline slugs to improve the sweep efficiency. Injection of materials that plug permeable channels may be required for injection profile control and to prevent or mitigate premature water or gas breakthrough.

Crosslinked or gelled polymers are pumped into injectors or producers for water shutoff or fluid diversion. Cement squeezes can often fix near wellbore water channeling problems. The design of chemical injection-EOR projects can be more complicated than that of waterflood projects. Downhole conditions are more severe than those for primary or secondary recovery production.

Well injectivity is complicated by chemicals in injected waters, so in addition to precautions used in waterfloods, chemical interactions, reduced injectivity, deleterious mixtures at producers, potential for accelerated corrosion, and possible well stimulations to cause reduced injectivity must be considered (Duncan and Bulkowski, 1995). Monographs on EOR technologies are

Petroleum Engineer's Guide to Oil Field Chemicals and Fluids. DOI: 10.1016/B978-0-12-383844-5.00016-7

TABLE 16.1 Estimated Production by Enhanced Oil Recovery and Heavy Oil

Region	BPD[a] (1996) (Moritis, 1996)	BPD[a] (1998) (Moritis, 1998)	BPD[a] (2006) (Sandrea and Sandrea, 2007)
United States	724,000	760,000	649,000
Canada	515,000	400,000	–
China	166,000	280,000	–
Former Soviet Union	200,000	200,000	–
Others	593,000	700,000	–
Total	2,198,000	2,340,000	2,500,000

a) Barrels of oil per day; includes in situ thermal heavy oil projects and primary heavy recovery oil projects

available (Alvarado and Manrique, 2010; Green and Willhite, 2008; Littmann, 1988; Sorbie, 1991).

WATERFLOODING

The surfactants described or characterized for waterflooding are summarized in Table 16.2. Commercial alkene sulfonates are a mixture of alkene sulfonate, hydroxyalkane sulfonate, and olefin disulfonate (Borchardt and Strycker, 1997).

Surfactants

Alkyl-aryl Sulfonates

Alkyl-aryl sulfonates have been recognized as being promising for EOR by surfactant flooding. They can be manufactured in large quantities and can generate low interfacial tensions (IFTs) in oils under favorable conditions.

While pure alkyl-aryl sulfonates, such as hexadecyl benzene sulfonate, can generate adequate phase behavior and low IFT with light alkanes, they are unsatisfactory when dealing with heavier crude oils, particularly those with a high wax content. They do not follow normal phase behavior when mixed with crude oil and brines of varying salinity. At low salinity, the surfactant stays predominantly in the aqueous phase, forming a lower-phase microemulsion, whereas at high salinity the surfactant stays predominantly in the oil phase, forming an upper-phase microemulsion.

Normally, a surfactant-oil-brine system with high oil recovery potential exhibits a lower-phase to middle-phase to upper-phase microemulsion transition as the salinity increases. Near the mid-range salinity, often termed optimal

TABLE 16.2 Surfactants for Waterflooding

Surfactant	References
Ethoxylated methylcarboxylates	Strycker (1990)
Propoxyethoxy glyceryl sulfonate	Jenneman and Clark (1994b)
Alkylpropoxyethoxy sulfate as surfactant, xanthan, and a copolymer of acrylamide (AAm) and sodium 2-acrylamido-2-methylpropane sulfonate	Austad et al. (1997)
Carboxymethylated ethoxylated surfactants (CME)	Gall
Polyethylene oxide as a sacrificial adsorbate	Austad et al. (1992)
Polyethylene glycols, propoxylated/ethoxylated alkyl sulfates	Osterloh and Jante (1992)
Mixtures of sulfonates and non-ionic alcohols	Austad et al. (1991) and Shpakoff and Raney (2009)
Combination of lignosulfonates and fatty amines	Debons and Whittington (1991)
Alkyl xylene sulfonates, polyethoxylated alkyl phenols, octaethylene glycol mono *n*-decyl ether, and tetradecyl trimethyl ammonium chloride	Campbell and Sinquin (2008) and Somasundaran (1994)
Anionic sodium dodecyl sulfate, cationic tetradecyl trimethyl ammonium chloride, non-ionic pentadecylethoxylated nonyl phenol (NP–15), and non-ionic octaethylene glycol *N*-dodecyl ether	Somasundaran (1995)
Dimethylalkyl amine oxides as cosurfactants and viscosifiers	Olsen (1989)
N-Dodecyltrimethylammonium bromide	Austad et al. (1998)
Petrochemical sulfonate	Ashrawi et al. (1992)
α-Olefin sulfonate	Ashrawi et al. (1992) and Sanz and Pope (1995)
Sugar-based surfactants (sorbitan monolaurate)	Shpakoff and Raney (2009)
Cocoamidopropyl betaine	Thompson et al. (2001)
1-Phenylalkane sulfonates	Zhang et al. (2003)
Heels of vegetable oil	Chen et al. (2003)
Linoleic acid	Thibodeau et al. (2003)
Naphthenic acid[a]	Horvath-Szabo et al. (2002)
Dodecyl benzene sulfonates	Elkamel et al. (2002)
Lauric acid	Amaya et al. (2002)

TABLE 16.2 Surfactants for Waterflooding–Cont'd

Surfactant	References
Naphthyl sulfonates	Berger and Lee (2002)
Gemini type aryl sulfonates	Berger and Lee (2002)
Dodecyltrimethylammonium bromide	Austad et al. (1998)
Ethoxylated nonyl phenols[b]	Lakatos-Szabo and Lakatos (1989)
Hybrid ionic non-ionic surfactants	Wang et al. (2001a,b)

a) Natural precursor
b) Non-ionic

salinity, a middle-phase microemulsion forms with appreciable amounts of oil and brine solubilized in the microemulsion phase. However, if the oil contains a significant fraction of wax, the above phase transition often does not occur and the solubilization capacity is low, resulting in high IFT and poor oil recovery capability (Chou and Campbell, 2001).

A series of homologous 1-phenylalkane sulfonates, i.e., 1-phenyldodecane sulfonate, 1-phenyltetradecane sulfonate, and 1-phenylhexadecane sulfonate were synthesized, and their IFT of 1-phenylalkane sulfonates was investigated against crude oil from the Daqing oil field (China).

Minima in the IFTs were observed with respect to changes of the concentrations of surfactant and with time. Alkali concentrations at which the lowest IFTs were achieved moved to low regions by increasing the chain length of the aliphatic chain in the sulfonate. The lowest concentration needed was observed with 1-phenylhexadecane sulfonate at about 0.3%.

On the other hand, no minima were observed when IFTs of the 1-phenylalkane sulfonates against alkanes themselves were measured. This behavior is quite distinct from that of the 1-phenylalkane sulfonates against crude oil (Zhang et al., 2003).

For waxy crudes, the use of a broad distribution of α-olefins greater than C_{10} are used for the alkylation of xylene sulfonate or toluene sulfonate, in contrast to conventionally used alkyl-aryl sulfonates, which generally have a narrow range of olefin carbon number, such as C_{12}-xylene sulfonate (Chou and Campbell, 2001).

Surfactants of High Activity

Various surfactants have been developed that can be used at very low concentrations to produce ultra-low IFTs for sandstone and limestone formations. These surfactants can be used for alkaline surfactant polymer floods, surfactant floods, and as an adjuvant for waterfloods (Berger and Lee, 2002).

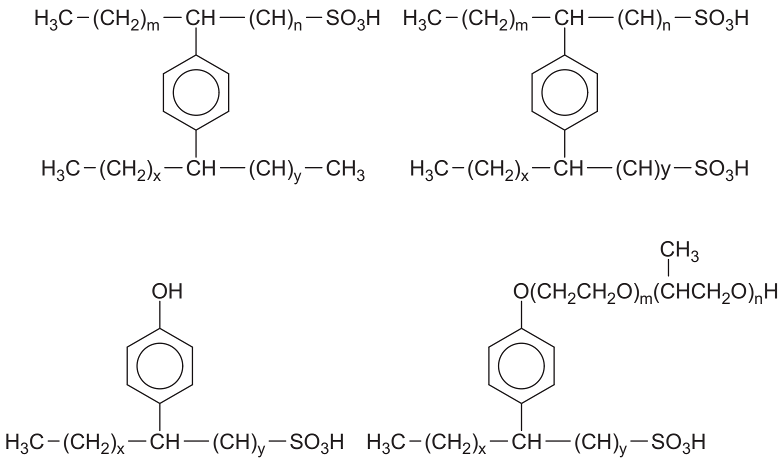


FIGURE 16.1 Sulfoalkylated phenol surfactants.

The new surfactants differ from conventional alkyl-aryl sulfonic acids, as the sulfonate group is attached to the end of the alkyl chain, as opposed to being attached directly to the aromatic ring. In general, the surface tensions and critical micelle concentrations are similar, but the solubility of the new alkyl-aryl sulfonic acids and their salts in water is generally greater than the corresponding conventional alkyl-aryl sulfonic acids and their salts. Because the sulfonate group is attached to the alkyl group instead of to the ring, more positions are available on the aromatic ring for additional substitution.

An olefinic sulfonic acid is used to simultaneously alkylate and sulfonate the aromatic compound. The aromatics that can be used include benzene, toluene, xylenes, naphthalene, phenol, and diphenylether, as well as substituted derivatives of these compounds. The olefinic sulfonic acid can be linear or branched with a range of chain lengths. Examples are shown in Figure 16.1. Several laboratory case studies have been performed for the evaluation and application of these compounds.

Sulfoalkylated nonyl phenol can be condensed with formaldehyde into oligomers (Zaitoun et al., 2003). The use of these oligomers, in combination with other surfactants reduces the adsorption of the surfactants.

Interactions between Crude Oil and Alkaline Solutions

The effectiveness of alkaline flooding for the recovery of an Arabian heavy crude oil has been studied. The alkaline reagents react with the acidic species in crude oil to form surface-active soaps in situ, leading to a lowering of the IFT and subsequent mobilization of the residual oil.

The equilibrium IFTs obtained through alkaline flooding have been compared with the IFTs when a synthetic surfactant, dodecyl benzene sulfonic acid sodium salt is used (Elkamel et al., 2002).

Effects of Connate Water in Alkaline Flooding

The effects of connate water on caustic flooding processes in porous media, by employing acidified paraffin oil as the oil phase and aqueous sodium hydroxide as the water phase, were studied. Displacement processes were performed in basic solution and with linoleic acid, in the absence and presence of connate water.

The results indicate that connate water has a greater effect on the displacement pattern for systems with higher IFTs. For lower IFTs, the patterns are similar both with and without connate water. Reducing the acid concentration has a considerable effect on the displacement, indicating that the organic acid is the limiting reagent. Generally, systems containing connate water increase the oil recovery. As the IFT decreases, the number of fingers increases and the finger width decreases (Thibodeau et al., 2003).

Combination of Primary and Secondary Surfactant Systems

The recovery of crude oil by an improved surfactant flooding process has been described. An alkaline polymer surfactant was used, which results in ultra-low IFTs with brine against crude oil even while the surfactant present is at or below its critical micelle concentration. This process is used in oil reservoirs; a primary surfactant system is diluted with brine and pumped downhole, where the alkali, which is usually sodium hydroxide or sodium carbonate, reacts with the residual acidic organic components in the oil to form a secondary surfactant system. This secondary surfactant helps the primary surfactant to further reduce the IFT between the residual oil and the injected fluid, thereby allowing the removal of residual oil from the pores of the reservoir.

The process utilizes a primary surfactant system (anionic surfactants, nonionic cosurfactants), solvents, and a strong base. An improved, concentrated surfactant formulation primarily containing a mixture of anionic surfactants demonstrated ultra-low ($< 10^{-2}\,\mathrm{mN\,m^{-1}}$) IFT against crude oils containing acidic organic components over a broad range of external parameters, such as surfactant, electrolyte and alkali concentrations, temperature, etc. The primary concentrated surfactant solution is a combination of a linear alkyl benzene sulfonate, a branched alkyl benzene sulfonate, and nonyl phenol (Hsu and Hsu, 2000).

Lignosulfonate Acrylic Acid Graft Copolymers as Sacrificial Agents

One of the most difficult problems in the use of surfactant flooding for EOR is the frequent, substantial loss of surfactant due to adsorption on the formation matrix and precipitation by polyvalent cations such as calcium and magnesium. A significant percentage of surfactants become physically entrapped within the pore spaces of the rock matrix. Surfactant adsorption on the formation matrix significantly decreases its efficiency, making greater quantities necessary, and hence increasing operational costs.

Most surfactants are only satisfactory for surfactant flooding if the calcium and magnesium concentrations of the formation water are less than about 500 ppm. Petroleum sulfonates, the most popular type of surfactants, precipitate where divalent ion concentrations exceed about 500 ppm. Such precipitation renders the sulfonates inoperative for recovering oil and in some instances, causes formation plugging.

The main cause of surfactant loss is adsorption due to physical contact with the formation matrix, or entrapment within its pores. Carbonate or sandstone matrices contain a range of adsorptive sites hence, adsorption is a particularly vexing problem here.

The most promising way of reducing this problem has been to use sacrificial agent compounds, either in a preflush solution injected before the surfactant-containing solution, or in the surfactant solution itself. The compounds are sacrificial because their adsorption and entrapment reduces the loss of the more expensive surfactants, solubilizers, and polymers contained within the surfactant solutions.

Various chemicals have been employed, including lignosulfonates, which are economically attractive because they are unwanted by-products of the pulp industry. A lignosulfonate acrylic acid graft copolymer has been used as such a sacrificial agent. It is believed that sacrificial agents generally work by several chemical mechanisms (Kalfoglou and Paulett, 1993):

- The sacrificial agent complexes with polyvalent cations in the formation fluids, so there will be less of these left for the surfactant to interact with;
- Electrostatic attraction of the matrix and the sacrificial agent for each other; and
- Blocking access to other sites onto which injected surfactants, solubilizers, and polymers could adsorb.

Silicone Compounds with Surfactants

Gas production from gas fields and underground gas storage is usually accompanied by unwanted water production, which often negatively affects the gas flow and recovery efficiency in wells operating in gas fields and hamper the environmental compatibility of the operation. Silicone compounds, such as silanes, siloxanes, silicone oils, and resins have been examined for their ability to restrict water production in gas wells.

Research has therefore been directed at developing a viable method to cure the problem. The methods can be categorized (Lakatos et al., 2003a) as:

1. Application of chain-like polymers,
2. Injection or in situ generation of weak polymer gels,
3. Application of alcohol-containing polymer solutions,
4. Treatment of wells with surfactant-stabilized oil-in-water emulsions,
5. Injection of silicone microemulsions, and
6. Hydrophobization of the formation rock.

The injection of a silicone microemulsion has been developed for the restriction of water production in gas wells. The treating solution was a surfactant-stabilized siloxane emulsion, which was driven into the formation by water and nitrogen.

According to the laboratory studies, the water retention is caused by disproportional permeability modification. This phenomenon is attributed to the inversion of the microemulsion into a macroemulsion initiated by spontaneous dilution by water and then entrapping siloxane droplets so formed by the pores. Field tests showed the beneficial effect of the silicone injection on gas production and gas/water ratio; the gas production tripled and was maintained for at least six months (Lakatos et al., 2002).

Non-ionic Tensides

The first non-ionic tensides were synthesized by C. Schöller at BASF by condensing oleic and stearic acid with polyoxyethylene glycol in 1930. Non-ionic surfactants are better than ionic surfactants in many respects, and their industrial application has been quite widespread during the past century.

The interfacial rheological properties of different Hungarian crude oil/water systems were determined over wide temperature and shear rate ranges, and in the presence of inorganic electrolytes, water-soluble polymers, non-ionic tensides and alkaline materials (Lakatos and Lakatos-Szabó, 2001a; Lakatos et al., 2003b).

Ethoxylated Nonyl Phenols

Ethoxylated nonyl phenols significantly reduce both the interfacial viscosity and the non-Newtonian character of the flow. Ethoxylated nonyl phenols with ethoxy groups of 10–40 were screened. The efficiency of ethoxylated nonyl phenols decreases with increasing ethoxy units and increasing concentration. This phenomenon can be explained by the formation of a closely packed adsorption layer between the phases (Lakatos and Lakatos-Szabó, 1997; Lakatos-Szabó and Lakatos, 1989). The activation energy of viscous flow in NaOH-containing oil-water systems is similar to those calculated for surfactant-containing systems (Lakatos-Szabó and Lakatos, 1999).

Interactions between Ethoxy Nonyl Phenol and Polyacrylamide

Micellization experiments on an ethoxylated nonyl phenol in the presence of partially hydrolyzed polyacrylamide (PHPA) showed that the presence of a highly hydrophilic polymer in an aqueous solution of non-ionic surfactants has only a negligible effect on the micelle structure and the mechanism of micelle formation. On the other hand, above the critical polymer concentration, the network structure is stabilized by the tenside. Therefore, the tenside exhibits positive effects on the performance of the polymer (Bedo et al., 1997).

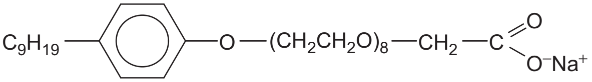


FIGURE 16.2 Phenolether as hybrid ionic non-ionic surfactant.

Hybrid Ionic Non-ionic Surfactants

In high salinity formations, the common non-ionic and anionic surfactants are inefficient because of salting out or cloud point phenomena. A hybrid ionic/non-ionic surfactant is shown in Figure 16.2. Such a surfactant has been synthesized, and found to be soluble in 30% NaCl brine, and to show good surface activity in brine. The IFT is particularly low if the surfactant is combined with petroleum sulfonate (Wang et al., 2001a,b).

Interphase Structure

To elucidate whether the phase behavior or the IFT is the governing criterion for an alkaline surfactant polymer flooding formulation, an experimental study has been performed (Li et al., 2000a). The volume and the color of the middle-phase liquid were observed, and the transient IFT at different salt and alkaline concentrations was measured. Finally, a coreflood test was performed in the laboratory. It was concluded that the primary and most important phenomenon affecting the oil recovery is the low or ultra-low minimum IFT at the crude oil/soluble phase interface.

The phase behavior and the IFT were investigated in the course of alkaline surfactant polymer flooding. The size distribution and structure analysis of the middle mixed layer were studied by a size analyzer and freeze-fracture transmission electron microscopy. Some correlations between the volume of the middle mixed layer and the concentration of each component could be established. The IFT between the middle mixed layer and the oil phase or water phase can reach a very low value (Mu et al., 2002).

Several systems of surfactant and alkaline combination flooding were studied by microscopy, polarizing microscopy, microcalorimetry, laser particles analysis instrument, and IFT meter.

Liquid crystals distributed on the surface of the small particles, which were formed, were observed. The small particles and the liquid crystals are responsible for the ultra low IFT (Li et al., 1999).

Sandwich Structures

Experimental evidence on the appearance of a third liquid crystal phase between the oil and water forming a sandwich like structure has been presented. The presence of this structure modifies both the equilibrium and the transport properties of oil-water systems.

Polarization microscopy was used to observe the sandwich structures. Naphthenic acid was used because it is the most important precursor of natural surfactants and its phase behavior is well known (Horvath-Szabó et al., 2001a,b). An equilibrium liquid crystal (LC) layer on an interface between crude oils and water was observed at high pH. This layer is composed mainly of sodium naphthenates formed in situ at the water/oil interface. The transient LC layer was also generated at the interface between aqueous sodium hydroxide solution and oleic naphthenic acid solution as result of a salt formation between NaOH and naphthenic acid. The chemical reaction causes a transport process resulting in a disturbance of the interface. The optical observation of this interfacial disturbance revealed that the interface covered with LC shows a considerably lower flexibility in comparison to an LC-free interface. The LC layer eventually dissolves in the water phase at low oil-to-water ratios, while at high oil-to-water ratio it can form an equilibrium phase, which spreads spontaneously at the oil-water interface (Horvath-Szabó et al., 2002).

Dynamic Interfacial Tension Behavior with In Situ Formed Surfactants

The time-dependent IFT has been investigated for an interfacially reactive immiscible system, composed of acidified oil and alkaline water. The acidified oil was composed of either lauric acid or linoleic acid dissolved in *n*-dodecane. Drop volume tensiometry was used to measure the IFT.

The rate of formation of the interfacial area depends on the alkali concentration. For lauric acid, the IFT value was found to decrease sharply with increasing alkali concentration, even at low drop formation times. In the case of linoleic acid, the decrease of the IFT with the drop formation time was more gradual, in particular at low alkali concentration (Amaya et al., 2002).

Interfacial Rheological Properties

In hydrocarbon reservoirs, interfacial phenomena play a fundamental role in displacement processes and phase-exchange mechanisms. Interfacial rheology is an efficient and powerful detection technique for these phenomena.

The positive effect of alkalis on microscopic displacement efficiency is attributed to Lakatos-Szabó and Lakatos (1999):

1. The alteration of the wettability,
2. The lowering of the IFT,
3. The restriction of rigid films at the oil-water interfaces,
4. The initiation of phase inversion in dispersed systems,
5. The formation of oil external emulsions,
6. Chemical reactions with some constituents of formation water and rocks, and
7. The sorption of naturally occurring surfactants.

Microemulsion Phase Diagrams

Tertiary oil recovery by means of microemulsions are concerned with

- The ability of a microemulsion to dissolve oil and water, and
- The attainment of very low IFTs.

So the understanding of chemical flooding processes for EOR relies on the knowledge of phase equilibria for such systems, which are composed of brine, oil, surfactant, and cosurfactant.

A thermodynamic analytical representation of the phase diagram of microemulsion systems similar to those used in EOR has been developed (Garcia-Sanchez et al., 2001). Since the system is basically a four component system, the data can be represented in Gibbs tetrahedral coordinates, and multiphase liquid equilibria can be estimated by excess Gibbs energy interaction parameters. An empirical expression was introduced into the selected excess Gibbs energy model to account for the specific role of the surfactant in these complex systems.

The results have been successfully tested for an oil-brine-surfactant-alcohol model system consisting of a sodium alkyl benzene sulfonate and *n*-butanol as co-surfactant.

Interfacial Tension

The oil-water IFT is one of the most important parameters for chemical-EOR. It has a strong time dependency, especially under alkaline conditions, so a knowledge of this behavior is necessary for the prediction of oil recovery.

The addition of sodium hydroxide to floodwater improves the oil or bitumen production because the alkaline additive activates the natural surfactants precursors, most likely acidic components, present in crude oil (Horvath-Szabó et al., 2002).

The IFT varies strongly with temperature and pressure and thus influences the transport of the fluid in a reservoir. It is probably the dominant factor that renders one-third of the total oil in place unrecoverable by gas drive or waterflooding (Amin and Smith, 1998).

Imbibition Experiments

Spontaneous imbibition experiments in nearly oil-wet chalk material of low permeability saturated with oil has been performed at ambient conditions with and without the cationic surfactant dodecyltrimethylammonium bromide present in the aqueous solution.

Without surfactant present the rate of imbibition is very small, and only approximately 13% of the oil could be expelled from the core within 90 days. After that time, a sudden increase in the oil production was observed by a 1.0% surfactant solution to the water. However, if the surfactant is present during the whole experiment, an oil production plateau of approximately to 65% recovery was obtained within 90 days (Austad et al., 1998).

CAUSTIC WATERFLOODING

Injection Strategies

To develop improved alkali surfactant flooding methods, several different injection strategies were tested for recovering heavy oils. Oil recovery was compared for four different injection strategies (French and Josephson, 1992):

- Surfactant followed by polymer,
- Surfactant followed by alkaline polymer,
- Alkaline surfactant followed by polymer, and
- Alkali, surfactant, and polymer mixed in a single formulation.

The effect of alkaline preflush was also studied under two different conditions. All of the oil recovery experiments were conducted under optimal conditions with a viscous, nonacidic oil and with Berea sandstone cores.

Foam-enhanced Caustic Waterflooding

The alkaline waterflooding process is enhanced by the injection of aqueous solutions of foam-forming surfactant and gases, or preformed foams, either ahead of or behind conventional alkaline slugs. A slug of an aqueous solution containing an alkaline agent, followed by a driving fluid, is injected into the formation, and this displaces oil through the relatively high-permeability zones of the formation, and this is recovered via the production well. Thereafter, a slug of an aqueous solution with a foaming agent is coinjected into the formation with a gas and creates a foam upon mixing with the gas. The foam will preferentially go into the formation zones that have a relatively high-permeability and low oil saturation, substantially plugging them. Then a slug of an aqueous alkaline agent is injected, followed by a driving fluid that displaces the alkaline solution and oil through the less permeable zones toward the production well (Hurd, 1991).

Alkaline Surfactant Polymer Flooding

Polymers can be used for mobility control. The interaction between polymers and surfactants is shown to be affected by pH, ionic strength, crude oil type, and the properties of the polymers and surfactants (French and Josephson, 1993).

Surfactants, whose major components are natural mixed carboxylates from the heels of vegetable oil and fats such as soybean oil, vegetable oil, animal oil, and tea oil, etc., have been developed. Optimal formulations were obtained using an orthogonal-test-design method to screen the alkaline surfactant polymer flooding systems. The transient IFTs at the oil/aqueous interface were measured. The oil recovery can be increased by 26.8% of the original oil in place in a coreflood experiment. The waste water resulting from the production of the natural mixed carboxylates also exhibits a high surface activity (Chen et al., 2003; Li et al., 2000b; Mu et al., 2001).

Interphase Properties

Alkaline agents can reduce surfactant losses and permit the use of low concentrations of surfactants. Laboratory tests show that alkali and synthetic surfactants produce interfacial properties that are more favorable for increased oil mobilization than either alkali or surfactant alone (French, 1990; French and Josephson, 1991).

Clay Dissolution

During caustic waterflooding, the alkali can be consumed by the dissolution of clay and is lost. The loss depends on the kinetics of the particular reaction. Several studies have been performed with kaolinite, using quartz as a yardstick, and the kinetic data are documented in the literature. The initial reaction rate has been found to be pH independent in the pH range of 11–13 (Drillet and Defives, 1991). The kinetics of silica dissolution could be quantitatively described in terms of pH, salinity, ion exchange properties, temperature, and contact time (Saneie, 1992).

ACID FLOODING

Hydrochloric Acid

Acid flooding can be successful in formations that are soluble in the particular acid mixture, thus opening the pores. Hydrochloric acid is commonly used, at a concentration of 6–30%, sometimes also with hydrofluoric acid and surfactants added (e.g., isononyl phenol) (Balakirov et al., 1992; Gorodnov et al., 1993). The acidic environment converts the sulfonates into sulfonic acid, which has a lower IFT toward oil, so giving greater efficiency in forcing out oil than is obtained from neutral, aqueous solutions of sulfonates. Cyclic injection can be applied (Abdulmazitov et al., 1997; Diyashev et al., 1996a), and sulfuric acid has also been used for acid treatment (Aleev, 1996; Aleev et al., 1996; Glumov et al., 1994). Injecting additional aqueous lignosulfonate increases the efficiency of a sulfuric acid treatment (Verderevskij et al., 1996).

Hydrochloric acid in combination with chlorine dioxide can be used as a treatment fluid in water injection wells that get impaired by the deposition of solid residues (Cavallaro et al., 2000, 2001). The treatment seems to be more effective than the conventional acidizing system when the plugging material contains iron sulfide and bacterial agents, because of the strongly oxidative effect of chlorine dioxide. Mixtures of chlorine dioxide, lactic acid, and other organic acids (Mason, 1991a,b) also have been described.

Iron control chemicals are used during acid stimulation to prevent the precipitation of iron-containing compounds, since this can decrease well productivity or injectivity. Acetic acid, citric acid, nitrilotriacetic acid, ethylene diamine tetraacetic acid, and erythorbic acid have all been used (Taylor and Nasr-El-Din, 1999; Taylor et al., 1998). A time dependence of iron (III) hydroxide precipitation was observed. Acetic acid can prevent the precipitation of iron (III) at high concentrations at low temperatures.

If the injected acid itself contains iron (III), a precipitation of asphaltic products can occur if it comes in contact with certain crude oils, which leads to practically irreversible damage to the treated zone. The amount of precipitate generally increases with the strength and concentration of the acid. Certain organic sulfur compounds, such as ammonium thioglycolate, mercaptoethanol, cysteamine, thioglycerol, cysteine, and thiolactic acid can reduce iron (III) (Feraud et al., 2001).

Sulfuric Acid

In contrast to hydrochloric acid, sulfuric acid, in particular in a thermal treatment, reacts with the crude oil itself and causes a reduction in the viscosity of the oil (Varadaraj, 2008). In laboratory experiments, crude oil was placed in an autoclave with 10–50 ppm sulfuric acid. After mixing and deaeration, the mixture was heated to 360°C for 2–6 h at elevated pressure. No significant changes were observed in the total acid number, distribution of naphthenic acids, toluene equivalence, and *n*-heptane insolubles between the thermally treated and sulfuric-acid-catalyzed, thermally treated samples. These data indicate that the chemistry of the crude oil is not significantly altered by sulfuric acid addition prior to thermal treatment.

A decrease in energy of activation of flow (viscosity) is observed, suggesting that the sulfuric acid catalyzed thermal treatment alters the fundamental aggregation properties of the species that are responsible for high viscosities of heavy crude oils.

EMULSION FLOODING

Optimizing the formulation of micellar surfactant solutions used for EOR aims to obtain IFTs as low as possible in multiphase systems, which can be achieved by mixing the injected solution with formation fluids. The solubilization of hydrocarbons by the micellar phases of such systems is directly linked to the interfacial efficiency of surfactants. Numerous research projects have shown that the amount of hydrocarbons that are solubilized by the surfactant is generally as great as the IFT between the micellar phase and the hydrocarbons. The solubilization of crude oils depends strongly on their chemical composition (Baviere and Rouaud, 1990).

Micellar flooding is a promising tertiary oil recovery method, perhaps the only method that has been shown to be successful in the field for depleted light oil reservoirs. As a tertiary recovery method, this process has desirable features of several chemical methods (e.g., miscible-type displacement) and is less susceptible to some of their drawbacks, such as adsorption.

It has been shown that a suitable preflush can considerably curtail the surfactant loss to the rock matrix. In addition, the use of multiple micellar solutions, selected on the basis of their phase behavior, can increase the oil recovery with respect to the amount of surfactant, in comparison with a single solution. Laboratory tests showed that volume ratios of oil recovery to slug as high as 15 can be achieved (Daharu et al., 1991).

A solids-stabilized water-in-oil emulsion may be used either as a drive fluid for displacing hydrocarbons from the formation, or to produce a barrier for diverting the flow of fluids in the formation. The solid particles may be formation or non-formation solid particles (Bragg, 1998, 1999).

Micellar Polymer Flooding

The factors affecting the equilibrium IFT at the oil/water interface were studied. The effect of parameters including reservoir temperature, pressure, surfactant concentration, and salinity were investigated. The pendant drop technique, enhanced by video imaging was employed for measuring the IFT.

The IFT decreases with temperature and salinity and decreases exponentially with surfactant concentration, but increases with pressure (Al-Sahhaf et al., 2002). The oil recovery performance of micellar floods is the highest, followed by polymer floods. Alkaline floods have been largely unsuccessful (Thomas and Ali, 1999).

Micellar and Alkaline Surfactant Polymer Flooding

The results for micellar flooding and alkaline surfactant polymer flooding processes were compared. Laboratory experiments on micellar floods in consolidated sandstone cores and in unconsolidated sand packs were performed using combinations of an alkali, a surfactant, and a polymer. Slugs were injected sequentially in a series of experiments, while the three components were mixed and injected as a single slug in other experiments. The oil recoveries in the two series of experiments were similar. Micellar flooding was found to be the superior process, with oil recoveries ranging from 50–80% (Thomas and Ali, 2001).

Scale-up Methods for Micellar Flooding

The design of micellar floods is largely based on laboratory experiments, which are usually unscaled. Dimensional and inspectional analysis is helpful for scaling up the design. General scaling criteria can be simplified for corefloods, and were verified by micellar floods in scaled models. Good agreement was obtained in most cases between the actual and predicted oil production histories, showing the validity of the scale-up. The scaling criteria that were derived can be also used for a micellar flood (Thomas et al., 2000).

CHEMICAL INJECTION

The state of the art in chemical oil recovery has been reviewed (Thomas and Farouq, 1999). More than two-thirds of the original oil remains unrecovered in an oil reservoir after primary and secondary recovery methods have been exhausted. Many chemically based oil recovery methods have been proposed and tested in the laboratory and field. Indeed, chemical oil recovery methods offer a real challenge in view of their success in the laboratory and lack of success in the field.

The problem lies in the inadequacy of laboratory experiments and the limited knowledge of reservoir characteristics. Field test performances of polymer, alkaline, and micellar flooding methods have been examined for nearly 50 field tests. The oil recovery performance of micellar floods is the best, followed by polymer floods. Alkaline floods have been largely unsuccessful. The reasons underlying success or failure are examined in the literature (Thomas and Farouq, 1999).

Ammonium Carbonate

Ammonium carbonate decomposes in an acid medium into ammonium salts and carbon dioxide. It is thus valuable for the in situ generation of carbon dioxide (Diyashev et al., 1996b; Stepanova et al., 1994a,b).

Hydrogen Peroxide

The physical properties of hydrogen peroxide indicate that hydrogen peroxide injection has the potential to combine the more favorable aspects of many enhanced oil recovery processes, namely:

1. Steam,
2. Combustion,
3. Oxygen-water combustion, and
4. Carbon dioxide injection.

Hydrogen peroxide decomposes to form water and oxygen. Both products are environmentally desirable and effective in recovering oil. Heat is generated in the oil reservoir when the decomposition reaction occurs, which supports steam and hot waterflooding operations, among others. Continued injection of liquid hydrogen peroxide advances the heat bank, steam zone, hot-water zone, oxygen-burning front, and CO_2 bank through the formation, effectively displacing oil (Moss and Moss, 1994).

Combinations of hydrogen peroxide, sulfuric acid, and urea have been proposed (Abasov et al., 1993). The temperature influences the urea decomposition into ammonia and carbon dioxide, which causes pressure buildup in a formation model and a 19% increase in oil-displacement efficiency in comparison with water.

Reactions of hydrogen peroxide with near-wellbore formation and liquids create high temperatures, which lower the oil viscosity and remove formation damage. The application of this chemical technique for heat-bank-type flooding is noted as being technically superior, but it is probably not economically viable (Bayless, 1998). There is a wide potential field for the application of hydrogen peroxide, including pressure generation, hydrate melting in subsea equipment, and metal cutting for offshore structure decommissioning (Bayless, 2000).

Alcohol–Waterflooding

Butanol

n-Butanol and other C_4 alcohols are suitable for hot waterflooding in medium to heavy oil reservoirs at depths greater than 1500 m (Richardson and Kibodeaux, 2001).

Isopropanol and Ammonia

A composition that includes ammonia and a low molecular weight alcohol, e.g., isopropanol, in an aqueous carrier solution has been proposed to be cost-effective for EOR (Cobb, 2010). The composition can be recovered and recycled to further decrease costs. Apparently, there is no reaction with oil nor is there a significant amount remaining trapped in the formation, so the mixture can be separated from the oil and recycled.

Residue from the Production of Glycerol or Ethylene glycol

Waste water-soluble alcohols are useful for miscible waterflooding (Ignateva et al., 1996).

Chemical Injection of Waste Gases

Waste gas produced from hydrocarbons can be safely disposed by reinjecting it into a formation. It is mixed with a surfactant to form a foam that is then placed within a disposal zone of a subterranean formation. The waste gas is trapped within the foam, thereby reducing its mobility, which in turn restricts its ability to flow out of the disposal zone and into the producing zone of the formation. The foam can be placed in the formation by coinjecting a surfactant and the waste gas together, or it can be formed in situ by first injecting the surfactant and then injecting the waste gas (Northrop, 1993).

Thermal conversion of organic waste material, such as plastics, or of biomass under the influence of oxygen, into crude synthesis gas yields a hydrogen product. The crude mixture can be injected into a depleted crude oil well, which still contains high molecular organic material. Hydrogen will crack the long chains of the sticking organics in situ and will make them more able to flow. In this way, improved oil recovery and plastics waste disposal by oxidative pyrolysis can be achieved, followed by in situ degradative hydrogenation of geopolymers. Thus more organic material can be recovered than was initially put into the well (Fink and Fink, 1998).

POLYMER WATERFLOODING

The polymer in a polymer waterflooding process acts primarily as a thickener. It decreases the permeability of the reservoir and thus improves the vertical and lateral sweep efficiency.

Associative copolymers of AAm with *N*-alkylacrylamides, terpolymers of AAm, *N*-decylacrylamide, and sodium-2-acrylamido-2-methylpropanesulfonate, sodium acrylate, or sodium-3-acrylamido-3-methylbutanoate have all been shown to possess the required rheological behavior for enhanced oil recovery processes (McCormick and Hester, 1990). Other copolymers of AAm with the zwitterionic 3-(2-acrylamido-2-methylpropyldimethyl ammonio)-1-propane sulfonate monomer also have been examined. Polymers used in polymer waterflooding are shown in Table 16.3.

Low-tension Polymer Flood Technique

This technique consists of combining low levels of polymer-compatible surfactants and a polymer with a waterflood. This affects mobility control and reduces front-end and total costs (Kalpakci et al., 1993). The synergy of surfactant polymer complex formation has been studied by gel permeation chromatography (Austad et al., 1993).

TABLE 16.3 Polymers Used in Polymer Waterflooding

Polymer	References
Polyacrylamide	Ma et al. (1996, 1999); Putz et al. (1994) and Ren et al. (1998)
Partially hydrolyzed polyacrylamide	Chen et al. (1997)
Polyacrylamide, bentonite clay	Gorodnov et al. (1992)
Polydimethyl diallyl ammonium chloride, biopolymers	Mamleev et al. (1997)
Exopolysaccharide produced by *Acinetobacter*	Starukhina et al. (1991)
Xanthan	Han et al. (1999) and Nashawi (1991)
Wellan	Hoskin et al. (1991)

Influence of Viscosity on Ionic Strength

The viscosity and non-Newtonian characteristics of polymer solutions decrease significantly in the presence of inorganic salts, alkali silicates, and multivalent cations. The effect is due to the decrease in dissociation of polyelectrolytes, to the formation of a badly dissociating polyelectrolyte metal complex, and to the separation of such a complex from the polymer solution (Lakatos and Lakatosne, 1991).

Modified Acrylics

A hydrophobically associating modified AAm polymer remarkably improved salt resistance and temperature resistance properties, compared with high molecular weight polyacrylamide (PAM) (Niu et al., 2001).

Biopolymers

Pseudozan

Pseudozan is an exopolysaccharide produced by a *Pseudomonas* species. It has high viscosity at low concentrations in formation brines, forms stable solutions over a wide pH range, and is relatively stable at temperatures up to 65°C. The polymer is not shear-degradable, and has a pseudoplastic behavior. The polymer has been proposed for enhanced oil recovery processes for mobility control (Lazar et al., 1993).

Xanthan

Xanthan interacts with anionic surfactants, which is a beneficial synergistic effect for mobility control in chemical-enhanced oil recovery processes (Liu and Zhang, 1995).

COMBINATION FLOODING

Combination flooding combines at least two of the basic techniques of gas flooding, caustic flooding, surfactant flooding, polymer flooding, or foam flooding. There may be synergy between the various chemical reagents used. There are specific terms that clarify the individual combination of the basic methods, such as surfactant-enhanced alkaline flooding, alkaline-assisted thermal oil recovery, and others. Methods for combined flooding are summarized in Table 16.4.

Low-tension Polymer Flood

Coinjecting a surfactant and a biopolymer, followed by a polymer buffer for mobility control, leads to reduced chemical consumption and high oil recovery. There may be synergistic effects between the surfactant and the polymer in a dynamic flood situation. The chromatographic separation of surfactant

TABLE 16.4 Methods Summarized Under Combined Flooding

Type
Alkali/polymer flooding
Alkali/surfactant/polymer flooding
Alkaline-assisted thermal oil recovery
Alkaline steamflooding
Polymer-assisted surfactant flooding
Water-alternating gas technology

and polymer is important for obtaining good oil recovery and low surfactant retention (Taugbol et al., 1994).

In buffered, surfactant-enhanced, alkaline flooding, it was found that the minimum in IFT and the region of spontaneous emulsification correspond to a particular pH range. Hence, buffering the aqueous pH against changes in alkali concentration allows a low IFT to be maintained when the amount of alkali decreases because of acids, rock consumption, and dispersion (Wason, 1990).

Effect of Alkaline Agents on the Retention

The effectiveness of any alkaline additives tends to increase with increasing pH. However, for most reservoirs, the reaction of these additives with minerals is a serious problem for strong alkalis, and a flood needs to be operated at the lowest effective pH, approximately 10. The ideal process by which alkaline agents reduce losses of surfactants and polymers in oil recovery by chemical injection has been detailed in the literature (Lorenz, 1991).

Alkaline Steamflooding

The performance of steamflooding often suffers from channeling and gravity segregation. Alkaline additives may be used with steam for certain types of crude oils to improve the steamflood performance. Experimental results show that sodium orthosilicate outperforms sodium hydroxide and sodium metasilicate (Mohanty and Khataniar, 1995).

Sediment-forming Materials

Aluminum trichloride and trisodium phosphate can be injected as sediment-forming material (Gorodilov et al., 1997).

Water-alternating Gas Technology

The oil production from thin under-gas cap zones with an active aquifer is not efficient because of the rapid breakthrough of gas or water. The water-alternating gas technology, based on the injection of a water solution with oil- and water-soluble polymers seems to be promising for the stimulation of such wells. For heavy oils, this technology can be considered as an alternative to thermal EOR (Stepanova et al., 1997).

Hydrocarbon-assisted Steam Injection

In steam injection, the mobility of the hydrocarbons is greater if a C_1–C_{25} hydrocarbon is added than if steam is used alone, under substantially similar formation conditions (Frolov et al., 1998; Nasr and Isaacs, 2001a,b).

FOAM FLOODING

Earlier reviews on the state of the art of foam flooding can be found in the literature (Schramm, 2000).

Basic Principles of Foam Flooding

Injection of a foam with oil-imbibing and transporting properties enhances the recovery of oil from a subterranean formation. The foam is selected either by determination of the lamella number or by micro visualization techniques. A suitable surfactant is selected by the following steps (Wang, 1999):

1. Determining the surface tension of the foaming solution,
2. Measuring the radius of a foam lamella plateau border where it initially contacts the oil or of an emulsified drop,
3. Determining the IFT between the foaming solution and the oil, and
4. Correlating these measurements with a mathematical model to obtain a value indicative of the oil-imbibing properties of the foam.

The foam, having a viscosity greater than the displacing medium, will preferentially accumulate in the well-swept and higher permeability zones of the formation. The displacing medium is thus forced to move into the unswept or underswept areas of the formation. It is from these latter areas that the additional oil is recovered. However, when a foam is used to fill a low oil-content area of the reservoir, the oil contained therein is, for all practical purposes, lost. This is because the foam diverts the displacement fluid from such areas (Schramm et al., 1991a,b,c).

Foam stability in the presence of oil can be described by thermodynamics in terms of the spreading and entering coefficients S and E, respectively. These coefficients are defined as follows:

$$S = Y_F^o - Y_{OF} - Y_O^o, \tag{16.1}$$

whereas Y_F^o is the foaming solution surface tension, Y_{OF} is the foaming solution-oil IFT, and Y_O^o is the surface tension of the oil.

$$E = Y_F^o + Y_{OF} - Y_O^o \tag{16.2}$$

Based on these coefficients, one can predict that three types of oil-foam interactions could take place. In the first type, (type A) an oil will neither spread over, nor enter, the surface of foam lamellae when E and S are less than zero. In (type B) the oil will enter but not spread over the surface of foam lamellae when E is greater than zero but S is less than zero. Thirdly, (type C) the oil will enter the surface of foam lamellae and then spread over the lamellae surfaces if both E and S are greater than zero. This latter behavior will destabilize the foam.

However, experimental results have not borne out these predictions. The theory was developed on the basis that the oil droplets are readily imbibed into the foam lamellae, but experimental results show that some foams, particularly those of type A, do not readily imbibe oil.

Therefore, there exists a need to distinguish between foams that are stable to oil but do not significantly imbibe oil, as in type A, foams that are stable to oil and do imbibe oil as in the second type above and finally, foams that are unstable to oil as in the third predicted type (Wang, 1999).

A foam drive method comprises the following steps (Wang, 1999):

1. Injecting into the reservoir an aqueous polymer solution as preceding slug;
2. Periodically injecting simultaneously or alternately a non-condensable gas and a foaming composition solution containing alkalis, surfactants, and polymers to form combined foam or periodically injecting the gas and the foam previously formed from the solution; and
3. Injecting a polymer solution as a protecting slug and then continuing with waterflooding.

Ambient Pressure Foam Tests

Several surfactants were studied by using ambient pressure foam tests, including alcohol ethoxylates, alcohol ethoxy sulfates, alcohol ethoxyethylsulfonates, and alcohol ethoxyglycerylsulfonates (Borchardt et al., 1987). The surfactants that performed well in the 1 atm foaming experiment were also good foaming agents in the site cell and core flood experiments that were performed in the presence of CO_2 and reservoir fluids under realistic reservoir temperature and pressure conditions.

Laboratory studies of foam flow in porous media suggest that the relative foam mobility is approximately inversely proportional to the permeability. This means that foam has potential as a flow-diverting agent, and could potentially sweep low-permeability regions as effectively as high-permeability regions (Goodyear and Jones, 1995).

Sand Pack Model

A one-dimensional sand pack model has been used to investigate the behavior of four anionic sulfonate surfactants of varying chemical structure in the presence of steam. The study was performed with a crude oil at a residual oil saturation of approximately 12% of the pore volume. The observed pressure drop across various sections of the pack was used to study the behavior of the surfactant. The tested surfactants varied in chain length, aromatic structure, and number of ionic charges.

A linear toluene sulfonate produced the strongest foam in the presence of oil at residual saturations, in comparison with α-olefin sulfonates. This contrasts with the behavior of the surfactants in the absence of oil, where the α-olefin sulfonates perform better. The reason for this change is the relative propagation rate of the foams produced by the surfactants (Razzaq and Castanier, 1992).

Foaming Agents

When an oil reservoir is subjected to steam injection, the steam tends to move up in the formation, whereas condensate and oil tend to move down due to the density difference between the fluids. Gradually, a steam override condition develops, in which the injected steam sweeps the upper portion of the formation but leaves the lower portion untouched. Injected steam will tend to follow the path of least resistance from the injection well to a production well (Osterloh, 1994).

Thus, areas of high permeability will receive more and more of the injected steam, which in turn raises the permeability of such areas. This phenomenon exists to an even larger degree with low injection rates and thick formations, and the problem worsens at greater radial distances from the injection well, because the steam flux decreases with increasing steam zone radius.

Although residual oil saturation in the steam-swept region can be as low as 10%, the average residual oil saturation in the formation remains much higher due to poor vertical conformance. This it is because of the creation of steam override zones.

A similar conformance problem exists with carbon dioxide flooding. CO_2 has a large tendency to channel through oil, since its viscosity may be 10–50 times lower than that of the oil. This channeling problem is exacerbated by the inherent tendency of a highly mobile fluid such as carbon dioxide to preferentially flow through more permeable rock sections.

These two factors, namely unfavorable mobility ratios between carbon dioxide and the oil in place and the tendency of carbon dioxide to take advantage of permeability variations, often make carbon dioxide flooding uneconomical. Conformance problems increase as the miscibility of the carbon dioxide with the oil in place decreases.

Although not much attention has been devoted to carbon dioxide conformance, it has long been the intention of the oil industry to improve the conformance of a steamflood by reducing the permeability of the steam swept zone by various means. The injection of numerous chemicals such as foams, foaming solutions, gelling solutions, or plugging or precipitating solutions have all been tried.

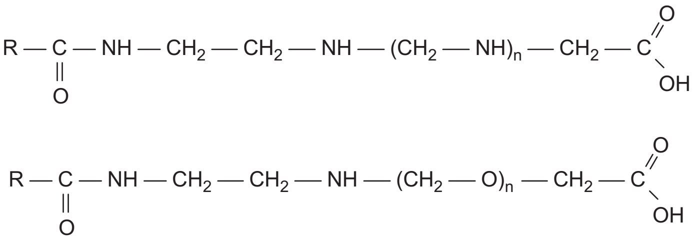
Because of the danger of damaging the reservoir, it is considered important to have a non-permanent method of lowering the permeability in the steam override zones. For this reason, certain plugging agents are deemed unacceptable. In order to successfully divert steam and improve the vertical conformance, the injected chemical should be:

1. Stable at high steam temperatures (150–315°C),
2. Effective in reducing permeability in steam swept zones,
3. Non-damaging to the oil reservoir, and
4. Economical.

The literature is replete with references to various foaming agents that are employed to lower permeability in steam swept zones, the vast majority of which require the injection of a non-condensable gas to generate the foam in conjunction with the injection of steam and the foaming agent (Osterloh, 1994).

C_{12} to C_{15} alcohols and α-olefin sulfonate are highly effective when used with steam or carbon dioxide foaming agents in reducing the permeability of flood-swept zones (Osterloh, 1994). The sodium salt of tall oil acid is suitable as a foam surfactant. Experimental results show that sodium tallates are effective foaming agents that can produce pressure gradients of hundreds of pounds per square inch per foot in a sand pack (Osterloh and Jante, 1995).

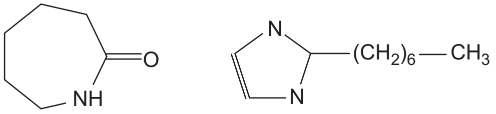
The foam-holding characteristics of foam from surfactants in oil field jobs can be tailored by adding an imidazoline-based amphoacetate surfactant, which are a special class of amphoteric tensides (Figure 16.3). Imidazoles, such as 2-heptylimidazoline, c.f., Figure 16.4, are reacted with fatty acids by ring opening. For alkylation, the imidazoline is reacted with, for example, chloroacetate (Dino and Homack, 1997). Residues from the production of caprolactam have been proposed as surfactants (Tulbovich et al., 1996).



$$\mathrm{R{-}C({=}O){-}NH{-}CH_2{-}CH_2{-}NH{-}(CH_2{-}NH)_n{-}CH_2{-}C({=}O){-}OH}$$

$$\mathrm{R{-}C({=}O){-}NH{-}CH_2{-}CH_2{-}NH{-}(CH_2{-}O)_n{-}CH_2{-}C({=}O){-}OH}$$

FIGURE 16.3 Amphoteric tensides.



Caprolactam 2-Heptylimidazoline

FIGURE 16.4 Nitrogen heterocycles.

Fluorocarbon Surfactant

A foam can be generated by using an inert gas and a fluorocarbon surfactant solution in admixture with an amphoteric or anionic hydrocarbon surfactant solution. A relatively small amount of the fluorocarbon surfactant is needed when mixed with the hydrocarbon surfactant and foamed. The foam has a better stability than a foam made with hydrocarbon surfactant alone when in contact with oil (Rendall et al., 1991).

Polymer-enhanced Foams

Polymer concentration, the chemical nature of the surfactants and their concentration, aqueous phase salinity and pH, and shear rate affect foam performance (Zhu et al., 1998). The performance of polymer-enhanced foams was shown to be much better than conventional foams. PAM polymers were used as an additive.

Higher foam resistance and longer persistence were achieved by using relatively low concentrations of polymers. Studies also showed that the foam performance was significantly improved over a broad range of polymer concentrations. Foams are severely affected by the presence of oil, but polymer-enhanced foam reduced the negative impact of oils on foam mobility. Polymer-enhanced foams are suitable for plugging fracture reservoirs (Sydansk, 1992).

CARBON DIOXIDE FLOODING

In the 1990s certain research groups focused on the development of CO_2-soluble polymers that could be used as direct thickeners, in particular, ionomers (Kovarik and Heller, 1990).

Sandstone rock surfaces are normally highly water-wet, but can be altered by treatment with solutions of chemical surfactants or by asphaltenes. Increasing the pH of the treating solution decreases the water wettability of the sandstone surface and, in some cases, makes the surface medium oil-wet (Smith and Comberiati, 1990). Thus, the chemical treatment of sandstone cores can increase the oil production when flooded with carbon dioxide.

A cosolvent used as a miscible additive for CO_2 changed the properties of the supercritical gas phase resulting in increased viscosity and density of the gas mixture and enhanced extraction of the oil compounds into the CO_2-rich phase. Gas phase properties were measured in an equilibrium cell with a capillary viscometer and a high-pressure densitometer. Cosolvent miscibility with CO_2, brine solubility, cosolvent volatility, and relative quantity of the cosolvent partitioning into the oil phase must all be considered for the successful application of cosolvents. The results indicate that additives with low molecular weight, such as propane, are the most effective cosolvents for increasing oil recovery (Raible, 1992).

By adding common solvents as chemical modifiers, the flooding fluid shows a marked improvement in solvent ability for heavy components of crudes because of its increased density and polarity (Hwang and Ortiz, 1999). Miscible or immiscible carbon dioxide injection is considered to be one of the most effective technologies for improving oil recovery from complicated formations and hard-to-recover oil reserves. Application of this technology can increase the ultimate oil recovery by 10–15%, and it can be applied in a wide range of geological conditions, for producing both light and heavy oils.

The main factors that restrict its application are the dependence on natural CO_2 sources, transportation of CO_2, safety and environmental problems, breakthrough of CO_2 to the production wells, and corrosion of well and field equipment.

A technology for in situ CO_2 generation has been developed and described. It is based on an exothermic chemical reaction between a gas-forming water solution and active acids at low concentrations (Dzhafarov et al., 1999).

Hydrocarbons and other fluids are recovered at a production well by mixing CO_2 and 0.1–20% trichloroethane at a temperature and pressure above the bubble point of the mixture, which ensures that the mixture will be in a single phase (Hsu, 1992).

STEAMFLOODING

Carbon Dioxide

When the temperature of a carbonate reservoir that is saturated with high-viscosity oil and water increases to 200°C or more, chemical reactions occur in the formation, resulting in the formation of considerable amounts of CO_2. This results from the dealkylation of aromatic hydrocarbons in the presence of water vapor, catalytic conversion of hydrocarbons by water vapor, and oxidation of organic materials.

Clay material and metals of variable valence, such as nickel, cobalt, or iron in the carbonate rock can serve as a catalyst. There is optimal amount of CO_2 for which maximal oil recovery is achieved (Ruzin et al., 1990). The performance of a steamflooding process can be improved by the addition of CO_2 or methane (Metwally, 1990).

Air Injection

Air used as a steam additive results in an increased rate of oil recovery because of low temperature oxidation reactions (Ivory et al., 1989).

Chemical Reactions

The reactivity of steam can be reduced via pH control. The injection or addition of a buffer, such as ammonium chloride, inhibits the dissolution of certain mineral groups, controls the migration of fines, inhibits the swelling of clays, controls chemical reactions in which new clay minerals are formed, and helps to prevent the precipitation of asphaltenes and the formation of emulsions (Wyganowski, 1991).

The reaction of sulfate with sulfide is strongly pH dependent, and the oxidation potential of sulfate at neutral pH is very low. At atmospheric pressure and temperatures up to the boiling points of the inorganic and organic media, no reaction takes place within 100 h. However, the reaction may proceed very slowly over geochemical time periods.

Large amounts of H_2S are produced, together with CO_2 and small amounts of elemental hydrogen in the steamflooding process. In the producing zones, the temperatures lie in the range of 250–270°C, which is significantly below the conditions described in the literature. H_2S production rises from 50 ppm to up to 300,000 ppm, causing enormous corrosion and health and safety risks (Hoffmann and Steinfatt, 1993). Addition of 2–5% urea with respect to water is claimed to reduce the viscosity of the heavy hydrocarbons by at least 50% (Campos and Hernandez, 1993).

IN SITU COMBUSTION

A significant increase in light oil production can be achieved by air injection. A total consumption of 5–10% of the remaining oil is expected to maintain a propagation of the in situ oxidation process. The flue gas and steam generated at the combustion front strip, swell, and heat the contacted oil. The light oil is displaced at near-miscible conditions with complete utilization of the injected oxygen (Surguchev et al., 1999).

SPECIAL TECHNIQUES

Viscous Oil Recovery

Special techniques, particularly thermal methods, have been developed for the recovery of viscous oils.

Low Temperature Oxidation

Cap Gas

Both crude and asphaltene-free oil were used to determine the consequences of low temperature oxidation. It was found that the oxygen contained in an artificial gas cap was completely consumed by chemical reactions, i.e., oxidation, condensation, and water formation, before the asphaltene content had reached equilibrium.

The application of a pillow (cap) gas containing air and oxygen for improving the gravitational segregation in offshore production technology may offer an appropriate alternative for increasing the recovery factor in heavy oil–bearing reservoirs (Lakatos et al., 1997).

Special Surfactant Formulations

An alkaline PAM solution in liquid hydrocarbons has been suggested for EOR (Almaev et al., 1996). Special surfactant formulations have been tried to recover heavy crude oils. Ternary surfactant formulations, so called mixed-surfactant-enhanced alkaline systems, were successful in reversing the trend of increasing IFT with time that is typical in additive-free alkaline crude oil systems.

At higher temperatures (65°C), these ternary surfactant formulations were capable of generating very low IFT values against the crude oil, which suggests that they could be suitable candidates for commercial heavy oil recovery processes (Chiwetelu et al., 1994).

Visbreaking

In situ visbreaking with steam and a catalyst can produce crude oils with reduced viscosity (Higuerey et al., 2001). A special variety of visbreaking that involves partial steam reforming, which produces smaller hydrocarbon components and additional hydrogen free radicals and carbon dioxide, has been described.

Low-permeability Flooding

Oil recovery from diatomaceous formations is usually quite limited because a significant portion of oil saturation may be bypassed using conventional production techniques such as primary, waterflooding, cyclic, or drive steaming. Significant improvement of oil recovery would require that a method of displacing oil from the interior of the diatoms into the flow channels between the diatoms be provided (Burcham et al., 1995; Northrop, 1995).

It would also be necessary to improve the permeability in the natural flow channels so that the oil can be recovered. A combination of chemical additives is used to increase the water wetness of a rock and so increase the capillary pressure that forces oil and water from the diatomaceous formation. The additives used include wetting agents such as mono-, di-, and tri-basic forms of sodium or potassium phosphate and sodium silicate.

Surfactants, including sulfonates, ammonium salts of linear alcohol, ethoxy sulfates, or calcium phenol ethoxylated alkyl sulfonates are also added to lower the IFT between oil and water, and allow oil to flow more freely through the diatomaceous matrix. Imbibition experiments with up to 3% of an active surfactant concentration indicate a 31% improvement in oil recovery over that obtainable with brine alone (Burcham et al., 1995; Northrop, 1995).

Injecting a solvent (Davis, 1992), for example, jet fuel, petroleum naphtha, aromatic hydrocarbons, or naphthenic hydrocarbons, before injecting the surfactant solution has also been proposed.

MICROBIAL-ENHANCED OIL RECOVERY TECHNIQUES

Microbiologists initially laid the foundations for microbial-enhanced oil recovery (MEOR), which increased after the petroleum crisis in 1973 (Lazar, 1993; Momeni et al., 1990; Zekri, 2001).

MEOR was first proposed in 1926 when Vadie (2002), Zobell (1937), and Zobell and Johnson (1979) laid down the foundations of the technique between 1943 and 1953. The results were then largely dismissed in the United States because there was little interest in finding methods to enhance the recovery of oil.

However, in some European countries, the interest for MEOR increased and several field trials were conducted. The first MEOR waterflood field project in the United States was initiated in 1986 in the Mink Unit of Delaware-Childers Field in Nowata County, Oklahoma (Bryant et al., 1991).

Basic Principles and Methods

The injection of microbes into the formation is a common MEOR technique. This should stimulate the in situ microflora, resulting in the production of certain compounds that increase the oil recovery of exhausted reservoirs. The following basic effects can be achieved by microbes (Vadie, 2002):

- In situ production of gels for selective water shutoff;
- In situ production of biosurfactants for surfactant flooding,
- In situ production of acids for dissolving carbonate rocks;
- In situ production of CO_2;
- In situ degradation of long chain molecules to reduce viscosity and paraffin content;
- Displacement of oil by metabolites of inoculated bacteria, grown in situ; and
- Huff and puff technique:
    1. Huff: Migration of cells and synthesis of metabolic products following inoculation and closing of injection well;
    2. Puff: Production and recovery of oil after incubation period.

It is often stressed that the technology is environmentally friendly. The stimulation of oil production by in situ bacterial fermentation is thought to be initialized by one or a combination of the following mechanisms:

1. Improvement of the relative mobility of oil to water by biosurfactants and biopolymers;
2. Partial repressurization of the reservoir by methane and CO_2 gases;

3. Reduction of oil viscosity through the dissolution of organic solvents in the oil phase;
4. Increase of reservoir permeability and widening of the fissures and channels through the etching of carbonaceous rocks in limestone reservoirs by organic acids produced by anaerobic bacteria;
5. Cleaning of the wellbore region by the acids and gas produced from in situ fermentation: the gas serves to push oil from dead space and dislodge debris that plugs the pores, the average pore size is increased, and, as a result, the capillary pressure near the wellbore is made more favorable for the flow of oil; and
6. Selective plugging of highly permeable zones by injecting slime-forming bacteria followed by sucrose solution that turns on the production of extracellular slimes.

Successful microbial MEOR requires (Sheehy, 1990):

1. The selection, injection, dispersion, metabolism, and persistence of organisms with properties that facilitate the release of residual oil and
2. The coinjection of growth-effective nutrients into the extreme environments that characterize petroleum reservoirs.

Economics

The most widely practiced technique for applying MEOR involves cyclic stimulation treatments of producing wells. Improvements in oil production can result from removal of paraffinic or asphaltic deposits from the near wellbore region, or from the mobilization of residual oil in the limited volume of the treated reservoir.

An alternative method involves applying microbes in an ongoing waterflood to improve oil recovery (Bryant et al., 1989). Microorganisms have been shown in the laboratory to produce chemicals such as surfactants, acids, solvents (alcohols and ketones), and gases, primarily CO_2, all of which could be effective in mobilizing crude oil under reservoir conditions. Microbial growth and polymer production in porous media have been shown to improve the sweep efficiency by permeability modification. In general, cost-effective MEOR methods are best applied in shallow, sandstone reservoirs in mature producing fields.

The function of aerobic MEOR is based on the ability of oil-degrading bacteria to reduce the IFT between oil and water. The process involves pumping water that contains oxygen and mineral nutrients into the oil reservoir to stimulate the growth of aerobic, oil-degrading bacteria. Based on coreflood experiments, the amount of bacterial biomass responsible for dislodging the oil can be calculated. The process is limited by the amount of oxygen available to the bacteria to degrade the oil. The bacterial biomass is more efficient than synthetic surfactants in dislodging the oil (Sunde et al., 1992).

Experiments have shown that bacterial cells may penetrate a solid porous medium with at least 140 mD permeability, and that a bacterial population can become established in such a medium if suitable substrates are supplied. The suitability of an organism for enhanced oil recovery is governed by parameters such as its capacity to produce a surfactant or cosurfactant, cell morphology and relationship of bacterial size to pore size, and pore size distribution of the porous rock. The activity of the organism is directly affected by conditions in the reservoir, such as oxygen availability, temperature, pressure, and substrate availability (Bubela, 1983).

A physical model to predict the results of large-scale application for MEOR has been developed. This model simulates both the radial flow of fluids toward the wellbore and bacteria transport through porous media (Momeni et al., 1988).

Field studies of MEOR processes require routine monitoring to determine the effects that microorganisms exert in the release of oil from petroleum-bearing formations. Careful monitoring of oil production, flow rates, oil/water ratios, temperature, pH, viscosity, ionic strength, and other factors allows observation of the real changes that occur as a result of microbial activities after selected microbes are injected. Simple microbial counts can be used to determine the viability and transport of injected microbes. The effect of injected energy sources, such as molasses, on indigenous microbes inhabiting a reservoir can also be detected (Cruze and Hitzman, 1987).

An example process for recovering hydrocarbons from a subterranean, hydrocarbon-bearing formation consists of the following:

1. Introducing microbes into the formation, the microbes being effective to render at least a portion of the hydrocarbons in the formation more easily recoverable;
2. Passing electrical energy through at least a portion of the formation to increase the mobility of the microbes in the formation; and
3. Recovering hydrocarbons from the formation.

The specific microbes chosen depends on many factors, for example, the particular formation involved, the specific hydrocarbons in the formation, and the desired action of the microbes. They may be aerobic or anaerobic and may or may not require one or more additional nutrients, either naturally occurring or injected, to be included in the formation. Highly mobile microbes, such as flagellated or ciliated bacilli, are useful. The microbes are sized so that they are mobile in the connate water of the formation (Killough, 1987).

Bacillus licheniformis produces a water-insoluble levan that has a potential application as a selective plugging agent in MEOR. The microorganisms grow on sucrose, glucose, and fructose but produce levan only on sucrose. Thus plugging may be selectively controlled in the reservoir by substrate manipulation. Oil reservoirs having a temperature of less than 55°C, a pH between 6 and 9, a pressure less than 500 atm, and a salt concentration of 4% or less are potentially suitable (Ramsay et al., 1989) for this treatment.

A possible approach to MEOR consists of the additional aeration of the water injected into the formation, together with the addition of mineral salts of nitrogen and phosphorus. The result is the activation of the aerobic microorganisms and the oxidation of the residual oil. The metabolic products of the petroleum-oxidizing bacteria are CO_2 and water-soluble organic compounds. These compounds enter the non-oxygenated zone of the formation and can act as oil recovery agents. The compounds also may serve as additional substrates for anaerobic bacteria, particularly for methanogens. The methane so formed can be easily recovered. It increases the mobility of the oil in place (Ivanov and Belyaev, 1989; Sorokin, 1989).

Potential Health Hazards of Bacteria

Practically all life forms may be infected by one or more kinds of microorganism, some of which confer a mutual advantage, such as in symbiosis, whereas some result in a disease of the host. The use of bacteria in MEOR operations necessitates a consideration of possible untoward effects against man and other living creatures. Because large numbers of bacteria are going to be placed into the ground and possibly come into direct contact with oil field workers who know little about them, it is necessary to closely examine possible hazards that may be associated with their use (Grula et al., 1989b).

Metabolism

MEOR methods mainly utilize the metabolites (biosurfactant, biopolymer, organic acid, and biogas) generated in situ or ex situ by bacteria to improve the mobility of the oil phase. In situ MEOR is mainly targeted toward the residual oil left after primary or secondary production, and its success depends strongly on the penetration and the stability of recovering agents. To contact the trapped oil with appropriate bacteria, the microbes must be transported from a wellbore to locations deep within the reservoir (Jang et al., 1989).

When microbial activity develops in a subsurface geologic environment, the geologic, mineralogic, hydrologic, and geochemical aspects of the environment will have a profound effect on the microorganisms and, in turn, the microbial population will have some effect on the rocks and fluids. The most significant geologic changes are (Bubela, 1989):

1. The precipitation of dissolved minerals, especially carbonates;
2. The change of permeability caused by precipitation in pore throats; and
3. A change of porosity, either an increase or decrease, depending on the equilibria of dissolved salts and products of organic acids.

Various bacterial species have proven useful in MEOR, depending on the biochemical materials produced by the the species, such as gases, surfactants, solvents, acids, swelling agents, and cosurfactants, which facilitate the displacement of oil. In field experiments, in situ fermentation is often desirable for producing a great quantity of gases. *Clostridium hydrosulfuricum 39E* was found to have surface active properties during simulated EOR experiments (Grula et al., 1989a; Yen et al., 1991).

Key mechanisms important for improved oil mobilization by microbial formulations have been identified, including wettability alteration, emulsification, oil solubilization, alteration in interfacial forces, lowering of the mobility ratio, and permeability modification. Aggregation of the bacteria at the oil-water-rock interface may produce locally high concentrations of metabolic chemicals that result in oil mobilization. A decrease in relative permeability to water and an increase in relative permeability to oil was usually observed in microbial-flooded cores, causing an apparent curve shift toward a more water-wet condition. Cores preflushed with sodium bicarbonate showed increased oil recovery efficiency (Chase et al., 1991).

Microorganisms inhabiting petroleum-bearing formations or that are introduced into subterranean environments are subject to extremes of redox potential, pH, salinity, temperature, pressure, ecologic pressure, geochemistry, and nutrient availability. Successful MEOR requires the selection, injection, dispersion, metabolism, and persistence of organisms that have the right properties to facilitate the release of residual oil (Sheehy, 1991).

Microbial Control of the Production of Sulfide

A microbial process was developed for controlling the production of hydrogen sulfide by sulfate-reducing bacteria, using mutant strains of *Thiobacillus denitrificans*. *T. denitrificans* oxidizes sulfide to sulfate, using oxygen or nitrate as the electron acceptor, but is inhibited by sulfide concentrations above 100–200 μ. A mutant of *T. denitrificans* that is resistant to glutaraldehyde ($40\,\mathrm{mg\,l^{-1}}$) and sulfide (1500 μ) was obtained by repeated subculturing at increasing concentrations of the inhibitors.

This strain prevented the accumulation of sulfide by *Desulfovibrio desulfuricans* when both organisms were grown in a liquid medium, or in Berea sandstone cores, which the wild-type strain did not. The mutant also prevented the accumulation of sulfide by a mixed population of sulfate-reducing bacteria enriched from an oil field brine.

Fermentation balances showed that this strain stoichiometrically oxidized the biogenically produced sulfide to sulfate. The mutant grew at temperatures up to 40°C, in salinities up to 2%, and at pressures up to 120 atm (McInerney et al., 1991). *C. hydrosulfuricum 39E* was found to have surface active properties during simulated enhanced oil recovery experiments (Yen et al., 1991).

Bacillus licheniformis

The *B. licheniformis JF-2* strain produces a very effective surfactant under conditions typical of oil reservoirs. The partially purified biosurfactant from JF-2 was shown to be the most active microbial surfactant found, and it gave an IFT against decane of $0.016\,\mathrm{mN\,m^{-1}}$. An optimal production of the surfactant was obtained in cultures grown in the presence of 5% NaCl at a temperature of 45°C and pH of 7.

The major end-products of fermentation were lactic acid and acetic acid, with smaller amounts of formic acid and acetoin. The growth and biosurfactant formation were also observed in anaerobic cultures supplemented with a suitable electron acceptor, such as $NaNO_3$ (Lin et al., 1991).

Microbial Ecology of Corrosion

The sulfur bacteria, which use sulfur compounds in their metabolism, are among the bacteria that can inhabit an oil reservoir. They produce hydrogen sulfide, which is responsible for extensive corrosion in the oil field, so the exclusion of these bacteria from MEOR is highly desirable. The net effect of souring a reservoir is a decrease in its economic value (Westlake, 1991).

B. licheniformis JF-2 and *Clostridium acetogutylicum* were investigated under simulated reservoir conditions. Sandstone cores were equilibrated to the desired conditions, saturated with oil and brine, and flooded to residual oil saturation. The waterflood brine was displaced with a nutrient solution. The MEOR efficiency was found to be directly related to the dissolved gas/oil ratio. The principal MEOR mechanism observed in this work was solution gas drive (Donaldson and Obeida, 1991).

Strict Anaerobic Bacteria

Several strict anaerobic bacteria belonging to different phylogenetic taxons were isolated from the Tatar and Siberian oil fields under different physicochemical conditions. All isolated strains are capable of producing oil-releasing compounds, such as: biopolymers, organic acids, or gases. Methanogenic bacteria were shown to produce polysaccharides. The polysaccharide of *Methanococcoides euhalobius* was partly purified and characterized. Some acetogenic strains capable of producing volatile fatty acids from CO_2 and H_2 were also isolated from stratal waters of the Tatar and Siberian oil fields (Belyaev et al., 1991).

Diverse populations of anaerobic, heterotrophic bacteria were present in highly saline brines collected from the Vassar Vertz Sand Unit, Payne County, Oklahoma. All strains grew in a mineral salts medium containing glucose, yeast extract, and casamino acids in the presence of NaCl concentrations of up to 20% (Bhupathiraju et al., 1991).

Shewanella putrefaciens

Many *S. putrefaciens* strains can reduce metal oxides, and *Shewanella* species that can utilize butane have been proposed for a method of bioremediation of petroleum contaminants. Biofilms of *Shewanella* species can sequester gases, in particular CO_2, in underground geological formations and prevent the release into the atmosphere (Cunningham et al., 2006).

S. putrefaciens grows under denitrifying anaerobic conditions on crude oil as the sole carbon source. This organism can assist the release of oil from a substrate when grown on either lactate or peptone as a carbon source, as shown by in vitro experiments. Thus, this strain can be used to improve oil recovery (Keeler et al., 2010).

Thauera Strains

Particular strains of denitrifying bacteria belonging to the genera *Azoarcus* and *Thauera* have been shown to grow on oil and or oil constituents under anaerobic conditions, without the need for nutrient supplementation (Anders et al., 1995). Enzymes that catalyze the metabolism of simple aromatic compounds have been identified in these species.

Enzymes from *Thauera aromatica* metabolize toluene and all cresols, but no xylene isomers. Most of the aromatic compounds are converted to the central intermediate benzoyl-CoA via different metabolic pathways. These strains may be useful in the maintenance of oil pipelines as well as in EOR (Hendrickson et al., 2010).

Methanohalophilus

A methanogenic bacterium was isolated from oil reservoir brines by enrichment with trimethylamine. Methane production occurred only with trimethylamine compounds or methanol as substrates. Sodium ions, magnesium ions, and potassium ions were all required for growth. This organism was considered to be a member of the genus *Methanohalophilus* on the basis of its substrate utilization and general growth characteristics (Gevertz et al., 1991).

Sulfate-reducing Desulfovibrio

A sulfate-reducing bacterium was isolated by enrichment with a lactate-sulfate medium containing 3% NaCl. The isolate utilized lactate as an electron donor for sulfate reduction and contained desulfoviridin, typical of the genus *Desulfovibrio* (Gevertz et al., 1991).

Ultramicrobacteria

Selective plugging of high-permeability areas in a reservoir rock will increase the oil recovery during waterflooding. The injected water flows through the low-permeability, oil-bearing zones, pushing oil along its path. Many plugging agents that have been developed do not penetrate the reservoir deeply and often wash out when the injection pressure is reduced. Ultramicrobacteria, however, can penetrate deep into formations and grow exponentially with nutrient stimulation to preferentially plug high-permeability zones (Cusack et al., 1991).

The microorganisms reduce the nitrate and produce sulfuric acid, which eventually dissolves the rock formation, thus releasing oil. The microorganisms can be denitrifying thiobacilli, such as *T. denitrificans* (Sperl and Sperl, 1991).

Lactic Acid Bacteria

Particularly preferred bacteria are those of the genera *Lactobacillus* or *Pediococcus*. Lactic acid produced by these bacteria may be used for removal of carbonate or iron scale in oil field equipment (Coleman et al., 1992).

Scale Inhibitors as a Microbial Nutrient

Organic phosphates and phosphonates are known to be scale inhibitors. Substances in this class can also be nutrients for certain bacteria, so a phosphorous nutrient injection system can both prevent scales and act as a nutrient in certain cases (Jenneman and Clark, 1994a,b).

Interfacial Properties

Interfacial Tension

The IFT plays an important role in the success of enhanced oil recovery methods, but additional complications arise when the components undergo a chemical reaction. The dynamic IFT behavior of reacting acidic oil-alkaline solutions has been studied for both an artificially acidified synthetic oil, and a real crude oil, at various concentrations, with either a drop volume or a spinning drop tensiometer (Ball, 1995; Ball et al., 1996).

The spinning drop technique measures the shape of an oil drop in the flooding solution in a capillary tube. An automatic measuring system has been developed that combines a video-image analysis, an automatic recording system, and a computer for calculation of the IFT (Yamazaki et al., 2000).

Interfacial Rheologic Properties

The interfacial rheology is very sensitive to the chemical composition of immiscible formation liquids (Lakatos and Lakatos-Szabó, 2001), hence an understanding of these factors may contribute significantly to an extension reservoir characterization, a better understanding of displacement mechanisms, development of more profitable enhanced and improved oil recovery methods, intensification of the surface technologies, optimization of the pipeline transportation, and improvement of refinery operations (Lakatos-Szabó et al., 1997).

Interfacial rheologic properties of different crude oil water systems were determined over wide ranges of temperature and shear rate, and in the presence of inorganic electrolytes, surfactants, alkaline materials, and polymers (Lakatos-Szabó et al., 1997).

Caustic Waterflooding

In caustic waterflooding, the interfacial rheological properties of a model crude oil-water system were studied in the presence of sodium hydroxide. The interfacial viscosity, non-Newtonian flow behavior, and activation energy of viscous flow were determined as a function of shear rate, alkali concentration, and aging time.

The interfacial viscosity drastically decreases in the presence of sodium hydroxide by up to three or four orders of magnitude. Sodium hydroxide also effectively suppresses the non-Newtonian flow behavior of the interfacial layer (Lakatos-Szabó and Lakatos, 1997).

Tracers

The addition of tracer chemicals to an injection fluid provides information about the permeability of a reservoir. Small amounts of a tracer are added to the injected fluid, and the distribution of the material at the production well is monitored with respect to time. Radioactive or nonradioactive tracers can be used.

Isotopically labeled tracers behave like the standard components in the fluid of interest; for example, tritium-labeled water behaves exactly like water. If less similar chemicals are used as tracers, their selective adsorption, chemical reaction, and liquid-liquid distribution must be considered. The tracer must be chosen so that the analytical method is sufficiently sensitive to detect it at the desired levels.

Tritiated or ^{14}C-tagged hydrocarbons (including tritium gas) can be measured by a liquid scintillation counter or a gas proportional counter (Tang and Harker, 1992a,b). Isotopic tracers are not exclusively radioactive; for instance, ^{13}C is often used.

Application of Tracers

Sensitive analytical procedures enable the detection and measurement of very low levels of tracer. In studies, an identifiable tracer material is injected through one or more injection wells into the reservoir being studied. Water is then injected to push the tracer to one or more recovery wells in the reservoir. The output of the recovery wells is then monitored to determine the tracer breakthrough and flow through the recovery wells. Analysis of breakthrough times and flows yields important information regarding how to perform the secondary or enhanced recovery processes. A sharp breakthrough of tracers in a two-well tracer test is achieved by the following method (Stegemeier and Perry, 1992):

1. A solution of a water-soluble tracer and a partitioning tracer that distributes between the formation oil and water into the formation is injected through a temporary injection well
2. This is stopped after a slug of the tracer solution has been injected,
3. Formation fluids are produced from the production well,
4. Monitoring the concentration of each tracer and the volumes of fluids produced from the producing wellborehole, and
5. Determining the formation of residual oil saturation from the chromatographic separation of the water-soluble tracer and the partitionable tracer.

Retention of the Tracer

To improve evaluation techniques in a water and gas pilot, tracers were injected in the gas phase at the beginning of the first two-gas injection periods. Perfluoromethylcyclopentane and perfluoromethylcyclohexane were used. In laboratory studies, these compounds were shown to have a higher partitioning to the oil phase than did tritiated methane. This caused a minor retention of the tracer (Dugstad et al., 1992; Ljosland et al., 1993).

Radioactive Tracers

Seven water tracers, namely tritiated water (HTO) and the ions $S^{14}CN^-$, $^{36}Cl^-$, $^{131}I^-$, $^{35}SO_4^{2-}$, $H^{14}CO^{3-}$, and $^{22}Na^+$ were tested for use in carbonate reservoirs. HTO is the ideal water tracer, although $S^{14}CN^-$ and $^{36}Cl^-$ were found to be near-ideal tracers for water flow in chalk. $^{131}I^-$ and $^{35}SO_4^{2-}$ show a more complicated behavior because of ion exclusion, adsorption, desorption, and chemical reactions (Bjornstad et al., 1994).

Nonradioactive Tracers

Analysis of halohydrocarbons, halocarbons, and sulfur hexafluoride is usually performed by gas chromatography with an electron capture detector. Complex metal anions, such as cobalt hexacyanide, are used as nonradioactive tracers in reservoir studies. The cobalt in the tracer compound must be in the complex anion portion of the molecule, because cationic cobalt tends to react with materials in the reservoir, leading to inaccurate analytic information (Miller et al., 1993).

In most production reservoirs, the brines produced are injected into the formation to maintain reservoir pressure and avoid subsidence and environmental pollution (Hutchins and Saunders, 1993), and, in the case of geothermal fields, to recharge the formation. These brines can, however, adversely affect the fluids produced from the reservoir. For example, in geothermal fields, the injected brine can lower the temperature of the produced fluids by mixing with the hotter formation fluids. In order to mitigate this problem, the subsurface paths of the injected fluids must be known.

Tracers have been used to label fluids in order to track their movement and monitor chemical changes in the injected fluid. Radioactive materials are one class of commonly used tracers, but they have several drawbacks.

They require special handling because of the danger posed to personnel and the environment. They also alter the natural isotope ratio that is indigenous to the reservoir. In addition, the half-life of radioactive tracers tends to be either too long or too short for practical use.

A number of organic compounds are suitable for use as tracers in a process for monitoring the flow of subterranean fluids. The following have been proposed: benzene tetracarboxylic acid, methylbenzoic acid, naphthalene sulfonic acid, naphthalene disulfonic acid, naphthalene trisulfonic acid, alkyl benzene sulfonic acid, alkyl toluene sulfonic acid, alkyl xylene sulfonic acid, α-olefin sulfonic acid, salts of the foregoing acids, naphthalenediol, aniline, substituted aniline, pyridine, and substituted pyridines (Hutchins and Saunders, 1993).

Thermal Stability of Alkyl Benzene Sulfonate

The thermal degradation of alkyl benzene sulfonates in alkaline media is important because of its potential application at elevated temperatures. The half-lives, with respect to thermal degradation, of several commercially available sulfonates have been estimated at hundreds to thousands of years at 204°C. The degradation mechanism is predominately a clipping of the alkyl chain to yield an alkyl benzene sulfonate with the phenyl group attached to the α-carbon; however, desulfonation also occurred (Shupe and Baugh, 1991).

Asphaltene Deposition

Asphaltenes are components of crude oils that contain numerous individual compounds, particularly high molecular weight condensed aromatic components including heteroatoms. Because of the complexity of their chemistry, asphaltenes are summarized as the oil fraction that is soluble in benzene, but not in *n*-pentane. In crude oil, asphaltenes are normally present as a colloidal dispersion stabilized by oleoresins. During the production, refining, transportation, and storage of crude oil, asphaltenes may precipitate.

Any precipitation caused by a temperature drop, or composition change in the porous media near the wellbore will reduce the permeability. Asphaltenes may also precipitate during flow through porous media, which may in particular, be stimulated by CO_2 flooding during the production process.

Partial esters of phosphoric acid with carboxylic acids are dispersants for asphaltenes (Miller et al., 1999), or the injection of organic aromatic solvents, and soaking is a feasible method for removing the precipitates (Ju et al., 2001). Alternatively, the precipitation of asphalt can be reduced by adding an *N*,*N*-dialkylamide of a fatty acid (Romocki, 1994, 1995). When asphaltenes are precipitated out, they can be removed from the walls of a well or a pipeline by washing with a hydrocarbon solvent. It has been shown that isopropyl benzoate is exceptionally useful as a solvent for asphaltene removal (Scovell et al., 2001).

Stabilizer Dispersant

The addition of hydrogenated castor oil to a copolymer of AAm and sodium acrylate formulation will suspend the copolymer and retard the settling process (Sommese and Nagarajan, 1995).

RESERVOIR PROPERTIES

Reservoir Models

There are several simulators for modeling the processes in EOR, which are indicated in Table 16.5.

Profile Control

Profile control occurs by artificially changing the permeability as is done in water shutoff. For more information, see Chapter 18.

AAm Polymers

The permeability of a high-permeability zone in a high-temperature oil can be reduced by placing an aqueous solution of a gellable polymeric and gelling this solution in situ (Lockhart and Burrafato, 1990b,c). The gel is made of a copolymer or a mixture of a synthetic polymer and a biopolymer (e.g., xanthan gum) (Lockhart and Burrafato, 1990a). Crosslinking agents are trivalent chromium ions or aldehydes (Sydansk, 1995). The pH is adjusted to 1.5–5.5, depending on the desired gelling time.

TABLE 16.5 Simulators and Models for Modeling Enhanced Oil Recovery

Simulator	References
Second-order Godunov-type finite difference for 2-dimensional, 3-component incompressible polymer floods	Holing et al. (1990)
Alkaline/surfactant/polymer compositional reservoir simulator, 3-dimensional compositional reservoir simulator, for alkaline chemical flooding processes	Bhuyan (1989)
New flux correcting (NFC)	Song (1992)
PC-GEL 3-dimensional, 3-phase (oil, water, and gas) permeability modification simulator	Chang and Gao (1993)
Fully implicit total variation diminishing high-order algorithm for compositional simulation and chemical flooding simulator	Liu et al. (1995)
Compositional chemical flooding simulator (UTCHEM)	Dakhlia (1995) and Rame and Delshad (1995)
Front-tracking model for in situ combustion oil recovery	Rocha et al. (1997)
Caustic waterflooding	Bhuyan et al. (1991), Islam and Chakma (1991) and Saneie and Yortsos (1993)

Anti-syneresis properties can be obtained with various organic acids and their alkali metal or ammonium salts. A delay in gelation also occurs when malonic acid is used (Albonico and Lockhart, 1993). AAms also can be crosslinked in situ by *o*-hydroxyphenylmethanol (Moradi-Araghi and Stahl, 1991b) or furfuryl alcohol and formaldehyde (Moradi-Araghi and Stahl, 1991a).

Melamine and Phenol-formaldehyde Resins

Melamine resins (Shu, 1990) and phenol-formaldehyde resins (Shu and Shu, 1991) can be gelled in situ to reduce the permeability of a formation. Various classes of polymers can be gelled by similar principles (Hutchins and Dovan, 1992).

Latex

Latex particles may flocculate when injected in to a reservoir at high formation temperatures. When the particles flocculate, shrink, and harden, they form a more effective blocking agent than the dispersed, expanded, and softer particles (Snowden et al., 1993).

In Situ Carbonate Precipitation

Carbon dioxide flooding is one of the most promising enhanced oil recovery method. To overcome the tendency of CO_2 to bypass the smaller pores containing residual oil, one approach is to plug the larger pores by chemical precipitation. Several, relatively inexpensive, water-soluble salts of alkaline earth metals react with CO_2 to form a precipitate.

Laboratory experiments have indicated that carbonate precipitation can alter the permeability of the core samples under reservoir conditions. The precipitation reduces the gas permeability in favor of the liquid permeability indicating that precipitation occurs preferentially in the larger pores.

Once the precipitate is formed, subsequent fluid flow will be diverted to smaller pores, thereby increasing the sweep efficiency. Additional experimental work with a series of connected cores suggested that the permeability profile can be modified successfully, but pH control plays a critical role in the propagation of the chemical precipitation reaction (Ameri et al., 1991).

In Situ Silica Cementation

The permeability profile of a formation where temperatures over 90°C are encountered can be modified by the following process: an aqueous solution of an alkali-metal hydroxide, ammonium hydroxide, or organo-ammonium hydroxide is injected into a zone of greater permeability in a formation. After this, a spacer volume of a water-miscible organic solvent is injected, followed by a water-miscible organic solvent containing an alkylpolysilicate in the greater permeability zone. A silica cement is formed in situ, which substantially closes off the higher permeability zone to fluid flow. Finally, a steamflooding, waterflooding, carbon dioxide stimulation, or fireflooding enhanced oil recovery operation is commenced in the lower permeability zone (Shu et al., 1993a,b).

Hydratable Clay

Hydratable clays may be used as plugging agents for profile control. The swelling of the clay is desirable, unlike when formation damage occurs (Zhou, 2000). First, an aqueous solution of the salts of cations such as K^+, Ca^{2+}, or Mg^{2+} that inhibit clay swelling is prepared.

The clay slurry is introduced into the formation, where it enters the channels of high permeability where it contacts the NaCl solution already present in natural or injected drive fluids. The inhibitive cations that are bound to the clay particles are replaced by Na^+ ions, which attract water molecules and promote clay swelling. The Na^+ clay swells up to 10 times its original volume, causing the slurry to acquire a gel-like consistency, which then blocks the flow of water. The gel can resist a differential pressure gradient of up to $500\,\mathrm{kPa\,m^{-1}}$.

Silicate Gel

Silicate gel enhances the sweep efficiency of a waterflood, gasflood, or steamflood operation by reducing the permeability of the high-permeability zones. Weak acids may be added to control gel generation rate (Chou and Bae, 1994).

Formation Damage

The in situ release of fine particles in a porous medium resulting from changes in the colloidal character of the fines has been studied. Changes in the electrolytic condition of the permeating fluid induce damage. The results showed that high pH and low salinity cause the fines to be released.

This release causes a drastic decline in the permeability of the medium. These findings establish the interplay between salinity changes, cation exchange, and pH during a water shock, and elucidate the vital role of the ion exchange process in formation damage (Vaidya and Fogler, 1990).

Formation damage caused by clay migration may be observed when the injected brine replaces the connate water during operations such as waterflooding, chemical flooding including alkaline, and surfactant and polymer processes. These effects can be predicted by a physicochemical flow model based on cationic exchange reactions that occur when the salinity decreases (Souto et al., 1993). Other models have also been presented (Chang and Civan, 1997; Moore, 2001).

The pH variation of the flowing fluid suggests that chemical reactions are occurring in the formation. A high pH promotes formation damage by particle deposition within porous media. The permeability reduction is minimized by using brines and high oil recoveries. Suspended solid particles are released and moved with the injection water when the salt concentration drops below critical levels, causing a reduction of permeability and eventually formation damage (Bagci et al., 2000).

Wettability

The wettability of the rock is responsible for the behavior of a reservoir subjected to any oil recovery process. Because the chemical composition of a mineral surface is mostly responsible for its wetting behavior, the relationship between wettability and chemical composition of the surface is key information.

X-ray photoelectron spectroscopy is a suitable technique for examining surfaces, whereas a detailed interpretation of coreflooding experiments and wettability index measurements gives the wettability. The results of such studies show that the organic carbon content of the surface correlates well with the wetting behavior of the material characterized by petrophysical measurements (Quet et al., 1991, 1992).

Flooding of Oil in Chalk

Chalk reservoirs encounter specific problems during secondary recovery of oil by waterflooding. Displacement experiments in several formations indicated that the shape of the leaching front depends not only on the nature of the fluids used, but also on the morphology of the formations. The following must be distinguished from each other:

- Voids filled with unrecoverable oil,
- Easily accessible pores, and
- Preferential paths.

Injecting water into oil-saturated chalk produces a regular front of leaching in some formations with a high percentage of preferential paths, especially when chalk contains a high proportion of rounded grains (Monjoie and Schroeder, 1997).

TREATMENT OF PRODUCED WATER

The liquid produced from an oil well is a mixture of oil and water. After dehydration, most of the crude oil is separated and a water phase that consists of oily waste water is formed. This needs to be treated, and can then be injected into the stratum again.

The amount of produced water can be appreciable. Experiments with a crude oil from the Daqing oil field (China) with a water content of less than 0.5%, a density of $850\,\mathrm{kg\,m^{-3}}$ and a viscosity of $60.89\,\mathrm{m\,Pa}$, at 45°C, and a PHPA with a degree of hydrolysis of about 25–30% were performed (Deng et al., 2002). The surfactant was an alkyl benzene sulfonate. The surfactant can decrease the ζ-potential of an oil droplet greatly, especially when its concentration is less than $200\,\mathrm{mgl^{-1}}$ The surfactant and the polymer increase interfacial elasticity between aqueous phase and oil phase. This indicates that the coalescence of the oil droplets is hindered.

SOIL REMEDIATION

A chemically enhanced oil recovery technology can be used to remove oily contaminants from soil. Laboratory studies have demonstrated that a variety of alkaline surfactant combinations can be used with a polymer to reduce the residual oil saturation in waterflooding (Pitts et al., 1993).

Polyaromatic hydrocarbons absorb strongly to humus and other soil components, making them difficult to remove by thermal, physical, or chemical means, and unavailable for biodegradation. To desorb polyaromatic hydrocarbons from soil, surfactant flooding and soil-washing processes, or treatments to enhance the biodegradation of polyaromatic hydrocarbons have been considered.

Surfactant flooding may contaminate ground water, and soil washing requires excavation and biodegradation of polyaromatic hydrocarbons and is incomplete even with surfactants. Biodegradable surfactants that can form reasonably stable foams in the presence of up to 50% ethanol have been developed. These ethanol-based foams can readily desorb the polyaromatic hydrocarbons from gas plant soils and move well through soils at pressure gradients of $1.5\,\mathrm{psi\,ft^{-1}}$ or less (Kilbane et al., 1996, 1997). A partially hydrolyzed copolymer of AAm and *n*-octylacrylamide together with sodium alkyl sulfates has also been described for in situ decontamination by flooding operations (Varadaraj, 1997).

REFERENCES

Abasov, M.T., Khismetov, T.V., Strekov, A.S., Mamalov, E.N., Bernshtein, A.M., 1993. New EOR methods based on hydrogen peroxide and urea solutions application. In: Proceedings Volume, vol. 1, 7th Eapg Impr. Oil Recovery Europe Symposium, Moscow, Russia, October 27–29, 1993, pp. 272–276.

Abdulmazitov, R.G., Muslimov, R.K., Zakirov, A.F., Khajretdinov, F.M., 1997. Oil recovery from carbonate oil-bearing seam – involves cyclic injection of acid solutions of increasing concentrations after reduction of seam pressure. RU Patent 2 073 791, assigned to Tartar Oil Inst., February 20, 1997.

Albonico, P., Lockhart, T.P., 1993. Aqueous gellable composition containing an anti- syneresis agent. EP Patent 544 377, assigned to Eniricerche SPA and Agip SPA, June 02, 1993.

Aleev, F.I., 1996. Oil displacement from heterogeneous seam by pumping sulphuric acid and water to seam - until sulpho-acids appear in liquid removed from wells. RU Patent 2 055 166, assigned to Orenburgneft Assoc. Cent. Lab, February 27, 1996.

Aleev, F.I., Andreev, V.V., Ivanov, S.V., Kivilev, P.P., Talalaev, N.A., Khodyrev, V.A., 1996. Chernoshtanov, I.F., Oil deposit water flooding with improved efficiency – by pumping of sulphuric acid and water into seam prior to periodic pumping of water into seam through injection well and liquid removal from producing well. RU Patent 2 055 165, assigned to Orenburgneft Assoc. Cent. Lab, February 27, 1996.

Al-Khafaji, A.H., 1999. Implementations of enhanced oil recovery techniques in the Arab world are questioned?. In: Proceedings Volume, 6th International Energy Found et al Mediter Petroleum Conference, Tripoli, Libya, November 23–25, 1999, pp. 124–133.

Almaev, R.K., Gabdrakhmanov, A.G., Kashapov, O.S., Bazekina, L.V., Kostilevskij, S.E., 1996. Extraction of viscous oil from oil strata – involves pumping-in aqueous alkalipolymericsolution containing fraction of liquid hydrocarbon(s) from oil processing and using polyacrylamide. RU Patent 2 068 084, assigned to Yuzharlanneft Oil Gas Conference, October 20, 1996.

Al-Sahhaf, T., Ahmed, A.S., Elkamel, A., 2002. Producing ultralow interfacial tension at the oil/water interface. Pet. Sci. Technol. 20 (7–8), 773–788.

Alvarado, V., Manrique, E., 2010. Enhanced Oil Recovery: Field Planning and Development Strategies. Elsevier Gulf Professional, Amsterdam.

Amaya, J., Rana, D., Hornof, V., 2002. Dynamic interfacial tension behavior of water/oil systems containing in situ-formed surfactants. J. Solut. Chem. 31 (2), 139–148.

Ameri, S., Aminian, K., Wasson, J.A., Durham, D.L., 1991. Improved CO_2 enhanced oil recovery – mobility control by in-situ chemical precipitation: Final report, US DOE Rep DOE/MC/22044-15, West Virginia Univ, June 1991.

Amin, R., Smith, T.N., 1998. Measurement of interfacial tension and spreading coefficient under reservoir conditions: experimental investigation. Colloid Surf. A 137 (1–3), 35–43.

Anders, H.J., Kaetzke, A., Kampfer, P., Ludwig, W., Fuchs, G., 1995. Taxonomic position of aromatic-degrading denitrifying pseudomonad strains K 172 and KB 740 and their descriptionas new members of the genera thauera, as thauera aromatica sp. nov., and azoarcus, as azoarcus evansii sp. nov., respectively, members of the beta subclass of the proteobacteria. Int. J. Syst. Evol. Microbiol. 45, 327–333.

Ashrawi, S.S., 1992. Hot water, surfactant, and polymer flooding process for heavy oil. US Patent 5 083 612, assigned to Texaco Inc., January 28, 1992.

Austad, T., Bjorkum, P.A., Rolfsvag, T.A., Oysaed, K.B., 1991. Adsorption: Pt.3: Nonequilibrium adsorption of surfactants onto reservoir cores from the North Sea. The effects of oil and clay minerals. J. Pet. Sci. Eng. 6 (2), 137–148.

Austad, T., Ekrann, S., Fjelde, I., Taugbol, K., 1997. Chemical flooding of oil reservoirs: Pt 9: Dynamic adsorption of surfactant onto sandstone cores from injection water with and without polymer present. Colloids Surf. 127 (1–3), 69–82.

Austad, T., Matre, B., Milter, J., Saevareid, A., Oyno, L., 1998. Chemical flooding of oil reservoirs: Pt 8: Spontaneous oil expulsion from oil- and water-wet low permeable chalk material by imbibition of aqueous surfactant solutions. Colloids Surf. 137 (1–3), 117–129.

Austad, T., Rorvik, O., Rolfsvag, T.A., Oysaed, K.B., 1992. Adsorption: Pt.4: An evaluation of polyethylene glycol as a sacrificial adsorbate towards ethoxylated sulfonates in chemical flooding. J. Pet. Sci. Eng. 4 (6), 265–276.

Austad, T., Veggeland, K., Fjelde, I., Taugbol, K., 1993. Physicochemical principles of low tension polymer flood. In: Proceedings Volume, vol. 1, 7th Eapg Impr. Oil Recovery Europe Symposium, Moscow, Russia, October 27–29, 1993, pp. 208–219.

Bagci, S., Kok, M.V., Turksoy, U., 2000. Determination of formation damage in limestone reservoirs and its effect on production. J. Pet. Sci. Eng. 28 (1–2), 1–12.

Balakirov, Y.A., Chernorubashkin, A.I., Makeev, G.A., Korolev, I.P., Glushchenko, V.N., 1992. Composition for treatment of stratum head zone – contains oxyethylated isononyl phenol, aqueous solution of hydrofluoric acid and aqueous solution of hydrochloric acid. SU Patent 1 770 555, assigned to Ukrgoproniineft Oil Ind. and Assoc. Ukr. Bioorg Chem. & Petrol., October 23, 1992.

Ball, S.D., 1995. Comparison of transient interfacial tension behaviours of oil/alkaline systems as measured by the drop volume and spinning drop tensiometers, Ph.D. thesis, Ottawa Univ.

Ball, S.D., Hornof, V., Neale, G.H., 1996. Transient interfacial tension behavior between acidic oils and alkaline solutions. Chem. Eng. Commun. 147, 145–156.

Baviere, M., Rouaud, T., 1990. Solubilization of hydrocarbons in micellar solutions. Influence of structure and molecular weight (solubilisation des hydrocarbures dans les solutions micellaires. Influence de la structure et de la masse moleculaire). Rev. Inst. Franc. Pet. 45 (5), 605–620.

Bayless, J.H., 1998. Hydrogen peroxide: A new thermal stimulation technique. World Oil 219 (5), 75–78.

Bayless, J.H., 2000. Hydrogen peroxide applications for the oil industry. World Oil 221 (5), 50–53.

Bedo, Z., Lakatos, I., Lakatos-Szabó, J., 1997. Interactions between an ethoxy-nonyl-phenol and a polyacrylamide in aqueous solutions. ACH-Models in Chemistry 134 (6), 735–752.

Belyaev, S.S., Charakchian, I.A., Kuznetsova, V.G., 1991. Strict anaerobic bacteria and their possible contribution to the enhancement of oil recovery. In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, vol. 31 of Developments in Petroleum Science, Elsevier Science Ltd., 1991, pp. 163–172.

Berger, P.D., Lee, C.H., 2002. Ultra-low concentration surfactants for sandstone and limestone floods. In: Proceedings Volume, SPE/DOE Thirteenth Improved Oil Recovery Symposium held in Tulsa, Oklahoma, April 13–17, 2002.

Bhupathiraju, V.K., Sharma, P.K., McInerney, M.J., Knapp, R.M., Fowler, K., Jenkins, W., 1991. Isolation and characterization of novel halophilic anaerobic bacteria from oil field brines. In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent 1990 International Conference on Microbial Enhancement of Oil Re Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, vol. 31 of Developments in Petroleum Science, Elsevier Science Ltd., 1991, pp. 131–143.

Bhuyan, D., 1989. Development of an alkaline/surfactant/polymer compositional reservoir simulator, Ph.D. thesis, Texas Univ, Austin.

Bhuyan, D., Pope, G.A., Lake, L.W., 1991. Simulation of high-pH coreflood experiments using a compositional chemical flood simulator. In: Proceedings Volume, SPE Oilfield Chemicals International Symposium, Anaheim, Calif, February 20–22, 1991, pp. 307–316.

Bjornstad, T., Haugen, O.B., Hundere, I.A., 1994. Dynamic behavior of radio-labelled water tracer candidates for chalk reservoirs. J. Pet. Sci. Eng. 10 (3), 223–238.

Borchardt, J.K., Bright, D.B., Dickson, M.K., Wellington, S.L., 1987. Surfactants for carbon dioxide foam flooding: Effects of surfactant chemical structure on one-atmosphere foaming properties. In: Proceedings Volume, no. 373, 61st Annual ACS Colloid & Surface Sci Symposium, Ann Arbor, MI, June 21–24, 1987, pp. 163–180.

Borchardt, J.K., Strycker, A.R., 1997. Olefin sulfonates for high temperature steam mobility control: Structure-property correlations. In: Proceedings Volume, SPE Oilfield Chemicals International Symposium, Houston, February 18–21, 1997, pp. 91–102.

Bragg, J.R., 1998. Oil recovery method using an emulsion. WO Patent 9 853 181, assigned to Exxon Production Res. Co., November 26, 1998.

Bragg, J.R., 1999. Oil recovery method using an emulsion. US Patent 5 855 243, assigned to Exxon Production Res. Co., January 05, 1999.

Bryant, R.S., Burchfield, T.E., 1989. Review of microbial technology for improving oil recovery. In: Proceedings Volume, Nat. Inst. Petrol. Energy Res. Microbial Enhanced Oil Recovery Short Course, Bartlesville, Okla, May 23, 1989.

Bryant, R.S., Burchfield, T.E., Porter, R.E., Dennis, D.M., Hitzman, D.O., 1991. Microbial enhanced waterflooding: A pilot study. In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, vol. 31 of Developments in Petroleum Science, Elsevier Science Ltd., 1991, pp. 399–419.

Bubela, B., 1989. Geobiology and microbiologically enhanced oil recovery. In: Donaldson, E.C., Chilingarian, G.V., Yen, T.F. (Eds.), Microbial Enhanced Oil Recovery, vol. 22 of Developments in Petroleum Science, Elsevier Science Ltd., 1989, pp. 75–97.

Bubela, B., 1983. In situ biological production of surfactants for enhanced oil recovery, Australia Dep Resources Energy End of Grant Rep 151, March 1983.

Burcham, C., Fast, R.E., Murer, A.S., Northrop, P.S., 1995. Oil recovery by enhanced imbibition in low permeability reservoirs. US Patent 5 411 086, assigned to Mobil Oil Corp., May 02, 1995.

Campbell, C.B., Sinquin, G.P., 2008. Alkylxylene sulfonates for enhanced oil recovery processes. US Patent 7 468 343, assigned to Chevron Oronite Company LLC, San Ramon, CA, December 23, 2008.

Campos, R.E., Hernandez, J.A., 1993. In-situ reduction of oil viscosity during steam injection process in eor. US Patent 5 209 295, assigned to Intevep, May 11, 1993.

Cavallaro, A.N., Baigorria, R., Curci, E., 2000. Design of an acid stimulation system with chlorine dioxide for the treatment of water-injection wells. In: Proceedings Volume, 51st Annual Cim Petroleum Society Technology Meeting, Calgary, Canada, June 4–8, 2000.

Cavallaro, A., Curci, E., Galliano, G., Vicente, M., Crosta, D., Leanza, H., 2001. Design of an acid stimulation system with chlorine dioxide for the treatment of water-injection wells. In: Proceedings Volume, 7th SPE Latin Amer. & Caribbean Petrol. Eng. Conference, Buenos Aires, Argentina, March 25–28, 2001.

Chang, F.F., Civan, F., 1997. Practical model for chemically induced formation damage. J. Pet. Sci. Eng. 17 (1–2), 123–137.

Chang, M.M., Gao, H.W., 1993. User's guide and documentation manual for "PCGel" simulator: Topical report, US DOE Fossil Energy Rep NIPER-705, NIPER, October 1993.

Chase, K.L., Bryant, R.S., Burchfield, T.E., Bertus, K.M., Stepp, A.K., 1991. Investigations of microbial mechanisms for oil mobilization in porous media. In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, vol. 31 of Developments in Petroleum Science, Elsevier Science Ltd., 1991, pp. 79–94.

Chen, T., Pu, W., Ping, K., Ye, Z., 1997. The rheological behavior of partially hydrolyzed polyacrylamide (HPAM) solutions in reservoir. J. Southwest Pet. Inst. 19 (3), 2A–3A, 28–34.

Chen, W.J., Li, G.Z., Mu, J.H., Zhai, L.M., Zhou, G.W., 2003. Effects of modified natural mixed carboxylates in ASP-flooding systems. J. Dispersion Sci. Technol. 24 (2), 197–202.

Chiwetelu, C.I., Hornof, V., Neale, G.H., George, A.E., 1994. Use of mixed surfactants to improve the transient interfacial tension behaviour of heavy oil/alkaline systems. Can. J. Chem. Eng. 72 (3), 534–540.

Chou, S., Bae, J., 1994. Method for silica gel emplacement for enhanced oil recovery. US Patent 5 351 757, assigned to Chevron Res. & Technol. Co., October 04, 1994.

Chou, S., Campbell, C.B., 2001. Oil recovery method for waxy crude oil using alkylaryl sulfonate surfactants derived from alpha-olefins and the alpha-olefin compositions. US Patent 6 269 881, assigned to Chevron U.S.A. Inc., San Francisco, CA, Chevron Chemical Company LLC, San Francisco, CA, August 7, 2001.

Cobb, H.G., 2010. Composition and process for enhanced oil recovery. US Patent 7 691 790, assigned to Coriba Technologies, L.L.C., North Little Rock, AR, April 6, 2010.

Coleman, J.K., Brown, M.J., Moses, V., Burton, C.C., 1992. Enhanced oil recovery. WO Patent 9 215 771, September 17, 1992.

Cruze, J.A., Hitzman, D.O., 1987. Microbial field sampling techniques for MEOR (microbial enhanced oil recovery) processes, US DOE Fossilenergy Rep NIPER-351 CONF-870858, US DOE, September 1987.

Cunningham, A.B., Spangler, L.H., Gerlach, R., Phillips, A.J., 2006. Use of bacteria to prevent gas leakage. US Patent Application 20060216811, September 28, 2006.

Cusack, F.M., Costerton, J.W., Novosad, J., 1991. Ultramicrobacteria enhance oil recovery. In: Proceedings Volume, 4th Inst. Gas Technol. Gas, Oil, & Environ. Biotechnol. International Symposium, Colorado Springs, CO, December 9–11, 1991, pp. 491–504.

Daharu, R., Thomas, S., Farouq, A.S.M., 1991. Micellar flooding for tertiary recovery: Recent advances and potential. In: Proceedings Volume, 10th SPE Trinidad & Tobago Sect. Tech. Conference, Port of Spain, Trinidad, June 26–28, 1991, pp. 414–428.

Dakhlia, H., 1995. A simulation study of polymer flooding and surfactant flooding using horizontal wells, Ph.D. thesis, Texas Univ, Austin.

Davis, B.W., 1992. In situ chemical stimulation of diatomite formations. CA Patent 1 308 550. Assigned to Chevron Res., October 13, 1992.

Debons, F.E., Whittington, L.E., 1991. Improved oil recovery surfactants based on lignin. J. Pet. Sci. Eng. 7 (1–2), 131–138.

Deng, S.B., Bai, R.B., Chen, J.P., Yu, G., Jiang, Z.P., Zhou, F.S., 2002. Effects of alkaline/surfactant/polymer on stability of oil droplets in produced water from ASP flooding. Colloid Surf. A 211 (2–3), 275–284.

Dino, D.J., Homack, A., 1997. Use of high purity imidazoline based amphoacetate surfactant as foaming agent in oil wells. US Patent 5 614 473, assigned to Rhone Poulenc Inc., March 25, 1997.

Diyashev, R.N., Sattarova, F.M., Mazitov, K.G., Khusainov, V.M., Mannanov, F.N., Diyashev, I.R., et al., 1996a. Extraction of oil from lens-shaped deposits – involves cyclic and portion-wise pumping-in of solutions of potassium carbonate and inhibited hydrochloric acid. RU Patent 2 065 942, assigned to Tartar Oil Inst., August 27, 1996.

Diyashev, R.N., Sattarova, F.M., Mazitov, K.G., Khusainov, V.M., Sulejmanov, K.I., Karimov, G.S., et al., 1996b. Recovering oil not exploited from reservoir – by injecting alternating portions of ammonium carbonate and hydrochloric acid and displacing formed carbon dioxide with water. RU Patent 2 065 940, assigned to Tartar Oil Inst., August 27, 1996.

Donaldson, E.C., Obeida, T., 1991. Enhanced oil recovery at simulated reservoir conditions, 3rd US DOE Microbial Enhancement of Oil Recovery International Conference (Norman, Okla, 5/27/90–6/1/90). In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, vol. 31 of Developments in Petroleum Science, Elsevier Science Ltd., 1991, pp. 227–245.

Drillet, V., Defives, D., 1991. Clay dissolution kinetics in relation to alkaline flooding. In: Proceedings Volume, SPE Oilfield Chemicals International Symposium, Anaheim, Calif, February 20–22, 1991, SPE Number: 21030, pp. 317–326.

Dugstad, O., Bjornstad, T., Hundere, I., 1992. Measurements and application of partition coefficients of compounds suitable for tracing gas injected into oil reservoirs. Rev. Inst. Franc. Pet. 47 (2), 205–215.

Duncan, G., 1994. Enhanced recovery engineering: Pt.1. World Oil 215 (9), 95, 97–100.

Duncan, G., Bulkowski, P., 1995. Enhanced recovery engineering: Pt.7. World Oil 216 (9), 77–84.

Dzhafarov, I.S., Brezitsky, S.V., Shakhverdiev, A.K., Panakhov, G.M., Suleimanov, B.A., 1999. New in-situ carbon dioxide generation enhanced oil recovery technology. In: Proceedings Volume, no. 106, 10th EAGE Improvement of Oil Recovery Europe Symposium, Brighton, UK, August 18–20, 1999.

Elkamel, A., Al-Sahhaf, T., Ahmed, A.S., 2002. Studying the interactions between an arabian heavy crude oil and alkaline solutions. Pet. Sci. Technol. 20 (7–8), 789–807.

Feraud, J.P., Perthuis, H., Dejeux, P., 2001. Compositions for iron control in acid treatments for oil wells. US Patent 6 306 799, assigned to Schlumberger Technology Corporation, Sugar Land, TX, October 23, 2001.

Fink, M., Fink, J., 1998. Usage of pyrolysis products from organic materials to improve recovery of crude oil. In: Extended Abstr Volume, vol. 2, 60th EAGE Conference, Leipzig, Ger, June 8–12, 1998, p. P553.

French, T.R., 1990. Design and optimization of phosphate-containing alkaline flooding formulations: Topical report, US DOE Fossil Energy Rep NIPER-446, NIPER, February 1990.

French, T.R., Josephson, C.B., 1991. Surfactant-enhanced alkaline flooding with weak alkalis, US DOE Rep NIPER-507, NIPER, February 1991.

French, T.R., Josephson, C.B., 1992. Alkaline flooding injection strategy, US DOE Fossil Energy Rep NIPER-563, NIPER, March 1992.

French, T.R., Josephson, C.B., 1993. The effect of polymer-surfactant interaction on the rheological properties of surfactant-enhanced alkaline flooding formulations: Topical report, US DOE Fossil Energy Rep NIPER-635, NIPER, February 1993.

Frolov, A.I., Khisamov, R.S., Rjabov, I.I., Taziev, M.Z., 1998. Recovery of oil from reservoir - by injection of water and surfactant solution also additionally of wide hydrocarbon(s) fraction and of surfactant solution. RU Patent 2 103 492, assigned to Tatneft Stock Co., January 27, 1998.

Gall, B., 1989. Use of sacrificial agents to reduce carboxymethylated ethoxylated surfactant loss during chemical flooding: Topical report, US DOE Fossil Energy Rep.

Garcia-Sanchez, F., Eliosa-Jimenez, G., Salas-Padron, A., Hernandez-Garduza, O., Apam-Martinez, D., 2001. Modeling of microemulsion phase diagrams from excess gibbs energy models. Chem. Eng. J. 84 (3), 257–274.

Gevertz, D., Paterek, J.R., Davey, M.E., Wood, W.A., 1991. Isolation and characterization of anaerobic halophilic bacteria from oil reservoir brines. In: Proceedings Volume, no. 31, 3rd US DOE Microbial Enhancement of Oil Recovery International Conference, Norman, Okla, May 27, 90–6, 1, 90, 1991, pp. 115–129.

Glumov, I.F., Ibatullin, R.R., Abdulkhairov, R.M., Slesareva, V.V., Kochetkov, V.D., Roshchektaeva, N.A., 1994. Working out of oil stratum – comprises pumping sulphuric acid into stratum through pressing-in wells, pressing-in with water and collecting oil through extraction wells. RU Patent 1 480 411, assigned to Tartar Oil Inst. and Tatnipineft, October 30, 1994.

Goodyear, S.G., Jones, P.I.R., 1995. Assessment of foam for deep flow diversion. In: Proceedings Volume, vol. 2, 8th Eapg Impr. Oil Recovery Europe Symposium, Vienna, Austria, May 15–17, 1995, pp. 174–182.

Gorodilov, V.A., Shevchenko, V.N., Tipikin, S.I., Makurov, A.D., Makeev, G.A., Fomichev, V.F., 1997. Method for high temperature seam oil deposit development – by pumping aluminium chloride and tri- sodium phosphate as sediment forming material. RU Patent 2 094 599, assigned to Noyabrskneftegeo Stock Co., October 27, 1997.

Gorodnov, V.P., Ryskin, A.Y., Kharlanov, G.P., Belov, A.A., Shein, A.V., 1992. Enhancing oil recovery from boreholes – by injecting into seam aqueous solution of polyacrylamide, chrome alum and bentonite clay for improved flow characteristics. SU Patent 1 731 942, assigned to Giprovostokneft Des. Inst., May 07, 1992.

Gorodnov, V.P., Ryskin, A.Y., Pavlov, M.V., 1993. Increasing oil extraction from stratum – by pumping- in hydrochloric acid solution or its mixture with hydrofluoric acid or ammonium fluoride, followed by pumping aqueous solution or surfactant. SU Patent 1 795 092, assigned to Giprovostokneft Des. Inst., February 15, 1993.

Green, D.W., Willhite, G.P., 2008. Enhanced Oil Recovery, fourth ed., vol. 8. of SPE Textbook Series, Society of Petroleum Engineers, Richardson, TX.

Grula, E.A., Russell, H.H., Bryant, D., Kenaga, M., 1989a. Oil displacement by anaerobic and facultatively anaerobic bacteria. In: Donaldson, E.C., Chilingarian, G.V., Yen, T.F. (Eds.), Microbial Enhanced Oil Recovery, vol. 22 of Developments in Petroleum Science, Elsevier Science Ltd., 1989, pp. 113–123.

Grula, E.A., Russell, H.H., Grula, M.M., 1989b. Potential health hazard of bacteria to be used in microbial enhanced oil recovery. In: Donaldson, E.C., Chilingarian, G.V., Yen, T.F. (Eds.), Microbial Enhanced Oil Recovery, vol. 22 of Developments in Petroleum Science, Elsevier Science Ltd., 1989, pp. 209–213.

Han, D.K., Yang, C.Z., Lou, Z.H., Zhang, Z.Q., Chang, Y.I., 1999. Recent development of enhanced oil recovery in china. J. Pet. Sci. Eng. 22 (1–3), 181–188.

Hendrickson, E.R., Jackson, R.E., Keeler, S.J., Luckring, A.K., Perry, M.P., Wolstenholme, S., 2010. Identification, characterization, and application of thauera sp. al9:8 useful in microbially enhanced oil recovery. US Patent 7 708 065, assigned to E.I. du Pont de Nemours and Company, Wilmington, DE, May 4, 2010.

Higuerey, I., Pereira, P., Leon, V., 2001. Comparative study of compositional changes between thermal cracking and aquaconversion(r) process. ACS Pet. Chem. Div. Preprints 46 (1), 64–65.

Hoffmann, G.G., Steinfatt, I., 1993. Thermochemical sulfate reduction at steam flooding processes – a chemical approach. In: ACS Pet. Chem. Div. Preprints, vol. 38, 205th ACS Nat. Mtg. Enhanced Oil Recovery Symposium, Denver, March 28, 93–4, 2, 1993, pp. 181–184.

Holing, K., Alvestad, J., Trangenstein, J.A., 1990. The use of second-order godunov-type methods for simulating EOR processes in realistic reservoir models. In: Proceedings Volume, 2nd Inst. Franc Du Petrol. Math. of Oil Recovery Europe Conference, Arles, Fr, September 11–14, 1990, pp. 101–111.

Horvath-Szabó, G., Czarnecki, J., Masliyah, J., 2001a. Liquid crystals in aqueous solutions of sodium naphthenates. J. Colloid Interface Sci. 236 (2), 233–241.

Horvath-Szabó, G., Masliyah, J.H., Czarnecki, J., 2001b. Phase behavior of sodium naphthenates, toluene, and water. J. Colloid Interface Sci. 242 (1), 247–254.

Horvath-Szabó, G., Czarnecki, J., Masliyah, J.H., 2002. Sandwich structures at oil-water interfaces under alkaline conditions. J. Colloid Interface Sci. 253 (2), 427–434.

Hoskin, D.H., Mitchell, T.O., Shu, P., 1991. Oil reservoir permeability profile control with crosslinked welan gum biopolymers. US Patent 4 981 520, assigned to Mobil Oil Corp., January 01, 1991.

Hsu, J.J.C., 1992. Recovering hydrocarbons with a mixture of carbon dioxide and trichloroethane. US Patent 5 117 907, June 02, 1992.

Hsu, O.Y., Hsu, N.S., 2000. Alkaline surfactant polymer flooding composition and process. US Patent 6 022 834, assigned to Oil Chemicals Technologies, Inc., Sugarland, TX, February 8, 2000.

Hurd, B.G., 1991. Method for using foams to improve alkaline flooding oil recovery. US Patent 4 981 176, assigned to Mobil Oil Corp., January 01, 1991.

Hutchins, R.D., Dovan, H.T., 1992. Method for reducing water production from wells. US Patent 5 161 615, assigned to Union Oil Co. California, November 10, 1992.

Hutchins, R.D., Saunders, D.L., 1993. Tracer chemicals for use in monitoring subterranean fluids. US Patent 5 246 860, assigned to Union Oil Co. California, September 21, 1993.

Hwang, R.J., Ortiz, J., 1999. Mitigation of asphaltics deposition during CO_2 flood by enhancing CO_2 solvency with chemical modifiers, Organic Geochem. 31 (12), 1451–1462.

Ignateva, V.E., Telin, A.G., Khisamutdinov, N.I., Safronov, S.V., Artemev, V.N., Ermilov, Y.A., 1996. Composition for oil extraction – contains hydrocarbon- or alcohol-containing solvent, water and vat residue from production of glycerine or ethylene glycol. RU Patent 2 065 941, assigned to Neftegaztek Res. Eng. Cent., August 27, 1996.

Islam, M.R., Chakma, A., 1991. Mathematical modelling of enhanced oil recovery by alkali solutions in the presence of cosurfactant and polymer. J. Pet. Sci. Eng. 5 (2), 105–126.

Ivanov, M.V., Belyaev, S.S., 1989. Biotechnology and enhanced oil recovery. Neft Khoz 10, 28–32.

Ivory, J., Derocco, M., Paradis, N., 1989. Investigation of the mechanisms involved in the steamair injection process. In: Preprints, no. 21, 3rd Cim Petroleum Society Technology Meeting, Regina, Canada, September 25–27, 1989.

Jang, L.K., Yen, T.F., Chilingarian, G.V., Donaldson, E.C., 1989. Bacterial migration through nutrient-enriched sandpack columns for in-situ recovery of oil. In: Donaldson, E.C., Chilingarian, G.V., Yen, T.F. (Eds.), Microbial Enhanced Oil Recovery, vol. 22 of Developments in Petroleum Science, Elsevier Science Ltd., 1989, pp. 151–164.

Jenneman, G.E., Clark, J.B., 1994a. Injection of scale inhibitors for subterranean microbial processes. US Patent 5 337 820, assigned to Phillips Petroleum Co., August 16, 1994.

Jenneman, G.E., Clark, J.B., 1994b. Utilization of phosphite salts as nutrients for subterranean microbial processes. US Patent 5 327 967, assigned to Phillips Petroleum Co., July 12, 1994.

Ju, B., Luan, Z., Wu, Z., Lu, G., 2001. A study of removal of organic formation damage by experiments and modeling approaches. In: Proceedings Volume, SPE Asia Pacific Oil & Gas Conference, Jakarta, Indonesia, April 17–19, 2001.

Kalfoglou, G., Paulett, G.S., 1993. Method of using lignosulfonate-acrylic acid graft copolymers as sacrificial agents for surfactant flooding. US Patent 5 251 698, assigned to Texaco Inc., White Plains, NY, October 12, 1993.

Kalpakci, B., Arf, T.G., Grist, D.M., Hyde, S.B., Vikane, O., Espedal, S., 1993. A preliminary evaluation of an LTPF (low tension polymer flood) process for Statfjord field, Norway. In: Proceedings Volume, vol. 1, 7th Eapg Impr. Oil Recovery Europe Symposium, Moscow, Russia, October 27–29, 1993, pp. 193–207.

Keeler, S.J., Hendrickson, E.R., Hnatow, L.L., Jackson, S.C., 2010. Identification, characterization, and application of shewanella putrefaciens (lh4:18), useful in microbially enhanced oil release. US Patent 7 776 795, assigned to E.I. du Pont de Nemours and Company, Wilmington, DE, August 17, 2010.

Kilbane II., J.J., Chowdiah, P., Kayser, K.J., Misra, B., Jackowski, K.A., Srivastava, V.J., et al., 1996. In-situ remediation of contaminated soils using foams as carriers for chemicals, nutrients, and other amendments. In: Proceedings Volume, 9th Inst. Gas Technol. Gas, Oil, & Environ. Biotechnol. International Symposium, Colorado Springs, CO, December 9–11, 1996.

Kilbane II., J.J., Chowdiah, P., Kayser, K.J., Misra, B., Jackowski, K.A., Srivastava, V.J., et al., 1997. Remediation of contaminated soils using foams. In: Proceedings Volume, 10th Inst. Gas Technol. Gas, Oil & Environ. Biotechnol. & Site Remediation Technol. International Symposium, Orlando, Florida, December 8–10, 1997.

Killough, J.E., 1987. Hydrocarbon recovery process. US Patent 4 678 033, July 07, 1987.

Kovarik, F.S., Heller, J.P., 1990. Improvement of CO_2 flood performance, US DOE Rep DOE/MC/21136-24, New Mex Inst Mining Techn, August 1990.

Lakatos, I., Bauer, K., Lakatos-Szabó, J., 1997. Potential application of oxygen containing gases to enhance gravity drainage in heavy oil bearing reservoirs. Erdöl Erdgas Kohle 113 (6), 260–263.

Lakatos, I., Lakatosne, S.J., 1991. Dynamical characteristics of the polymer flooding: Pt.2 (a polimeres elarasztas kinamikus jellemzoi: 2. resz). Koolaj Foldgaz 24 (6), 170–178.

Lakatos, I., Lakatos-Szabó, J., 1997. Effect of ethoxylated nonyl-phenols on interfacial rheological properties of oil/water systems. Colloid Polym. Sci. 275 (5), 493–501.

Lakatos, I., Lakatos-Szabó, J., 2001a. Effect of IOR/EOR [improved oil recovery/enhanced oil recovery] chemicals on interfacial rheological properties of crude oil/water systems. In: Proceedings Volume, SPE Oilfield Chemicals International Symposium, Houston, TX, February 13–16, 2001, SPE Number: 65391.

Lakatos, I., Lakatos-Szabó, J., 2001b. Effect of IOR/EOR chemicals on interfacial rheological properties of crude oil/water systems. In: Proceedings Volume, SPE International Symposium on Oilfield Chemistry held in Houston, Texas, February 13–16, 2001.

Lakatos, I., Lakatos-Szabó, J., Bedo, Z., 2003b. Application of nonionic tenside homologues in IOR/EOR and oilfield chemistry: Fundamental and engineering aspects. In: Proceedings Volume, SPE International Symposium on Oilfield Chemistry, Houston, Texas, U.S.A., February 5–7, 2003.

Lakatos, I., Tóth, J., Bauer, K., Lakatos-Szabó, J., Kosztin, B., Palásthy, G., et al., 2003a. Comparative study of different silicone compounds as candidates for restriction of water production in gas wells. In: Proceedings Volume, SPE International Symposium on Oilfield Chemistry, Houston, Texas, U.S.A., February 5-7, 2003.

Lakatos, I., Tóth, J., Lakatos-Szabó, J., Kosztin, B., Palásthy, G., H.Wöltje, 2002. Application of silicone microemulsion for restriction of water production in gas wells. In: Proceedings Volume, SPE 13th European Petroleum Conference, Aberdeen, Scotland, U.K., October 29–31, 2002.

Lakatos-Szabó, J., Lakatos, I., 1989. Effect of non-ionic surfactants on interfacial rheological properties of water/oil systems. Erdöl Erdgas Kohle 105 (10), 406–410.

Lakatos-Szabó, J., Lakatos, I., 1997. Effect of sodium hydroxide on interfacial rheological properties of oil-water systems. In: Colloids and Surfaces, vol. 149, 9th Surface & Colloid Sci International Conference, Sofia, Bulgaria, July 6–12, 1997, pp. 507–513.

Lakatos-Szabó, J., Lakatos, I., 1999. Effect of sodium hydroxide on interfacial rheological properties of oil-water systems. Colloid Surf. A 149 (1–3), 507–513.

Lakatos-Szabó, J., Lakatos, I., Kosztin, B., 1997. Role of interfacial rheological properties of oil/water systems in mechanism and design of EOR/IOR technologies. In: Proceedings Volume, no. 057, 9th EAGE Impr. Oil Recovery Europe Symposium, The Hague, Neth, December 20–22, 1997, Proc.

Lazar, I., 1993. The microbiology of MEOR: (microbial enhanced oil recovery): Practical experience in europe. In: Proceedings Volume, vol. 2, Minerals, Metals & Mater Soc. et al Biohydromet Technol. International Symposium, Jackson Hole, WY, August 22–25, 1993, pp. 329–338.

Lazar, I., Voicu, A., Archir, G., Toma, T., Lazar, I.G., Blanck, L., et al., 1993. Investigations on a new Romanian biopolymer (pseudozan) for use in enhanced oil recovery (EOR). In: Proceedings Volume, vol. 2, Minerals, Metals & Mater Soc. et al Biohydromet Technology International Symposium, Jackson Hole, WY, August 22–25, 1993, pp. 357–364.

Li, G.Z., Mu, J.H., Li, Y., Xiao, H.D., Gu, Q., 2000a. What is the criterion for selecting alkaline/surfactant/polymer flooding formulation: Phase behavior or interfacial tension. J. Dispersion Sci. Technol. 21 (3), 305–314.

Li, G.Z., Mu, J.H., Li, Y., Yuan, S.L., 2000b. An experimental study on alkaline/surfactant/polymer flooding systems using nature mixed carboxylate. Colloid Surf. A 173 (1–3), 219–229.

Li, Z.P., Zeng, H.X., Zhao, R.B., Jiao, L.M., 1999. The nature of colloid and interface of miscible phase system in alkaline-surfactant combination flooding. J. Dispersion Sci. Technol. 20 (4), 1143–1162.

Lin, S.C., Goursaud, J.C., Kramer, P.J., Georgiou, G., Sharma, M.M., 1991. Production of biosurfactant by bacillus licheniformis strain jf-2. In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, vol. 31 of Developments in Petroleum Science, Elsevier Science Ltd., 1991, pp. 219–226.

Littmann, W., 1998. Polymer Flooding, vol. 24. of Developments in Petroleum Science, Elsevier Science, New York.

Liu, H., Zhang, Y., 1995. Rheological property of the xanthan biopolymer flooding systems, J. Univ. Pet., China 19 (4), 41–44.

Liu, J., Pope, G.A., Sepehrnoori, K., 1995. A high-resolution, fully implicit method for enhanced oil recovery simulation. In: Proceedings Volume, 13th SPE Reservoir Simulation Symposium, San Antonio, February 12–15, 1995, pp. 35–50.

Ljosland, E., Bjornstad, T., Dugstad, O., Hundere, I., 1993. Perfluorocarbon tracer studies at the Gullfaks field in the North Sea. J. Pet. Sci. Eng. 10 (1), 27–38.

Lockhart, T.P., Burrafato, G., 1990a. Gellable buffered aqueous composition and its use inenhanced petroleum recovery. EP Patent 390 281, assigned to Eniricerche SPA and Agip SPA, October 03, 1990.

Lockhart, T.P., Burrafato, G., 1990b. Method and composition for reducing the permeability of a high-permeability zone in an oil reservoir. CA Patent 2 013 468, assigned to Eniricerche SPA and Agip SPA, September 30, 1990.

Lockhart, T.P., Burrafato, G., 1990c. Method and composition for reducing the permeability of a high permeability zone in an oil reservoir. EP Patent 390 280, assigned to Eniricerche SPA and Agip SPA, October 03, 1990.

Lorenz, P.B., 1991. The effect of alkaline agents on retention of EOR chemicals, US DOE Rep NIPER-535, NIPER.

Ma, G., 1996. Laboratory study on polymer flooding in oil reservoir with high salinity. Oil Gas Recovery Technol. 3 (2), I, 1–4, 33.

Ma, G., Zuo, K., Xu, Z., 1999. Polymer flooding test in low permeability and high salinity reservoir of maling oilfield. Oil Drilling Prod. Technol. 21 (1), 89–93, 109–110.

Mamleev, R.A., Yulbarisov, E.M., Fakhretdinov, R.N., Zagidullina, L.N., Kulikov, A.N., Kutushev, Z.R., 1997. Composition for pumping into oil stratum – contains specified biopolymer, polydimethyldiallyl ammonium chloride, water and formaldehyde. SU Patent 1 828 161, assigned to Oil Strata Geolog. Phys., January 10, 1997.

Mason, J.A., 1991a. Use of chlorous acid in oil recovery. CA Patent 2 007 218, July 05, 1991.

Mason, J.A., 1991b. Use of chlorous acid in oil recovery. GB Patent 2 239 867, July 17, 1991.

McCormick, C.L., Hester, R.D., 1990. Polymers formobility control in enhanced oil recovery: Final report, US DOE Fossil Energy Rep DOE/BC/10844-20, Southern Mississippi Univ.

McInerney, M.J., Montgomery, A.D., Sublette, K.L., 1991. Microbial control of the production of sulfide. In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, vol. 31 of Developments in Petroleum Science, Elsevier Science Ltd., 1991, pp. 441–449.

Metwally, M., 1990. Effect of gaseous additives on steam processes for lindbergh field, alberta. J. Can. Pet. Technol. 29 (6), 26–30.

Miller, D., Vollmer, A., Feustel, M., Klug, P., 1999. Synergistic mixtures of phosphoric acid esters with carboxylic acid derivatives as dipersants for asphaltenes. EP Patent 0 967 361, assigned to Clariant GmbH, December 29, 1999.

Miller, J.F., Sheely, C.O., Wimberley, J.W., Howard, R.A., 1993. Use of nonradioactive complex metal anion as tracer in subterranean reservoirs. US Patent 5 246 861, assigned to Conoco Inc., September 21, 1993.

Mohanty, S., Khataniar, S., 1995. Sodium orthosilicate: An effective additive for alkaline steamflood. J. Pet. Sci. Eng. 14 (1–2), 45–49.

Momeni, D., Chen, J.R., Yen, T.F., 1988. MEOR (microbial enhanced oil recovery) studies in a radial flow system – the research outlook. In: Proceedings Volume, no. NIPER-351 CONF-870858, US Dep Energy et al Appl of Microorganisms to Petrol. Technol. Symposium, Bartlesville, Okla, August 12–13, 1987, 1988, pp. XVII–1–XVII–7.

Momeni, D., Yen, T.F., Jang, L.K., McDavid, R., Kuo, J.F., Huang, V., et al., 1990. Microbial Enhanced Oil Recovery: Principle and Practice. CRC Press, Inc, Boca Raton, FL.

Monjoie, A., Schroeder, C., 1997. Flooding of oil in chalk (deplacement des hydrocarbures dans la craie). Soc. Geol. Nord. Ann. 5 (4), 325–329.

Moore, C.H., 2001. Computer simulation of formation damage resulting from thermal recovery. In: Proceedings Volume, SPE International Therm Oper. & Heavy Oil Symposium, Margarita Island, Venezuela, March 12–14, 2001.

Moradi-Araghi, A., Stahl, G.A., 1991a. Gelation of acrylamide-containing polymers with furfuryl alcohol and water dispersible aldehydes. EP Patent 447 967, assigned to Phillips Petroleum Co., September 25, 1991.

Moradi-Araghi, A., Stahl, G.A., 1991b. Gelation of acrylamide-containing polymers with hydroxyphenyl alkanols. EP Patent 446 865, assigned to Phillips Petroleum Co., September 18, 1991.

Moritis, G., 1996. EOR survey and analysis. Oil Gas J. 94 (16), 39–42, 44–61.

Moritis, G., 1998. EOR oil production up slightly. Oil Gas J. 96 (16), 49–77.

Moss Jr., J.T., Moss, J.T., 1994. Enhanced oil recovery using hydrogen peroxide injection, US DOE Fossil Energy Rep NIPER/BDM-0086, Tejas Petrol. Engineers In.

Mu, J.H., Li, G.Z., Li, Y., 2001. An experimental study on alkaline/surfactant/polymer flooding systems using natural mixed carboxylate. Chin. J. Chem. Eng. 9 (2), 162–166.

Mu, J.H., Li, G.Z., Liao, G.Z., Huang, L., Zhao, K.S., 2002. Phase behavior and structure analysis of the middle mixed layer for ASP flooding system at low surfactant concentration. Sci. China Ser. B 45 (2), 184–190.

Nashawi, I.S., 1991. Laboratory investigation of the effect of brine composition on polymer solutions: Pt.2: Xanthan gum (XG) case, SPE Unsolicited Pap SPE-23534, United Arab Emirates Univ, August 1991.

Nasr, T.N., Isaacs, E.E., 2001a. Process for enhancing hydrocarbon mobility using a steam additive. US Patent 6 230 814, assigned to Alta Oil Sand Tech. Res. Aut, May 15, 2001.

Nasr, T.N., Isaacs, E.E., 2001b. Process for enhancing hydrocarbon mobility using a steam additive. WO Patent 0 127 439, assigned to Alberta Sci Res. Tech. Auth, April 19, 2001.

Niu, Y., Ouyang, J., Zhu, Z., Wang, G., Sun, G., Shi, J., 2001. Research on hydrophobically associating water-soluble polymer used for EOR. In: Proceedings Volume, SPE Oilfield Chemicals International Symposium, Houston, TX, February 13–16, 2001.

Northrop, P.S., 1993. Method for disposing of waste gas in subterranean formations. US Patent 5 267 614, assigned to Mobil Oil Corp., December 07, 1993.

Northrop, P.S., 1995. Imbibition process using a horizontal well for oil production from low permeability reservoirs. US Patent 5 411 094, assigned to Mobil Oil Corp., May 02, 1995.

Olsen, D.K., 1989. Use of amine oxide surfactants for chemical flooding EOR: Topical report, US DOE Fossil Energy Rep NIPER-417, National Inst. for Petroleum and Energy Research, Bartlesville, OK, November 1989.

Osterloh, W.T., 1994. Long chain alcohol additives for surfactant foaming agents. US Patent 5 333 687, assigned to Texaco Inc., August 02, 1994.

Osterloh, W.T., Jante Jr., M.J., 1992. Surfactant-polymer flooding with anionic po/eo surfactant microemulsions containing polyethylene glycol additives. In: Proceedings Volume, vol. 1, 8th SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, April 22–24, 1992, pp. 485–494.

Osterloh, W.T., Jante, M.J., 1995. Low-cost foam surfactant from wood pulping by-products. In: Proceedings Volume, vol. 2, 8th Eapg Impr. Oil Recovery Europe Symposium, Vienna, Austria, May 15–17, 1995, pp. 191–199.

Pitts, M.J., Wyatt, K., Sale, T.C., Piontek, K.R., 1993. Utilization of chemical-enhanced oil recovery technology to remove hazardous oily waste from alluvium. In: Proceedings Volume, SPE Oilfield Chemicals International Symposium, New Orleans, March 2–5, 1993, pp. 33–44.

Putz, A.G., Pedron, B.M., Bazin, B., 1994. Commercial polymer injection in the Courtenay field, 1994 update. In: Proceedings Volume, Vol. 1, 69th Annual SPE Technical Conference, New Orleans, September 25–28, 1994, pp. 403–413.

Quet, C., Cheneviere, P., Bourrel, M., Glotin, G., 1991. Core surface analysis for wettability assessment. In: Proceedings Volume, Advances in Core Evaluation II: Reservoir Appraisal (2nd Soc. Core Anal et al Europe Core Anal Symposium, (Eurocas II), London, England, May 20–22, 1991), Gordon & Breach Science Publishers, 1991, pp. 119–131.

Quet, C., Cheneviere, P., Glotin, G., Bourrel, M., 1992. Pore surface chemistry and wettability. In: Proceedings Volume, 6th Inst. Francais Du Petrole Explor. & Prod. Res. Conference, Saint-Raphael, France, September 4–6, 1991, 1992, pp. 81–88.

Raible, C., 1992. Improvement in oil recovery using cosolvents with CO_2 gas floods, US DOE Fossil Energy Rep NIPER-559, NIPER, January 1992.

Rame, M., Delshad, M., 1995. A compositional reservoir simulator on distributed memory parallel computers. In: Proceedings Volume, 13th SPE Reservoir Simulation Symposium, San Antonio, February 12–15, 1995, pp. 89–100.

Ramsay, J.A., Cooper, D.G., Neufeld, R.J., 1989. Effects of oil reservoir conditions on the production of water-insoluble levan by bacillus licheniformis. Geomicrobiol. J. 7 (3), 155–165.

Razzaq, A., Castanier, L.M., 1992. Characterization of surfactants in the presence of oil for steam foam application, US DOE Fossil Energy Rep DOE/BC/14600-37, Stanford Univ.

Ren, Z.C., Shi, A.P., Leng, S.L., Zhang, W.S., Qin, L.P., 1998. Formulation of crosslinking polyacrylamide solution for EOR. Oilfield Chem. 15 (2), 146–149.

Rendall, W.A., Ayasse, C., Novosad, J., 1991. Surfactant-stabilized foams for enhanced oil recovery. US Patent 5 074 358, assigned to Alta Oil Sand Tech. Res. Aut, December 24, 1991.

Richardson, W.C., Kibodeaux, K.R., 2001. Chemically assisted thermal flood process. US Patent 6 305 472, assigned to Texaco Inc., October 23, 2001.

Rocha, P.S., Miller, M.A., Sepehrnoori, K., 1997. A succession-of-states front-tracking model for the in-situ combustion recovery process. In Situ 21 (1), 65–100.

Romocki, J., 1994. Application of *N*, *N*-dialkylamides to reduce precipitation of asphalt from crude oil. WO Patent 9 418 430, assigned to Buckman Labs Internat. Inc., August 18, 1994.

Romocki, J., 1995. Application of *N*, *N*-dialkylamides to reduce precipitation of asphalt from crude oil. US Patent 5 388 644, assigned to Buckman Labs Internat. Inc., February 14, 1995.

Ruzin, L.M., Pleshkova, O.E., Konovalova, L.V., 1990. Generation of carbon dioxide during thermal steam treatment of carbonate reservoirs containing high- viscosity oil. Neft Khoz (11), 59–62.

Sandrea, I., Sandrea, R., 2007. Global oil reserves – recovery factors leave vast target for EOR technologies. Oil & Gas J. 105 (41), 44.

Saneie, S., 1992. Alkaline assisted thermal oil recovery: Kinetic and displacement studies, Ph.D. thesis, Southern California Univ.

Saneie, S., Yortsos, Y.C., 1993. Alkaline assisted thermal oil recovery: Kinetic and displacement studies: Topical report, US DOE Rep DOE/BC/14600-45, Southern California Univ, June 1993.

Sanz, C.A., Pope, G.A., 1995. Alcohol-free chemical flooding: From surfactant screening to coreflood design. In: Proceedings Volume, SPE Oilfield Chemicals International Symposium, San Antonio, February 14–17, 1995, pp. 117–128.

Schramm, L.L. (Ed.), 2000. Surfactants: Fundamentals and Applications in the Petroleum Industry. Cambridge University Press, Cambridge.

Schramm, L.L., Ayasse, C., Mannhardt, K., Novosad, J., 1991a. Method for improving enhanced recovery of oil using surfactant-stabilized foams. CA Patent 2 006 482, June 20, 1991.

Schramm, L.L., Ayasse, C., Mannhardt, K., Novosad, J., 1991b. Method for improving enhanced recovery of oil using surfactant-stabilized foams. US Patent 5 060 727, assigned to Alta Oil Sand Tech. Res. Aut, October 29, 1991.

Schramm, L.L., Ayasse, C., Mannhardt, K., Novosad, J., 1991c. Recovery of oil using surfactantstabilized foams. GB Patent 2 239 278, assigned to Alta Oil Sand Tech. Res. Aut, June 26, 1991.

Scovell, E.G., Grainger, N., Cox, T., 2001. Maintenance of oil production and refining equipment. WO Patent 0 174 966, assigned to Imperial Chemical Inds Pl, October 11, 2001.

Sheehy, A.J., 1990. Microbial physiology and enhanced oil recovery. In: Proceedings Volume, 3rd US DOE Microbial Enhancement of Oil Recovery International Conference, Norman, Okla, May 27, 90–6, 1, 1990.

Sheehy, A.J., 1991. Microbial physiology and enhanced oil recovery. In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, vol. 31 of Developments in Petroleum Science, Elsevier Science Ltd., 1991, pp. 37–44.

Shpakoff, P.G., Raney, K.H., 2009. Method and composition for enhanced hydrocarbons recovery. US Patent 7 612 022, assigned to Shell Oil Company, Houston, TX, November 3, 2009.

Shu, P., 1990. Programmed gelation of polymers using melamine resins. US Patent 4 964 461, assigned to Mobil Oil Corp., October 23, 1990.

Shu, P., Ng, R.C., Phelps, C.H., 1993a. In-situ cementation for profile control. US Patent 5 211 231, assigned to Mobil Oil Corp., May 18, 1993.

Shu, P., Phelps, C.H., Ng, R.C., 1993b. In-situ silica cementation for profile control during steam injection. US Patent 5 211 232, assigned to Mobil Oil Corp., May 18, 1993.

Shu, W.R., Shu, P., 1991. Method for steam flooding profile control. CA Patent 2 041 584, November 03, 1991.

Shupe, R.D., Baugh, T.D., 1991. Thermal stability and degradation mechanism of alkylbenzene sulfonates in alkaline media. J. Colloid Interface Sci. 145 (1), 235–254.

Smith, D.H., Comberiati, J.R., 1990. Chemical alteration of the rock surfaces by asphaltenes or surfactants, and its effect on oil recovery by CO_2 flooding. In: Proceedings Volume, Annual Aiche Meeting, Chicago, Ill, November 11–16, 1990.

Snowden, M.J., Vincent, B., Morgan, J.C., 1993. Conformance control in underground reservoirs. GB Patent 2 262 117, assigned to British Petroleum Co. Ltd., June 09, 1993.

Somasundaran, P., 1994. Surfactant loss control in chemical flooding: Spectroscopic and calorimetric study of adsorption and precipitation on reservoir minerals – annual report for the reporting period September 30, 1992 to September 30, 1993, US DOE Fossil Energy Rep DOE/BC/14884-5, Columbia Univ.

Somasundaran, P., 1995. Surfactant loss control in chemical flooding spectroscopic and calorimetric study of adsorption and precipitation on reservoir minerals: Annual report, September 30, 1993–September 30, 1994, US DOE Fossil Energy Rep DOE/BC/14884-12, Columbia Univ.

Sommese, A.G., Nagarajan, R., 1995. Settling stabilization of polymer containing particle dispersions in oil. US Patent 5 438 088, assigned to Nalco Chemical Co., August 01, 1995.

Song, J., 1992. A new flux correcting method for reducing numerical dispersion – application to EOR (enhanced oil recovery) by chemical processes (reduction de la dispersion numerique par correction des flux massiques – application au probleme de la recuperation d'hydrocarbures par procedes chimiques), Ph.D. thesis, Paris VI Univ.

Sorbie, K.S., 1991. Polymer-Improved Oil Recovery, CRC Press, Inc., Boca Raton, FL.

Sorokin, V.A., 1989. Microbiological technology of oil recovery. Neft Khoz (6), 49–50.

Souto, E., Bazin, B., Sardin, M., 1993. Ion exchange between hydrogen and homoionic brines related to permeability reduction. In: Proceedings Volume, SPE Oilfield Chemicals International Symposium, New Orleans, March 2–5, 1993, pp. 491–500.

Sperl, G.T., Sperl, P.L., 1991. Enhanced oil recovery using denitrifying microorganisms. US Patent 5 044 435, assigned to Injectech Inc., September 03, 1991.

Starukhina, L.A., Deriabin, V.V., Titov, V.J., 1991. New biopolymer for EOR Moscow. In: Proceedings Volume, vol. 1, 6th Europe Impr. Oil Recovery Symposium, Stavanger, Norway, May 21–23, 1991, pp. 371–393.

Stegemeier, G.L., Perry, G.E., 1992. Method utilizing spot tracer injection and production induced transport for measurement of residual oil saturation. US Patent 5 168 927, assigned to Shell Oil Co., December 08, 1992.

Stepanova, G.S., Mamedov, Y.G., Babayeva, I.A., Mosina, A.A., Nenartovich, T.L., Li, A.A., 1997. Thin under gas oil rims – new technology for efficient oil production using foam generating oil/water polymers. In: Proceedings Volume, no. 050, 9th EAGE Impr. Oil Recovery Europe Symposium, The Hague, Neth, October 20–22, 1997, Proc.

Stepanova, G.S., Rozenberg, M.D., Boksha, O.A., Gubkina, G.F., Nenartovich, T.L., Safronov, S.V., 1994a. Development of oil field – comprises pumping down well portion of aqueous solution of ammonium carbonate and displacing solution into seam with water, giving increased oil recovery. RU Patent 2 021 495, assigned to Oil Gas Res. Inst., October 15, 1994.

Stepanova, G.S., Rozenberg, M.D., Boksha, O.A., Gubkina, G.F., Nenartovich, T.L., 1994b. Chemical treatment of oil strata – comprises pumping-in ammonium carbonate and nitrate solution followed by aqueous solution of ammonium nitrate-sulphuric acid mixture, and water. RU Patent 2 021 496, assigned to Oil Gas Res. Inst., October 15, 1994.

Strycker, A., 1990. Selection and design of ethoxylated carboxylates for chemical flooding: Topical report, Government Report NIPER-449, US Dept Energy.

Sunde, E., Beeder, J., Nilsen, R.K., Torsvik, T., 1992. Aerobic microbial enhanced oil recovery for offshore use. In: Proceedings Volume, vol. 2, 8th SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, April 22–24, 1992, pp. 497–502.

Surguchev, L.M., Koundin, A., Yannimaras, D., 1999. Air injection – cost effective IOR method to improve oil recovery from depleted and waterflooded fields. In: Proceedings Volume, SPE Asia Pacific Improvement of Oil Recovery Conference (Apiorc 99), Kuala Lumpur, Malaysia, October 25–26, 1999, SPE Number: 57296.

Sydansk, R.D., 1992. Enhanced liquid hydrocarbon recovery process. US Patent 5 129 457, assigned to Marathon Oil Co., July 14, 1992.

Sydansk, R.D., 1995. Hydrocarbon recovery process utilizing a gel prepared from a polymer and a preformed crosslinking agent. US Patent 5 415 229, assigned to Marathon Oil Co., May 16, 1995.

Tang, J.S., Harker, B.C., 1992a. Use of tracers to monitor in situ miscibility of solvent in oil reservoirs during eor. CA Patent 1 310 140, assigned to Esso Resources Canada Ltd., November 10, 1992.

Tang, J.S., Harker, B.C., 1992b. Use of tracers to monitor in situ miscibility of solvent in oil reservoirs during eor. US Patent 5 111 882, assigned to Exxon Production Res. Co., May 12, 1992.

Taugbol, K., Zhou, H.H., Austad, T., 1994. Low tension polymer flood. the influence of surfactant-polymer interaction. In: Proceedings Volume, Recent Advances in Oilfield Chemistry, 5th Royal Soc. Chemicals International Symposium, Ambleside, England, April 13–15, 1994, pp. 281–294.

Taylor, K.C., Nasr-El-Din, H.A., 1999. A systematic study of iron control chemicals: Pt 2. In: Proceedings Volume, SPE Oilfield Chemicals International Symposium, Houston, February 16–19, 1999, pp. 649–656.

Taylor, K.C., Nasr-El-Din, H.A., Al-Alawi, M.J., 1998. A systematic study of iron control chemicals used during well stimulation. In: Proceedings Volume, SPE Formation Damage Contr. International Symposium, Lafayette, LA, February 18–19, 1998, pp. 19–25.

Thibodeau, L., Sakanoko, M., Neale, G.H., 2003. Alkaline flooding processes in porous media in the presence of connate water. Powder Technol. 132 (2–3), 101–111.

Thomas, S., Ali, S.M.F., 1999. Status and assessment of chemical oil recovery methods. Energy Sources 21 (1–2), 177–189.

Thomas, S., Ali, S.M.F., 2001. Micellar flooding and ASP-chemical methods for enhanced oil recovery. J. Can. Pet. Technol. 40 (2), 46–52.

Thomas, S., Ali, S.M.F., Thomas, N.H., 2000. Scale-up methods for micellar flooding and their verification. J. Can. Pet. Technol. 39 (2), 18–27.

Thomas, S., Farouq, A.S.M., 1999. Status and assessment of chemical oil recovery methods. Energy Sources 21 (1–2) 177–189.

Thompson Sr., J.E., Brannon, H.D., Woo, G.T.-C., Wood, W.R., Dawson, J.C., Ault, M.G., 2001. Surfactant compositions and uses therefor. US Patent 6 302 209, assigned to BJ Services Company, Houston, TX, October 16, 2001.

Tulbovich, B.I., Kazakova, L.V., Kozhevskikh, V.I., 1996. Foam-forming composition – contains surfactant, in form of alkali effluent from caprolactam production, and solvent, in form of e.g. stratal water. RU Patent 2 061 859, assigned to Perm Oil Ind. Res. Des. Inst., June 10, 1996.

Vadie, A., 2002. Microbial enhanced oil recovery, [electronic] http://www.msstate.edu/dept/wrri/meor/.

Vaidya, R.N., Fogler, H.S., 1990. Formation damage due to colloidally induced fines migration. Colloids Surf. 50, 215–229.

Varadaraj, R., 1997. Polymer-surfactant fluids for decontamination of earth formations. US Patent 5 614 474, assigned to Exxon Research & Eng. Co., March 25, 1997.

Varadaraj, R., 2008. Mineral acid enhanced thermal treatment for viscosity reduction of oils (ecb-0002). US Patent 7 419 939, assigned to ExxonMobil Upstream Research Company, Houston, TX, September 2, 2008.

Verderevskij, Y.L., Valeeva, T.G., Khabirov, R.A., Gusev, V.I., Arefev, Y.N., Golovko, S.N., et al., 1996. Development of oil-bearing strata – comprises pumping in spent sulphuric acid, preceded by additional aqueous lignosulphonate(s) to increase efficiency. SU Patent 1 448 783, assigned to Oil Ind. Chem. Process Asso and Perm Paper Res. Inst., November 20, 1996.

Wang, D., 1999. A foam drive method. WO Patent 9 951 854, assigned to Daqing Petroleum Admin. Bu, October 14, 1999.

Wang, Y., Li, J., Zhao, F., 2001a. Surfactants oil displacement system in high salinity formations. In: Proceedings Volume, SPE Asia Pacific Oil and Gas Conference and Exhibition, Jakarta, Indonesia, April 17–19, 2001.

Wang, Y., Wang, L., Li, J., Zhao, F., 2001b. Surfactants oil displacement system in high salinity formations: Research and application. In: Proceedings Volume, SPE Permian Basin Oil and Gas Recovery Conference, Midland, Texas, May 15–16, 2001.

Wason, D.T., 1990. Enhanced oil recovery through in-situ generated surfactants augmented by chemical injection, US DOE Rep DOE/BC/10847-20, Inst Gas Technol, Chicago, August 1990.

Westlake, D.W.S., 1991. Microbial ecology of corrosion and reservoir souring. In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, vol. 31 of Developments in Petroleum Science, Elsevier Science Ltd., pp. 257–263.

Wyganowski, M.W., 1991. Method of reducing the reactivity of steam and condensate mixtures in enhanced oil recovery. US Patent 5 036 915, assigned to Alberta Energy Co. Ltd., Amoco Canada Petroleum Co., and Diminex Ltd., Canada, August 06, 1991.

Yamazaki, T., Aso, K., Okabe, H., Akita, Y., 2000. Automatic continuous-measuring system of interfacial tension by spinning drop technique. In: Proceedings Volume, SPE Asia Pacific Conference, Yokohama, Japan, April 25–26, 2000.

Yen, T.F., Park, J.K., Lee, K.I., Li, Y., 1991. Fate of surfactant vesicles surviving from thermophilic, halotolerant, spore forming, clostridium thermohydrosulfuricum. In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, vol. 31 of Developments in Petroleum Science, Elsevier Science Ltd., pp. 297–309.

Zaitoun, A., Fonseca, C., Berger, P., Bazin, B., Monin, N., 2003. New surfactant for chemical flood in high-salinity reservoir. In: Proceedings Volume, SPE International Symposium on Oilfield Chemistry, Houston, Texas, February 5–7, 2003.

Zekri, A.Y., 2001. Microbial enhanced oil recovery – a short review. Oil Gas Europe Mag. 27 (1), 22–25.

Zhang, S.B., Qiao, W.H., Li, Z.S., Cheng, L.B., Hu, J.Z., 2003. 1-Phenylalkane sulfonates for studying interfacial tensions. Pet. Sci. Technol. 21 (7–8), 1043–1054.

Zhou, Z., 2000. Process for reducing permeability in a subterranean formation. US Patent 6 143 699, assigned to Alta Oil Sand Tech. Res. Auth, November 07, 2000.

Zhu, T., Strycker, A., Raible, C.J., Vineyard, K., 1998. Foams for mobility control and improved sweep efficiency in gas flooding. In: Proceedings Volume, vol. 2, 11th SPE/DOE Improvement of Oil Recovery Symposium, Tulsa, April 19–22, 1998, pp. 277–286.

Zobell, C.E., 1937. Bacterial action in seawater. Proc. Soc. Exp. Biol. Med. (34), 113–116.

Zobell, C.E., Johnson, F.H., 1979. The influence of hydrostatic pressure on the growth and viability of terestrial and marine bacteria. J. Bacteriol. Bioeng. (57), 1979.

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Chapter 17

Fracturing Fluids

Hydraulic fracturing is a technique used to stimulate the productivity of a well. A hydraulic fracture is a superimposed structure that remains undisturbed outside the fracture, so the effective permeability of a reservoir remains unchanged by this process. The increased wellbore radius increases its productivity, because a large contact surface between the well and the reservoir is created.

STRESSES AND FRACTURES

Hydraulic fracturing is one of the newer techniques in petroleum sciences, not being used for more than approximately 50 years. The classic treatment (Hubbert and Willis, 1957) of hydraulic fracturing states that the fractures are approximately perpendicular to the axis of the least stress. For most deep reservoirs, the minimal stresses are horizontal, hence vertical stresses will occur in fracturing.

The actual stress can be calculated by balancing the (vertical) geostatic stress and the horizontal stress by the common tools of the theory of elasticity. For example, the geostatic stress must be corrected in a porous medium filled with a liquid having a poroelastic constant and hydrostatic pressure. The horizontal stress can be calculated from the corrected vertical stress by using the *Poisson's ratio*. Under some circumstances, in particular in shallow reservoirs, horizontal stresses can be created, as well as vertical stresses. The possible stress modes are summarized in Table17.1.

Knowledge of the stresses in a reservoir is essential to find the pressure at which initiation of a fracture can take place. The upper bound of this pressure can be estimated using a formula given by Terzaghi (von Terzaghi, 1923), which states that:

$$p_b = 3s_{H,min} - s_{H,max} + T - p \tag{17.1}$$

The closure pressure indicates the pressure at which the width of the fracture becomes zero. This is normally the minimal horizontal stress.

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TABLE 17.1 Modes of Stresses in Fractures

p_b	Fracture Initialization Pressure
$3s_{H,min}$	Minimal horizontal stress
$s_{H,max}$	Maximal horizontal stress (= minimal horizontal stress + tectonic stress)
T	Tensile strength of rock material
p	Pore pressure

The pressure response during fracturing provides important information about the success of the operation. The fluid efficiency can be estimated from the closure time.

COMPARISON OF STIMULATION TECHNIQUES

In addition to hydraulic fracturing, there are other stimulation techniques, such as acid fracturing or matrix stimulation, and hydraulic fracturing is also used in coal seams to stimulate the flow of methane.

Fracturing fluids are often divided into water-based, oil-based, alcohol-based, emulsion, or foam-based fluids. Several reviews are available in the literature dealing with the basic principles of hydraulic fracturing, and the guidelines that are used to select a formulation for a specific job (Ebinger and Hunt, 1989; Ely, 1989; Lemanczyk, 1991).

Polymer hydration, crosslinking, and degradation are the key processes that these materials undergo. Technological improvements over the years have focused primarily on improved rheological performance, thermal stability, and clean-up of crosslinked gels.

Action of a Fracturing Fluid

Fracturing fluids must meet a number of conditions simultaneously. They must be stable at high temperatures, high pumping rates, and shear rates, which can cause the fluids to degrade and prematurely settle out the proppant before the fracturing operation is complete.

Most commercially used fracturing fluids are aqueous liquids that have been either gelled or foamed. Typically, the fluids are gelled by a polymeric gelling agent. The thickened or gelled fluid helps keep the proppants within the fluid during the fracturing operation. Fracturing fluids are injected into a subterranean formation for the following purposes (Kelly et al., 2007):

- To create a conductive path from the wellbore extending into the formation and
- To carry proppant material into the fracture to create a conductive path for produced fluids.

Stages in a Fracturing Job

A fracturing job has several stages, including injecting a prepad, a pad, a proppant containing fracturing fluid, and finally, a treatment with flush fluids. A prepad is a low viscosity fluid used to condition the formation, which may contain fluid loss additives, surfactants, and have a defined salinity to prevent formation damage. The generation of the fractures takes place by injecting the pad, a viscous fluid, but without proppants.

After the fractures develop, a proppant must be injected to keep them permeable. When the fracture closes, the proppant left there creates a large flow area and a highly conductive pathway for hydrocarbons to flow into the wellbore. Thus, the proppant is utilized to maintain an open fracture. Viscous fluids are utilized to transport, suspend, and eventually allow the proppant to be trapped inside the fracture. These fluids typically exhibit a power law behavior for the range of shear rates encountered in hydraulic fracturing treatments.

A uniform proppant distribution is needed in order to get a uniformly conductive fracture along the wellbore height and fracture half-length, but the complicated nature of proppant settling in non-Newtonian fluids often leads to a higher concentration of proppant in the lower part of the fracture. This often leads to a lack of adequate proppant coverage of the upper portion of the fracture and the wellbore. Clustering of proppant, encapsulation, bridging, and embedment are all phenomena that lower the potential conductivity of the proppant pack (Watters et al., 2010).

The job ends eventually with a clean-up stage, in which flush fluids and other clean-up agents are applied. The actual detailed time schedule depends on the particular system used.

After the completion the fluid viscosity should decrease to allow the placement of the proppant and a rapid fluid return through the fracture. It is important to control the time at which the viscosity break occurs. In addition, the degraded polymer should produce little residue to restrict the flow of fluids through the fracture.

TYPES OF HYDRAULIC FRACTURING FLUIDS

Generally, a hydraulic fracturing treatment involves pumping a proppant-free viscous fluid, or pad, which is usually water with some fluid additives, in order to generate high viscosity, into a well faster than the fluid can escape into the formation. This causes the pressure to rise and the rock to break, creating artificial fractures or enlarging existing ones.

After fracturing the formation, a propping agent such as sand is added to the fluid. This forms a slurry that is pumped into the newly formed fractures in the formation to prevent them from closing when the pumping pressure is released. The proppant transportability of a base fluid depends on the type of viscosifying additives that have been added to the water base (Lukocs et al., 2007).

Since the late 1950s, more than half of fracturing treatments have been conducted with fluids comprising guar gums, or guar derivatives such as hydropropyl guar (HPG), hydroxypropyl cellulose (HPC), carboxymethyl guar, and carboxymethyl hydropropyl guar.

Crosslinking agents based on boron, titanium, zirconium, or aluminum complexes are typically used to increase the effective molecular weight of the polymers and make them better suited for use in high-temperature wells.

Cellulose derivatives, such as hydroxyethyl cellulose (HEC) or HPC and carboxymethylhydroxyethyl cellulose are also used, with or without crosslinkers. Xanthan and scleroglucan have also been shown to have excellent proppant-suspension ability, but they are more expensive than guar derivatives and therefore used less frequently.

Polyacrylamide (PAM) and polyacrylate polymers and copolymers are typically used for high-temperature applications or as friction reducers at low concentrations for all temperatures ranges (Lukocs et al., 2007).

Polymer-free, water-based fracturing fluids can be obtained by using viscoelastic surfactants (VES). These fluids are normally prepared by mixing appropriate amounts of suitable surfactants such as anionic, cationic, non-ionic, and zwitterionic surfactants. Their viscosity is attributed to the three-dimensional structure formed by the components in the fluids. The viscosity increases when the surfactant concentration exceeds a critical concentration. Then the surfactant molecules aggregate into micelles, which can interact to form a network that exhibits viscous and elastic behavior.

Cationic VESs – typically consisting of long chain quaternary ammonium salts such as cetyltrimethylammonium bromide (CTAB) – have so far been the type attracting most commercial interest. Other common reagents that generate viscoelasticity in surfactant solutions include salts, such as ammonium chloride, potassium chloride, sodium chloride, sodium salicylate, and sodium isocyanate, and also non-ionic organic molecules such as chloroform. The electrolyte content of surfactant solutions is also important for controlling their viscoelastic behavior (Lukocs et al., 2007).

Fluids showing this type of cationic VESs tend to lose their viscosity at high brine concentrations, hence they have seen limited use as gravel-packing or drilling fluids. Anionic VESs are also used.

Amphoteric/zwitterionic surfactants (Allan et al., 2008) and an organic acid, salt, or an inorganic salt can also impart viscoelastic properties. The surfactants could be, for dihydroxyl alkyl glycinate, alkyl ampho acetate or VESs propionate, alkyl betaine, alkyl amidopropyl betaine, and alkylamino mono- or dipropionates derived from certain waxes, fats, and oils. They are used in conjunction with an inorganic water-soluble salt or organic additives such as phthalic acid, salicylic acid, or their salts.

Amphoteric/zwitterionic surfactants, in particular those comprising a betaine moiety, are useful for temperatures up to about 150°C and are therefore of particular interest for medium to high temperature wells. Betaine is shown in Figure 17.1. However, like the cationic VES mentioned above, anionic surfactants are usually not compatible with high brine concentrations.

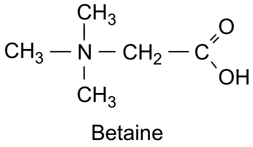


FIGURE 17.1 Betaine.

Proppants can be sand, intermediate strength ceramic proppants, or sintered bauxites, which can be coated with a resin to improve their clustering ability. They can be coated with resin or a proppant flowback control agent such as fibers. By selecting proppants having a contrast a property such as density, size, or concentration, different settling rates will be achieved.

Waterfrac treatments combine low-cost, low-viscosity fluids to stimulate very low permeability reservoirs. The treatments rely on the mechanisms of asperity creation (rock spalling), shear displacement of rock, and localized high concentration of proppant to create adequate conductivity, with the last mechanism being mostly responsible for the success of the treatment. The mechanism can be described as analogous to a wedge splitting wood.

A viscous well treatment fluid is generally composed of a polysaccharide or synthetic polymer in an aqueous solution, which is crosslinked by an organometallic compound. Examples of well treatments in which metal crosslinked polymers are used are hydraulic fracturing, gravel packing operations, water blocking, and other well completion operations.

In order for the treatment to be successful, the fluid viscosity should eventually diminish to levels approaching that of water after the proppant is placed. This allows a portion of the treating fluid to be recovered without producing excessive amounts of proppant after the well is opened and returned to production. If the viscosity of the fluid is low, it will flow naturally from the formation under the influence of formation fluids. This viscosity reduction or conversion is referred to as breaking, and is accomplished by incorporating chemical agents, referred to as breakers, into the initial gel.

Some fracturing fluids, such as those based upon guar polymers, break naturally without the intervention of a breaking agent, but their breaking time is generally somewhere in the range from greater than 24 hours, to weeks, months, or years depending on the conditions in the reservoir.

To decrease this break time, chemical agents are usually incorporated into the gel. These are typically either oxidants or enzymes that degrade the polymeric gel structure. Oxidizing agents, such as persulfate salts, chromous salts, organic peroxides or alkaline earth or zinc peroxide salts, or enzymes are the most effective.

The timing of the break is also of great importance. Gels that break prematurely can cause suspended proppant material to settle out. They penetrate before a sufficient distance into the produced fracture. Premature breaking can also lead to a premature reduction in the fluid viscosity, resulting in an inadequate fracture width. On the other hand, gelled fluids that break too slowly can cause slow recovery of the fracturing fluid, with attendant delay in resuming production.

Additional problems may occur, such as the tendency of proppant to become dislodged from the fracture, resulting in at least partial closing and decreased efficiency of the fracturing operation. The fracturing gel should preferably, begin to break when the pumping operations are finished, and be completely broken within about 24 hours after completion of the treatment.

Fracturing fluid compositions comprise a solvent, a polymer-soluble or hydratable in the solvent, a crosslinking agent, an inorganic breaking agent, an optional ester compound, and a choline carboxylate. The solvent may be an aqueous potassium chloride solution, and the inorganic breaking agent may be a metal-based oxidizing agent, such as an alkaline earth metal or a transition metal, or it may be magnesium, calcium, or zinc peroxide. The ester compound may be an ester of a polycarboxylic acid, such as an ester of oxalate, citrate, or ethylene diamine tetraacetate. Those having hydroxyl groups can also be acetylated, for instance, citric acid can be acetylated to form acetyl triethyl citrate, which is a preferred ester.

The hydratable polymer can be a water-soluble polysaccharide, such as galactomannan or cellulose, and the crosslinking agent may be a borate, titanate, or zirconium-containing compound, such as $Na_3BO_3 \times n H_2O$.

A general review of commercially available additives for fracturing fluids is given in the literature (Anonymous, 1999). Possible components in a fracturing fluid are listed in Table 17.2, which indicates the complexity of a fracturing fluid formulation. Some additives may not be used together, such as oil-gelling additives in a water-based system. More than 90% of the fluids are based on water. Aqueous fluids are economical and can provide control of a broad range of physical properties if used with additives. Additives for fracturing fluids serve two purposes (Harris, 1988):

1. They enhance fracture creation and proppant-carrying capability and
2. They minimize formation damage.

Viscosifiers, such as polymers and crosslinking agents, temperature stabilizers, pH control agents, and fluid loss control materials assist the creation of a fracture. Formation damage is reduced by gel breakers, biocides, surfactants, clay stabilizers, and gases. Table 17.3 summarizes the various types of fluids and techniques used in hydraulic fracturing.

Comparison of Different Techniques

The optimal technique to be used depends on the type of reservoir. Reports that compare the techniques in a related environment are available. In the Kansas

TABLE 17.2 Components in Fracturing Fluids

Component/Category	Function/Remark
Water-based polymers	Thickener, to transport proppant, reduces leak-off in formation
Friction reducers	Reduce drag in tubing
Fluid loss additives	Form filter cake, reduce leak-off in formation if thickener is not sufficient
Breakers	Degrade thickener after job or disable crosslinker (wide variety of different chemical mechanisms)
Emulsifiers	For diesel premixed gels
Clay stabilizers	For clay-bearing formations
Surfactants	Prevent water-wetting of formation
Nonemulsifiers	
pH-Control additives	Increase the stability of fluid (e.g., for elevated temperature applications)
Crosslinkers	Increase the viscosity of the thickener
Foamers	For foam-based fracturing fluids
Gel stabilizers	Keep gels active longer
Defoamers	
Oil-gelling additives	Same as crosslinkers for oil-based fracturing fluids
Biocides	Prevent microbial degradation
Water-based gel systems	Common
Crosslinked gel systems	Increase viscosity
Alcohol-water systems	
Oil-based systems	Used in water sensitive formation
Polymer plugs	Used also for other operations
Gel concentrates	Premixed gel on diesel base
Resin coated proppants	Proppant material
Ceramics	Proppant material

Hugoton field (Mesa Limited Partnership), several hydraulic fracturing methods were tested (Cottrell et al., 1988).

A method in which a complexed gelled water fracture was applied was the most successful when compared with a foam technique and with older and

TABLE 17.3 Various Types of Hydraulic Fracturing Fluids

Type	Remarks
Water-based fluids	Predominant
Oil-based fluids	Water sensitive; increased fire hazard
Alcohol-based fluids	Rarely used
Emulsion fluids	High pressure, low temperature
Foam-based fluids	Low pressure, low temperature
Noncomplex gelled water fracture	Simple technology
Nitrogen-foam fracture	Rapid clean-up
Complexed gelled water fracture	Often the best solution
Premixed gel concentrates	Improve process logistics
In situ precipitation technique	Reduces scale-forming ingredients Hrachovy (1994)

simpler techniques. The study covers some 56 wells where such techniques were applied.

Expert Systems for Assessment

A PC-based, interactive computer model has been developed to help engineers choose the best fluid and additives and the most suitable propping agent for a given set of reservoir properties (Holditch et al., 1993; Xiong et al., 1996). The model also optimizes treatment volume, based on reservoir performance and economics. To select the fluids, additives, and propping agents, the expert system surveys stimulation experts from different companies, reviews the literature, and then incorporates the knowledge so gained into rules, using an expert system shell.

In addition, the fluid leak-off during hydraulic fracturing can be modeled, calculated, and measured experimentally. Procedures for converting laboratory data to an estimate of the leak-off under field conditions have been given in the literature (Penny and Conway, 1989).

WATER-BASED SYSTEMS

Thickeners and Gelling Agents

A gelling agent is also known as a viscosifying agent, and refers to a material that can make the fracturing fluid into a gel, thereby increasing its viscosity (Welton et al., 2010).

TABLE 17.4 Summary of Thickeners Suitable for Fracturing Fluids

Thickener	References
Hydroxypropyl guar[a]	
Galactomannans[b]	Mondshine (1987)
HEC-modified vinylphosphonic acid	Holtmyer and Hunt (1992)
Carboxymethyl cellulose	
Polymer from *N*-vinyl lactam monomers, vinylsulfonates[c]	Bharat (1990)
Reticulated bacterial cellulose[d]	Westland et al. (1993)
Bacterial xanthan[e]	Hodge (1997)

a) General purpose eightfold power of thickening in comparison to starch
b) Increased temperature stability, used with boron-based crosslinkers
c) High-temperature stability
d) Superior fluid performance
e) Imparts high viscosity

Suitable gelling agents include guar gum, xanthan gum, welan gum, locust bean gum, gum ghatti, gum karaya, tamarind gum, and tragacanth gum. Guar gum can be functionalized to hydroxyethyl guar, hydroxypropyl guar, or carboxymethyl guar. Examples of water-soluble cellulose ethers include methyl cellulose, carboxymethyl cellulose (CMC), HEC, and hydroxyethyl carboxymethyl cellulose (Welton et al., 2010).

Artificial polymers, such as copolymers from acrylamide, methacrylamide, acrylic acid (AA), or methacrylic acid, or those from 2-acrylamido-2-methyl-1-propane sulfonic acid (AMPS) derivates and *N*-vinylpyridine have all been used (Welton et al., 2010), but also naturally occurring polysaccharides and their derivatives (Lemanczyk, 1992). They can increase the viscosity of the fluid when used in comparatively small amounts. Table 17.4 summarizes suitable polymers.

Guar is shown in Figure 17.2. In hydroxypropyl guar, some of the hydroxyl groups are etherified with oxopropyl units. Compositions for gelling a hydrocarbon fracturing fluid are basically different from those for aqueous fluids. A possible formulation consists of a gelling agent, a phosphate ester, a crosslinking agent, a multivalent metal ion, and a catalyst, a fatty quaternized amine (Lawrence and Warrender, 2010).

Guar

Guar is a branched polysaccharide from the guar plant *Cyamopsis tetragonolobus*, which originated in India, and is now found in the southern United States. It has a molar mass of approximately 220 kDalton, and it consists of mannose in the main chain and galactose in the side chain. The ratio of mannose to galactose is 2:1.

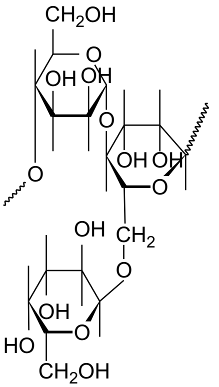


FIGURE 17.2 Structural unit of guar.

Polysaccharides having this structure are referred to as *heteromannans*, and in particular as *galactomannans*. Derivatives of guar are therefore sometimes called *galactomannans*.

Guar-based gelling agents, typically hydroxypropyl guar, are widely used to viscosify fracturing fluids because of their desirable rheological properties, economics, and ease of hydration. Nonacetylated xanthan is a variant of xanthan gum, which interacts synergistically with guar to give superior viscosity and particle transport at lower polymer concentrations.

Static leak-off experiments with borate crosslinked and zirconate-crosslinked hydroxypropyl guar fluids showed practically the same leak-off coefficients (Zeilinger et al., 1991). An investigation of their stress-sensitive properties showed that zirconate filter cakes have viscoelastic properties, but borate filter cakes are merely elastic. Non-crosslinked fluids show no filter cake-type behavior for a large range of core permeabilities, but rather, a viscous flow that is dependent on characteristics of the porous medium.

The addition of glycols, such as ethylene glycol (EG), to aqueous fluids gelled with guar gum can increase the viscosity of the fluid and stabilize the fluid brines. Such fluids are more stable at high temperatures from 27–177°C (80–350°F). The formation damage is minimized after hydraulic fracturing operations, as less of the guar polymer can be used, but the same viscosity is achieved by the addition of a glycol (Kelly et al., 2007).

The crosslinker can be a borate, a titanate, or a zirconate. The stability of the gel is improved by the addition of sodium thiosulfate. The development of the viscosity at 93°C (200°F) of brine fluids with $2.4\,\mathrm{kg\,m^{-3}}$ guar and 5% KCl, with varying amounts of EG, is shown in Figure 17.3.

By using the sodium derivative of ethylene diamine tetraacetic acid (EDTA) as gel breaker in these compositions with EG, the decay of viscosity with time can be adjusted accordingly (Kelly et al., 2007).

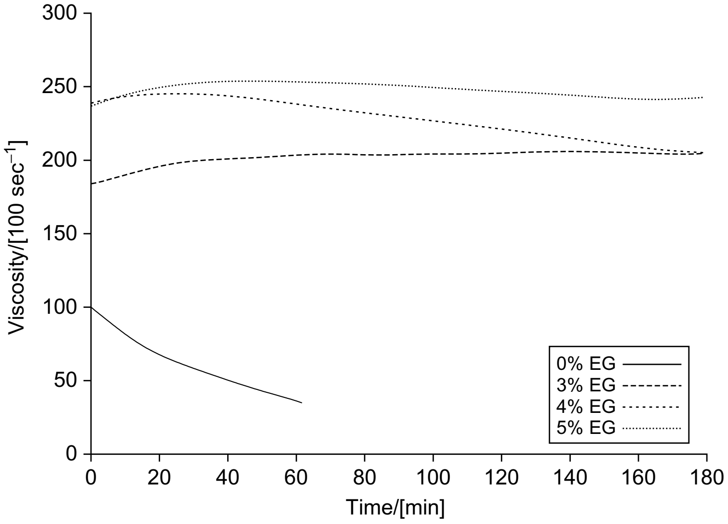


FIGURE 17.3 Viscosity of guar brines with varying amounts of ethylene glycol (EG) (Kelly et al., 2007).

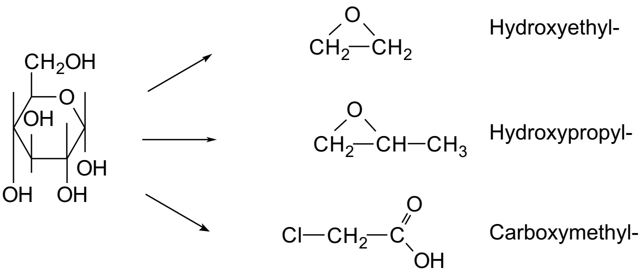
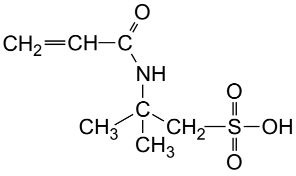


FIGURE 17.4 Modification of polyhydroxy compounds.

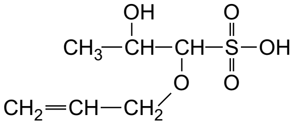
Anionic galactomannans, which are derived from guar gum by partially esterifying hydroxyl groups with sulfonate groups that result from AMPS and 1-allyloxy-2-hydroxypropyl sulfonic acid (Yeh, 1995), have been claimed to be suitable as thickeners. The composition is capable of producing enhanced viscosities, when used alone, or in combination with a cationic polymer and distributed in a solvent.

Polyhydroxy compounds can be modified by various reactions. Etherification, exemplified with dextrose as the model compound, is shown in Figure 17.4. Vinyl compounds used for the modification of guar are shown in Figure 17.5.

The temperature stability of fracturing fluids containing galactomannan polymers is increased by adding a sparingly soluble borate with a slow solubility

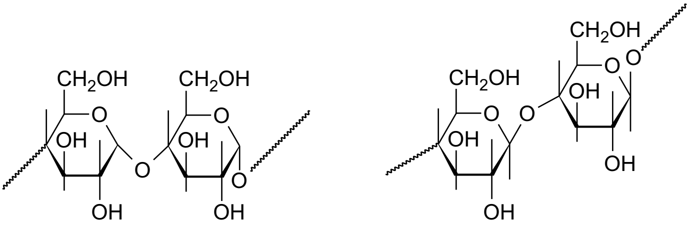


2-Acrylamido-2-methylpropane sulfonic acid



1-Allyloxy-2-hydroxypropyl sulfonic acid

FIGURE 17.5 Vinyl modifiers for guar gum.



Amylose

Cellulose

FIGURE 17.6 Amylose and cellulose.

rate. This provides a source of boron for solubilizing at elevated temperatures, thus enhancing the crosslinking of the galactomannan polymer.

Hydroxyethyl Cellulose

HEC can be chemically modified by reaction with vinylphosphonic acid in the presence of the reaction product of hydrogen peroxide and a ferrous salt. The HEC forms a graft copolymer with the vinylphosphonic acid.

Amylose and cellulose are shown in Figure 17.6. Amylose is a linear polymer of glucose, and is water-soluble. The difference between amylose and cellulose is the way in which the glucose units are linked; amylose has α-linkages whereas cellulose contains, β-linkages. Because of this difference, amylose is soluble in water and cellulose is not. Chemical modification allows cellulose to become water-soluble.

Modified HEC has been proposed as a thickener for hydraulic fracturing fluids (Holtmyer and Hunt, 1992). Polyvalent metal cations may be employed to crosslink the polymer molecules to further increase the viscosity of the aqueous fluid.

Biotechnological Products

Gellan Gum and Wellan Gum

Gellan gum is the generic name for an extracellular polysaccharide produced by the bacterium *Pseudomonas elodea*. It is a linear anionic polysaccharide with a molecular mass of 500 kDalton, consisting of 1,3-β-*D*-glucose, 1,4-β-*D*-glucuronic acid, 1,4-β-*D*-glucose, and 1,4-α-*L*-rhamnose.

Wellan gum is produced by aerobic fermentation. The backbone of wellan gum is identical to gellan gum, but it has a side chain of *L*-mannose or *L*-rhamnose. It is used in fluid loss additives and is extremely compatible with calcium ions in alkaline solutions.

Reticulated Bacterial Cellulose

A cellulose produced from bacteria, with an intertwined reticulated structure, has unique properties and functionalities unlike conventional cellulose. It improves fluid rheology and particle suspension over a wide range of conditions in aqueous systems (Westland et al., 1993).

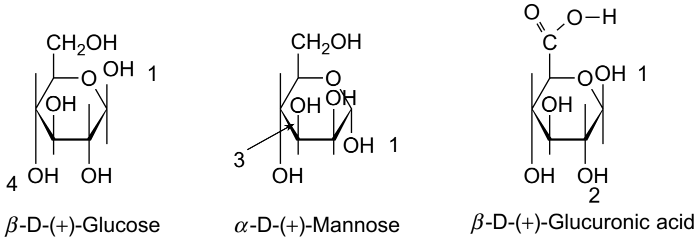
Xanthan Gum

Xanthan gum is produced by the bacterium *Xanthomonas campestris*, and has been used commercially since 1964. Xanthans are water-soluble polysaccharide polymers with the repeating units (Doherty et al., 1992) shown in Table 17.5 and Figure 17.7.

The *D*-glucose moieties are linked in a β-(1,4) configuration, and the inner *D*-mannose moieties are linked in an α-(1,3) configuration, generally alternating

TABLE 17.5 Variant Xanthan Gums

Number	Repeating Units	Ratio
Pentamer	*D*-glucose: *D*-mannose: *D*-glucuronic acid	2:2:1
Tetramer	*D*-glucose: *D*-mannose: *D*-glucuronic acid	2:1:1



β-D-(+)-Glucose α-D-(+)-Mannose β-D-(+)-Glucuronic acid

FIGURE 17.7 Carbohydrates and derivates.

with glucose moieties. The *D*-glucuronic acid moieties are linked in a β-(1,2) configuration to the inner mannose moieties. The outer mannose moieties are linked to the glucuronic acid moieties in a β-(1,4) configuration.

Xanthan gum is used in oil field applications in the form of a fermentation broth containing 8–15% of the polymer. The viscosity is less dependent on the temperature than for other polysaccharides.

Viscoelastic Formulations

VES fluids have the following advantages over conventional polymer formulations (Li et al., 2010):

- Higher permeability in the oil-bearing zone,
- Lower formation or subterranean damage,
- Higher viscosifier recovery after fracturing,
- No need for enzymes or oxidizers to break down viscosity, and
- Easier hydration and faster build up to optimum viscosity.

Disadvantages and drawbacks of VES fluids are their high costs, their low tolerance to salts, and stability against high temperatures as found in deep well applications. However there are recent formulations that overcome these difficulties, at least to some extent.

The components of a viscoelastic fluid are a zwitterionic surfactant, erucyl amidopropyl betaine, an anionic polymer, or *N*-erucyl-*N*,*N*-bis-(2-hydroxyethyl)-*N*-methyl ammonium chloride, poly(napthalene sulfonate), and cationic surfactants, methyl poly(oxyethylene) octadecanammonium chloride, and poly(oxyethylene) cocoalkylamines (Couillet and Hughes, 2008; Li et al., 2010). The corresponding fluids exhibit a good viscosity performance.

Typical VESs are *N*-erucyl-*N*,*N*-bis(2-hydroxyethyl)-*N*-methyl ammonium chloride and potassium oleate, solutions of which form gels when mixed with corresponding activators such as sodium salicylate and potassium chloride (Jones and Tustin, 2010).

The cationic surfactant should be soluble in both organic and inorganic solvents. Solubility in hydrocarbon solvents is promoted by attaching multiple long chain alkyl groups to the active surfactant unit (Jones and Tustin, 2010). Examples are hexadecyltributylphosphonium and trioctylmethylammonium ions. In contrast, cationic surfactants have a single, long, linear hydrocarbon moiety attached to the surfactant group.

Obviously, there is a conflict between the structural requirements for achieving solubility in hydrocarbons and for the formation of viscoelastic solutions. As a compromise, surfactant compounds that are suitable for reversibly thickening water-based wellbore fluids and also soluble in both organic and aqueous fluids have been designed.

Tallow amido propylamine oxide (McElfresh and Williams, 2007) is a suitable, non-ionic surfactant gelling agent. Non-ionic fluids are inherently less damaging to the producing formations than cationic fluid types, and are more efficacious than anionic gelling agents.

The synthesis of branched oleates have been described. 2-methyl oleic acid methyl ester, or 2-methyl oleate, can be prepared from methyl oleate and methyl iodide in presence of a pyrimidine-based catalyst (Jones and Tustin, 2010). The methyl ester is then hydrolyzed to obtain 2-methyl oleic acid.

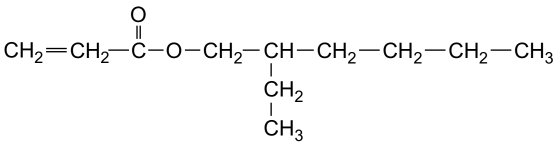
It is sometimes believed that contact with a VES-gelled fluid instantaneously reduces the viscosity of the gel, but it has been discovered that mineral oil can be used as an internal breaker for VES-gelled fluid systems (Crews et al., 2010). The rate of viscosity breaking at a given temperature is influenced by the type and amount of salts present. In the case of low molecular weight mineral oils, it is important to add them after the VES component is added to the aqueous fluid.

By using combinations of internal breakers, both the initial and final break of the VES fluid may be customized. Fatty acid compounds or bacteria may be used in addition to mineral oil (Crews, 2006; Crews et al., 2010).

Miscellaneous Polymers

A copolymer of 2-ethylhexyl acrylate and AA is not soluble in water or in hydrocarbons. The ester units are hydrophobic and the acid units are hydrophilic. An aqueous suspension with a particle size smaller than 10 μ can be useful in preparing aqueous hydraulic fracturing fluids (Harms and Norman, 1988). 2-Ethylhexyl acrylate is shown in Figure 17.8.

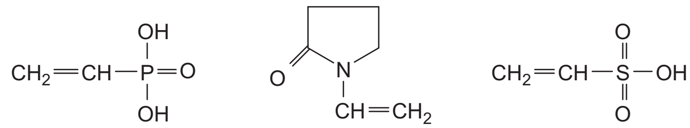
A water-soluble polymer of *N*-vinyl lactam or vinyl-containing sulfonate monomers reduces the water loss and enhances other properties of well-treating fluids in high-temperature subterranean environments (Bharat, 1990). Lignites, tannins, and asphaltic materials are added as dispersants. Vinyl monomers are shown in Figure 17.9.



$$CH_2{=}CH_2{-}\overset{\overset{\large O}{\|}}{C}{-}O{-}CH_2{-}\underset{\begin{array}{c}|\\CH_2\\|\\CH_3\end{array}}{CH}{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

2-Ethylhexylacrylate

FIGURE 17.8 2-Ethylhexyl acrylate.



Vinyl phosphonic acid *N*-Vinylpyrrolidinon Vinylsulfonic acid

FIGURE 17.9 Monomers for synthetic thickeners.

Lactide Polymers

Degradable thermoplastic lactide polymers are used for fracturing fluids. Hydrolysis is the primary mechanism used for the degradation of the lactide polymer (Cooke, 2009).

Biodegradable Formulations

Biodegradable drilling fluid formulations have been suggested, which consist of a polysaccharide in a concentration that is insufficient to permit contamination by bacteria. The polymer is a high-viscosity CMC that is sensitive to bacterial enzymes produced by the degradation of the polysaccharide (Pelissier and Biasini, 1991).

The biodegradability of seven kinds of mud additives was studied by determining the content of dissolved oxygen in water, a simple biochemical oxygen demand testing method. The biodegradability is high for starch but lower for polymers of allyl monomers and additives containing an aromatic group (Guo et al., 1996).

Concentrates

Historically, fracture stimulation treatments have been performed by using conventional batch mix techniques, which involves premixing chemicals into tanks and circulating the fluids until a desired gelled fluid rheology is obtained. This method is time-consuming and burdens the oil company with disposal of the fluid if the treatment ends prematurely.

Environmental damage during spillage or disposal can be avoided if the fluid is capable of being gelled as needed. Thus gelling-as-needed technology has been developed with water, methanol, and oil (Gregory et al., 1991). This procedure eliminates batch mixing and minimizes handling of chemicals and base fluid. The customer is charged only for products used, and environmental concerns regarding disposal are virtually eliminated. Computerized chemical addition and monitoring, combined with on-site procedures, ensure quality control throughout treatment. Fluid rheologies can be accurately varied during the treatment by varying polymer loading.

The use of a diesel-based concentrate with hydroxypropyl guar gum has been evolved from batch-mixed dry powder procedures (Harms et al., 1988). The application of such a concentrate reduces system requirements, and companies can benefit from the reduced logistic burden that comes from using the diesel hydroxypropyl guar gum concentrate.

A fracturing fluid slurry concentrate has been proposed (Brannon, 1988) that consists of the components shown in Table 17.6. Such a polymer slurry concentrate will readily disperse and hydrate when admixed with water at the proper pH, thus producing a high-viscosity aqueous fracturing fluid. This concentrate is useful for producing large volumes of high-viscosity treating fluids at the well site on a continuous basis. Suitable surfactants are shown in Figure 17.10.

TABLE 17.6 Components of a Slurry Concentrate

Component	Example
Hydrophobic solvent base	Diesel
Suspension agent	Organophilic clay
Surfactant	Ethoxylated nonyl phenol
Hydratable polymer	Hydroxypropyl guar gum

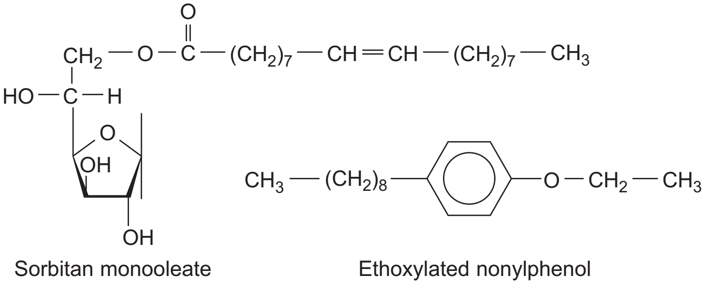


FIGURE 17.10 Surfactants in a slurry concentrate.

Fluidized aqueous suspensions of 15% or more of HEC, hydrophobically modified cellulose ether, hydrophobically modified HEC, methyl cellulose, hydroxypropylmethyl cellulose, and polyethylene oxide (PEO) are prepared by adding the polymer to a concentrated sodium formate solution containing xanthan gum as a stabilizer (Burdick and Pullig, 1993).

The xanthan gum is dissolved in water before sodium formate is added. Then the polymer is added to the solution to form a fluid suspension of the polymers. The polymer suspension can serve as an aqueous concentrate for further use.

Friction Reducers

Low pumping friction pressures are achieved by delaying crosslinking, but specific additives are also available to reduce the drag in the tubings. Gaur was first applied as a drag reducer in oil well fracturing, which is now a routine practice.

Relatively small quantities of a bacterial cellulose (0.60–1.8 $g l^{-1}$) in hydraulic fracturing fluids enhance their rheologic properties (Penny et al., 1991). The suspension of the proppant is enhanced and friction loss through well casings is reduced.

Fluid Loss Additives

Fluid loss additives are widely used additives for drilling fluids. High-permeability fracturing zones can easily be damaged by deeply penetrating fluid leak-off along the fracture, or by the materials in the fluid to minimize the amount of leak-off.

Several fracturing treatments in high-permeability formations exhibit positive post-treatment skin effects. This is the result of fracture face-damage (Aggour and Economides, 1996). If the invasion of the fracturing fluid is minimized, the degree of damage is of secondary importance. So if the fluid leak-off penetration is small, even severe permeability impairments can be tolerated without exhibiting positive skin effects. The first priority in designing fracture treatments should be to maximize the conductivity of the fracture. In high-permeability fracturing, the use of high concentrations of polymer crosslinked fracturing fluids with fluid loss additives and breakers is recommended.

Materials used to minimize leak-off can also damage the conductivity of the proppant pack. High shear rates at the tip of the fracture may prevent the formation of external filter cakes, hence increasing the magnitude of spurt losses in highly permeable formations, so non-damaging additives are needed. Enzymatically degradable fluid loss additives are available. Table 17.7 summarizes some fluid loss additives suitable for hydraulic fracturing fluids.

Degradation of Fluid Loss Additives

A mixture of natural starch (cornstarch) and chemically modified starches (carboxymethyl and hydroxypropyl derivatives) plus an enzyme, has been described as a fluid loss additive for fracturing fluids (Williamson and Allenson, 1989;

TABLE 17.7 Fluid Loss Additives for Hydraulic Fracturing Fluids

Chemical	References
Calcium carbonate and lignosulfonate[a]	Johnson (1996), and Johnson and Smejkal (1993)
Natural starch	Elbel et al. (1995), Navarrete et al. (1996), and Navarrete and Mitchell (1995)
Carboxymethyl starch	Elbel et al. (1995), Navarrete et al. (1996), and Navarrete and Mitchell (1995)
Hydroxypropyl starch[b]	Elbel et al. (1995), Navarrete et al. (1996), and Navarrete and Mitchell (1995)
HEC with crosslinked guar gums[c]	Cawiezel et al. (1999)
Granular starch and particulate mica	Cawiezel et al. (1999)

a) Wellan or xanthan gum polymer can be added to keep the calcium carbonate and lignosulfonate in suspension
b) Synergistic effect, see text
c) 500 mD *permeability*

Williamson et al., 1991b). The enzyme degrades the α-linkage of starch but not the β-linkage of guar and modified guar gums.

The starches can be coated with a surfactant, such as sorbitan monooleate, ethoxylated butanol, or ethoxylated nonyl phenol, to facilitate dispersion in the fracturing fluid. Modified starches or blends of modified and natural starches with a broad particulate size distribution have been found to maintain the injected fluid within the created fracture more effectively than natural starches (Williamson et al., 1991a). The starches can be degraded by oxidation or by bacterial attack.

pH Control Additives

Buffers, necessary to adjust and maintain the pH, can be salts of a weak acid and a weak base, such as carbonates, bicarbonates, and hydrogen phosphates (Nimerick, 1996), or weak acids such as formic acid, fumaric acid, and sulfamic acid. Common aqueous buffers are shown in Table 17.8 and in Figures 17.11 and 17.12.

Increased temperature stability of various gums can be achieved by adding sodium bicarbonate to the fracturing fluid and thus raising its pH to 9.2–10.4.

TABLE 17.8 Common Buffer Solutions

Buffer	pK_A
Sulfamic acid/sulfamate	1.0
Formic acid/formate	3.8
Acetic acid/acetate	4.7
Dihydrogenphosphate/hydrogenphosphate	7.1
Ammonium ammonia	9.3
Bicarbonate/carbonate	10.4
Fumaric acid/hydrogen fumarate	3.0
Benzoic acid/benzoate	4.2

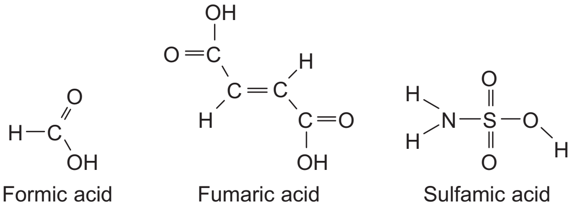
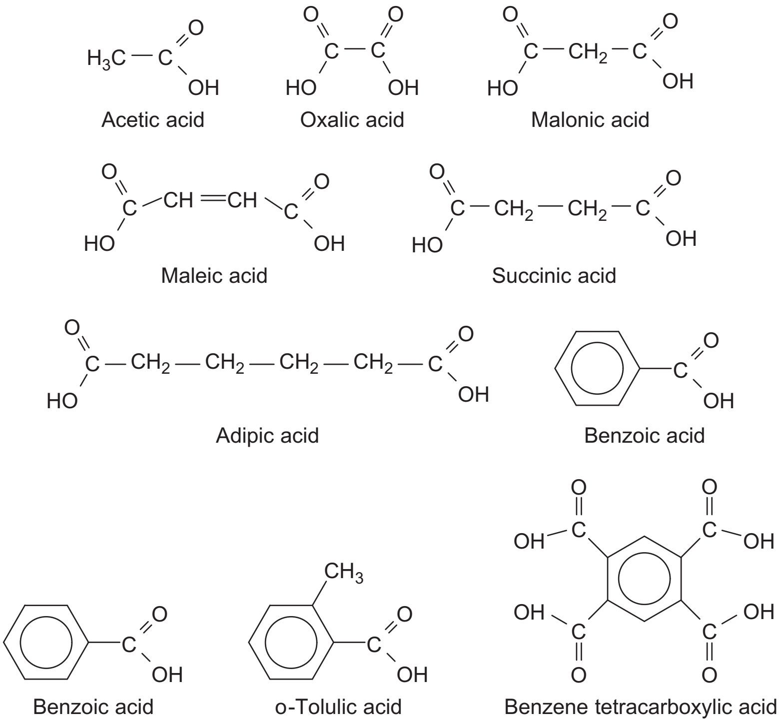


FIGURE 17.11 Weak organic acids.



Acetic acid

Oxalic acid

Malonic acid

Maleic acid

Succinic acid

Adipic acid

Benzoic acid

Benzoic acid

o-Tolulic acid

Benzene tetracarboxylic acid

FIGURE 17.12 Carbonic and dicarbonic acids.

Clay Stabilizers

Advances in treating clay-bearing formations have led to the development of numerous clay-stabilizing treatments and additives. Most additives are high molecular weight cationic organic polymers, but it has been shown that these stabilizers are less effective in low-permeability formations (Himes et al., 1989).

The use of salts such as potassium chloride and sodium chloride, as temporary clay stabilizers during oil well drilling, completion, and servicing, has been practiced for many years. Because of the bulk and potential environmental hazards associated with the salts, many operators have looked for alternatives. Recent research has shown a relationship between the physical properties of various cations (e.g., K^+, Na^+) and their efficiency as temporary clay stabilizers. These properties were used to synthesize an organic cation (Table 17.9) with a higher efficiency as a clay stabilizer.

These additives provide additional benefits when used in conjunction with acidizing and fracturing treatments, since a much lower salt concentration can be used (Himes et al., 1990; Himes and Vinson, 1991), and the liquid product is

TABLE 17.9 Clay Stabilizers

Compound	References
Ammonium chloride	
Potassium chloride[a]	Yeager and Bailey (1988)
Dimethyl diallyl ammonium salt[b]	Thomas and Smith (1993)
N-Alkyl pyridinium halides	
N,N,N-Trialkylphenylammonium halides	
N,N,N-Trialkylbenzylammonium halides	
N,N-Dialkylmorpholinium halides[c]	Himes (1992), and Himes and Vinson (1989)
Reaction product of a homopolymer of maleic anhydride and an alkyl diamine[d]	Schield et al. (1991)
Tetramethylammonium chloride and methyl chloride quaternary salt of ethylene-ammonia condensation polymer[d]	Aften and Gabel (1992)
Quaternary ammonium compounds[e]	Hall and Szememyei (1992)

a) Added to a gel concentrate with a diesel base
b) Minimum 0.05% to prevent swelling of clays
c) Alkyl equals methyl, ethyl, propyl, and butyl
d) Synergistically retards water absorption by the clay formation
e) Hydroxyl-substituted alkyl radials

much easier to handle and transport. It is also environmentally compatible and biodegradable in its diluted form.

Biocides

A hydraulic fracturing fluid containing guar gum or other natural polymers can be stabilized against bacterial attack by adding heterocyclic sulfur compounds, thus preventing any undesired degradation of the fracturing fluid, such as reduction of its rheological properties at high temperatures. Biocides suitable for fracturing fluids are shown in Table 17.10 and Figure 17.13.

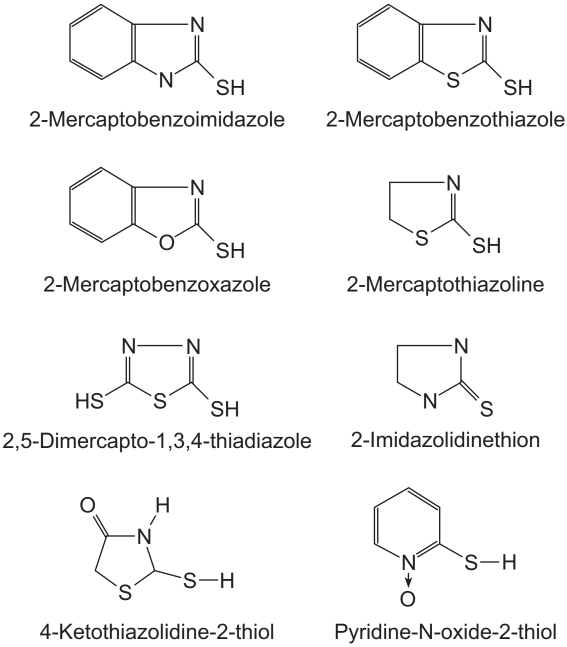
Surfactants

Surface active agents are included in most aqueous treating fluids to improve their compatibility with the hydrocarbon-containing reservoir. The formation must be water-wet to achieve maximal conductivity of hydrocarbons.

TABLE 17.10 Biocides

Compound	References
Mercaptobenzimidazole[a]	Kanda et al. (1986)
1,3,4-Thiadiazole-2,5-dithiol[a,b]	Kanda and Kawamura (1988, 1989), and Kanda et al. (1988)
2-Mercaptobenzothiazole	
2-Mercaptothiazoline	
2-Mercaptobenzoxazole	
2-Mercaptothiazoline	
2-Thioimidazolidone	
2-Thioimidazoline	
4-Ketothiazolidine-2-thiol	
N-Pyridineoxide-2-thiol	

a) For Guar gum
b) For Xanthan gum



2-Mercaptobenzoimidazole
2-Mercaptobenzothiazole
2-Mercaptobenzoxazole
2-Mercaptothiazoline
2,5-Dimercapto-1,3,4-thiadiazole
2-Imidazolidinethion
4-Ketothiazolidine-2-thiol
Pyridine-N-oxide-2-thiol

FIGURE 17.13 Biocides for hydraulic fracturing fluids.

Alkylamino phosphonic acids and fluorinated alkylamino phosphonic acids adsorb onto solid surfaces, particularly of carbonate materials in subterranean hydrocarbon-containing formations, in a layer only one molecule thick. This is significantly thinner than a layer of water or a water-surfactant mixture on water-wetted surfaces (Penny, 1987; Penny and Briscoe, 1987). These compounds resist or substantially reduce the wetting of the surfaces by water and hydrocarbons, and provide high interfacial tensions between the surfaces and water and hydrocarbons. The hydrocarbons displace injected water, leaving a lower water saturation and an increased flow of hydrocarbons through capillaries and flow channels in the formation.

A methyl quaternized erucyl amine is useful for aqueous VES-based fracturing fluids in high-temperature and high-permeability formations (Gadberry et al., 1999).

Crosslinkers

Kinetics of Crosslinking

The rheology of hydroxypropyl guar is greatly complicated by crosslinking reactions with titanium ions. A study of the rheology of this system has been performed (Barkat, 1987). Continuous flow and dynamic data suggest a crosslinking reaction order of approximately 4/3 and 2/3, with respect to the crosslinker and hydroxypropyl guar concentration. Dynamic tests have shown that the shearing time is important in determining the final gel properties. Continued steady shear and dynamic tests show that high shear irreversibly destroys the gel structure, and the extent of the crosslinking reaction decreases with increasing shear. Studies at shear rates below 100 s^{-1} suggest a shear-induced structural change in the polymer that affects the chemistry of the reaction and the nature of the product molecule.

Delayed Crosslinking

Delayed crosslinking is desirable because the fluid can be pumped more easily. A delay is a retarded reaction rate of crosslinking, which can be achieved with the methods explained in the following section.

Borate Systems

Boric acid can form complexes with hydroxyl compounds as shown in Figure 17.14. Three hydroxyl units form an ester and one unit forms a complex bond, releasing a proton that lowers the pH. The scheme is valid also for polyhydroxy compounds, where two polymer chains are connected via such a link.

The control of the delay time requires the pH, or the availability of borate ions, or both to be controlled. Control of pH can be effective in fresh water systems (Ainley et al., 1993), but the control of borate is effective in both fresh

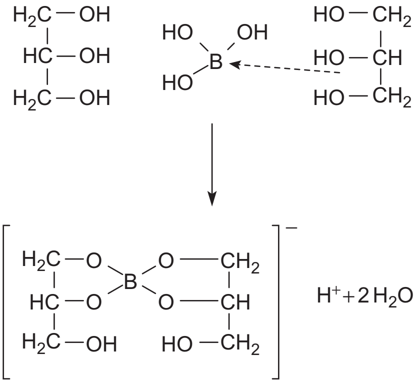


FIGURE 17.14 Complexes of boric acid with glycerol.

water and sea water. This may be accomplished by using sparingly soluble borate species or by complexing the borate with a variety of organic species.

Borate-crosslinked fracturing fluids have been used successfully in fracturing operations. These fluids provide excellent rheological, fluid loss, and fracture conductivity properties over fluid temperatures up to 105°C. The mechanism of borate crosslinking is an equilibrium process that can produce very high fluid viscosities under conditions of low shear (Cawiezel and Elbel, 1990). A fracturing fluid containing borate is prepared in the following way (Harris et al., 1994):

1. Adding a polysaccharide (sea) water to produce a gel,
2. Adding an alkaline agent to the gel to obtain a pH of at least 9.5, and
3. Adding a borate crosslinking agent to the gel to crosslink the polymer.

A dry granular composition can be prepared in the following way (Harris and Heath, 1994):

1. Dissolving 0.2–1.0% of a water-soluble polysaccharide in aqueous solution,
2. Admixing a borate source with the aqueous gel formed in step 1,
3. Drying the borate crosslinked polysaccharide formed in step 2, and
4. Granulating the product.

The crosslinking agent can be boric acid, borax, an alkaline earth metal borate, or an alkali metal alkaline earth metal borate. The borate source must be present at 5–30% calculated as boric oxide.

Borated starch compositions are useful for controlling the rate of crosslinking of hydratable polymers in aqueous media. They are prepared by reacting starch and a borate source in an aqueous medium. The complex provides a source of borate ions, which cause crosslinking of hydratable polymers in aqueous media (Sanner et al., 1996). Delayed crosslinking takes place at low temperatures.

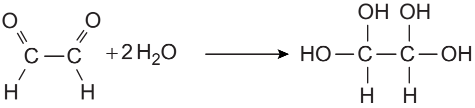


FIGURE 17.15 Glyoxal and hydrate formation.

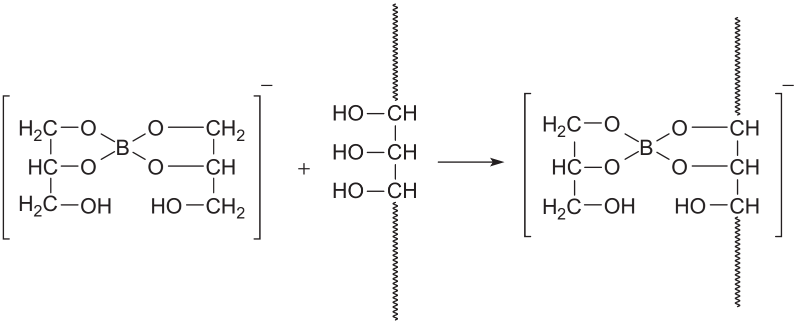


FIGURE 17.16 Delayed crosslinking.

Glyoxal (Dawson, 1992, 1995) shown in Figure 17.15 is effective as a delay additive within a certain pH range. It bonds chemically with both boric acid and borate ions to limit the number of borate ions that are initially available in solution for subsequent crosslinking. The subsequent rate of crosslinking can be controlled by adjusting the pH of the solution. The mechanism of delayed crosslinking is shown in Figure 17.16. If two hydroxyl compounds with low molecular weight are exchanged with high molecular weight compounds, and the hydroxyl units belonging to different molecules, then a crosslink is formed.

Other dialdehydes, keto aldehydes, hydroxyl aldehydes, ortho-substituted aromatic dialdehydes, and ortho-substituted aromatic hydroxyl aldehydes are claimed to be active in a similar way .

Borate-crosslinked, guar-fracturing fluids have been reformulated to allow use at higher temperatures in both fresh water and sea water. The temporary temperature range is extended for the use of magnesium oxide-delayed borate crosslinking of a galactomannan gum fracturing fluid by adding fluoride ions that precipitate insoluble magnesium fluoride (Nimerick et al., 1993). Alternatively, a chelating agent for the magnesium ion may be added. With the precipitation of magnesium fluoride or the chelation of the magnesium ion, insoluble magnesium hydroxide cannot form at elevated temperatures, which would otherwise lower the pH and reverse the borate crosslinking reaction. The addition effectively extends the use of such fracturing fluids to temperatures of 135–150°C.

Polyols, such as glycols or glycerol, can delay the crosslinking of borate in hydraulic fracturing fluids based on galactomannan gum (Ainley and McConnell, 1993). This is suitable for high-temperature applications up to

150°C. In this case, low molecular weight borate complexes initially are formed but exchange slowly with the hydroxyl groups of the gum.

Titanium Compounds

Organic titanium compounds are useful as crosslinkers (Putzig and Smeltz, 1986). Aqueous titanium compositions often consist of mixtures of compounds.

Zirconium Compounds

Various zirconium compounds are used as delayed crosslinkers, as shown in Table 17.11. The complexes initially form with low molecular weight compounds, and are then exchanged with intermolecular polysaccharide complexes, which cause delayed crosslinking.

A diamine-based compound for complex forming is shown in Figure 17.17, and hydroxy acids are shown in Figure 17.18. Polyhydroxy compounds suitable for complex formation with zirconium compounds are shown in Figure 17.19.

TABLE 17.11 Zirconium Compounds Suitable as Delayed Crosslinkers

Zirconium Crosslinker/Chelate	References
Hydroxyethyl-tris-(hydroxypropyl) ethylene diamine[a]	Putzig (1988)
Zirconium halide chelates	Ridland and Brown (1990)
Boron zirconium chelates[b]	Dawson and Le (1998) and Sharif (1993, 1995)

a) Good high-temperature stability
b) High-temperature application, enhanced stability

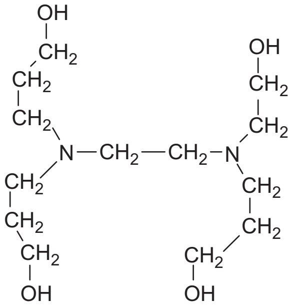
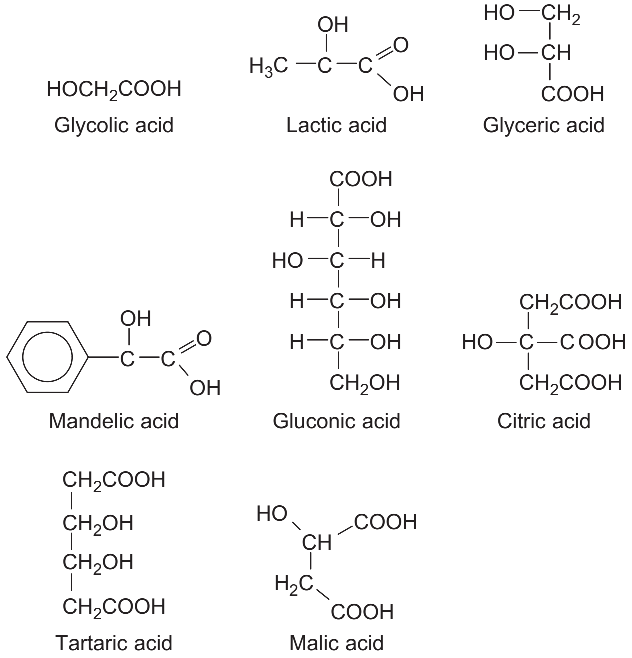


FIGURE 17.17 Hydroxyethyl-tris-(hydroxypropyl) ethylene diamine.

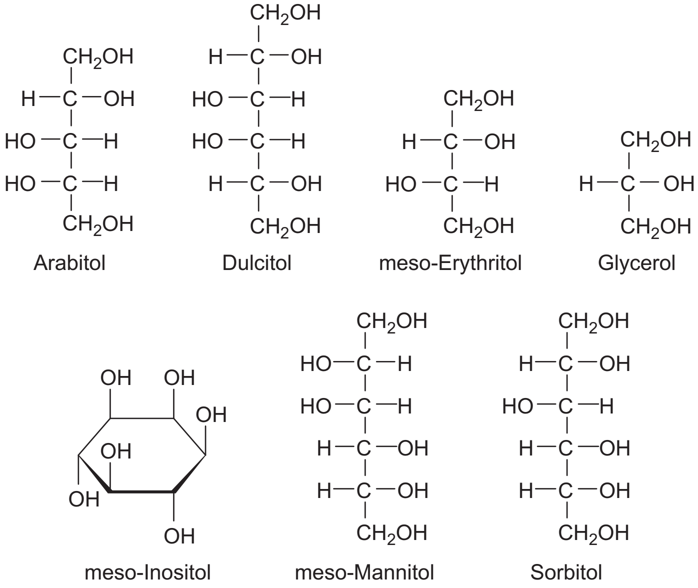


Glycolic acid Lactic acid Glyceric acid

Mandelic acid Gluconic acid Citric acid

Tartaric acid Malic acid

FIGURE 17.18 Hydroxy acids.



Arabitol Dulcitol meso-Erythritol Glycerol

meso-Inositol meso-Mannitol Sorbitol

FIGURE 17.19 Polyalcohols for complex formation.

Borozirconate complexes can be prepared by the reaction of tetra-*n*-propyl zirconate with triethanol amine and boric acid (Putzig, 2010). They can be used at a pH of 8–11.

Gel Breaking in Water-based Systems

In general, there are two methods for combining a fracturing fluid and a breaker (Carpenter, 2009):

1. Mixing the breaker with the fracturing fluid prior to sending the fracturing fluid downhole or
2. Sending the fracturing downhole first, followed by the breaker.

The first method is favored because of convenience, but a disadvantage of this method is that the breaker can act to decrease the viscosity of the fracturing fluid before the desired time.

In the second method, the fracturing fluid is dispatched first, and the breaker is sent downhole later. While inconvenient, this prevents premature decrease in the viscosity (Carpenter, 2009).

The properties of the formation should be restored after fracturing. Maximal well production can be achieved only when the solution viscosity and the molecular weight of the gelling agent are significantly reduced after the treatment, that is, the fluid is degraded.

Basic Studies

Comprehensive research on the degradation kinetics of a hydroxypropyl guar fracturing fluid by enzyme, oxidative, and catalyzed oxidative breakers has been performed (Craig, 1991; Craig and Holditch, 1993a,b). Changes in viscosity were measured as a function of time. The studies revealed that enzyme breakers are effective only in acid media at temperatures of 60°C or below. In an alkaline medium and at temperatures below 50°C, a catalyzed oxidative breaker system was the most effective breaker. At temperatures of 50°C or higher, hydroxypropyl guar fracturing fluids can be degraded by an oxidative breaker without a catalyst.

Oxidative Breakers

Alkali metal hypochlorites and inorganic and organic peroxides have been described in literature. These materials degrade the polymer chains by oxidative mechanisms. CMC, guar gum, or partially hydrolyzed polyacrylamides were used for testing a series of oxidative gel breakers in a laboratory study (Bielewicz and Kraj, 1998).

Hypochlorite Salts

Hypochlorites are powerful oxidants and therefore may degrade polymeric chains. They are often used in combination with tertiary amines (Williams et al.

1987), which increases the reaction rate above that achievable with the application of a hypochlorite alone. A tertiary amino galactomannan may serve as an amine source (Langemeier et al., 1989), which also serves as a thickener before breaking. Hypochlorites are also effective for breaking stabilized fluids (Walker and Shuchart, 1995). Sodium thiosulfate has been proposed as a stabilizer for high-temperature applications.

Peroxide Breakers

Alkaline earth metal peroxides have been described as delayed gel breakers in alkaline aqueous fluids containing hydroxypropyl guar (Mondshine, 1993). The peroxides are activated by increasing the temperature of the fluid.

Perphosphate esters or amides can be used for oxidative gel breaking (Laramay et al., 1995). The salts of the perphosphate ion interfere with the action of the crosslinkers, but the esters and amides do not. Fracturing fluids that contain these breakers and using metal ion crosslinkers are useful for fracturing deeper wells that operate at temperatures of 90–120°C such as titanium and zirconium. Breaker systems based on persulfates have also been described (Harms, 1992).

Organic peroxides are also suitable for gel breaking (Dawson and Le, 1995). They need not be completely soluble in water. The time needed to break is kept in the range 4–24 h by adjusting the amount of breaker added to the fluid.

Redox Gel Breakers

Gel breakers act basically, according to a redox reaction. Copper (II) ions and amines can degrade various polysaccharides (Shuchart et al., 1999).

Delayed Release of Acid

Regained permeability studies with HEC polymer in high-permeability cores revealed that persulfate-type oxidizing breakers and enzyme breakers do not adequately degrade the polymer. Sodium persulfate breakers were found to be thermally decomposed, and the decomposition was accelerated by minerals present in the formation.

The enzyme breaker adsorbed onto the formation but still partly functioned as a breaker. Dynamic fluid loss tests at reduced pH with borate crosslinked gels suggest that accelerated leak-off away from the wellbore could be obtained through the use of a delayed release acid. Rheological measurements confirmed that a soluble, delayed release acid could be used to convert a borate crosslinked fluid into a linear gel (Noran et al., 1995).

A condensation product of hydroxyacetic acid can be used as a fluid loss material in a fracturing fluid where another hydrolyzable aqueous gel is used (Cantu and Boyd, 1989; Cantu et al., 1990a,b, 1993). The hydroxyacetic acid condensation product degrades under formation conditions to release hydroxyacetic acid, which breaks the aqueous gel. This mechanism may be used for

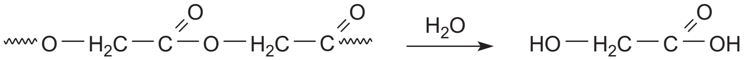


FIGURE 17.20 Hydrolysis of polyglycolic acid.

TABLE 17.12 Polymer Enzyme Systems

Polymer	References
Xanthan[a]	Ahlgren (1993)
Mannan-containin hemicellulose[b]	Fodge (1996)

a) Elevated temperatures and salt concentrations
b) High alkalinity and elevated temperature

delayed gel breaking, as shown in Figure 17.20. Here the permeability is restored without the need for the separate addition of a gel breaker, and the condensation product acts a fluid loss additive.

Enzyme Gel Breakers

Enzymes cleave the backbone structure of the thickeners specifically and eventually that of the fluid loss additive. They offer several advantages over other breaker systems, because of their inherent specificity and the infinite polymer-degrading activity. Initially their application has been limited to low-temperature fracturing treatments, because of pH and temperature constraints, but recently, extreme temperature-stable and polymer-specific enzymes have been developed (Brannon and Tjon-Joe-Pin, 1994).

Basic Studies

Basic studies have been performed to investigate the performance of enzymes. The products and kinetics of degradation, and limits of application, such as temperature and pH, have been analyzed (Craig et al., 1992; Slodki and Cadmus, 1991). Enzymes degrade chemical linkages highly selectively, hence no general-purpose enzyme exists, but one must be selected for each thickener. Enzymes suitable for particular systems are shown in Table 17.12.

Enzymes break the chains of the thickener directly or degrade polymers into organic acid molecules (Harris and Hodgson, 1995).

Interactions

Despite their advantages over conventional oxidative breakers, enzyme breakers have limitations because of interferences and incompatibilities with other additives. Interactions between enzyme breakers and fracturing fluid additives

TABLE 17.13 Use of Encapsulation in Delayed Gel Breaking

Breaker system	References
Ammonium persulfate[a]	Gulbis et al. (1990a,b, 1992), and King et al. (1990)
Enzyme breaker[b]	Gupta and Prasek (1995)
Complexing agents[c]	Boles et al. (1996)

a) Guar or cellulose derivatives
b) Open cellular coating
c) For titanium and zirconium; wood resin encapsulated

including biocides, clay stabilizers, and certain types of resin-coated proppants have been reported (Prasek, 1996).

Encapsulated Gel Breakers

The chemical in encapsulated gel breakers is contained with in a membrane that is impermeable, or is only slightly permeable to the breaker that does not come in initial contact with the polymer to be degraded. The breaker diffuses, slowly out from the capsulation, or the capsulation is destroyed so that the breaker can act successfully.

Encapsulated gel breakers are widely applied for delayed gel breaking. The breaker is encapsulated by a water-resistant coating, which shields the fluid from the breaker, so that a high concentration can be added without causing premature loss of fluid properties.

The barrier properties of the coating, release mechanisms, and the properties of the reactive chemicals are critical factors in the design of encapsulated breakers. For example, a hydrolytically degradable polymer can be used as the membrane (Muir and Irwin, 1999). This method of delayed gel breaking has been reported both for oxidative breaking and for enzyme gel breaking. Formulations of encapsulated gel breakers are shown in Table 17.13, and membranes for encapsulators are shown in Table 17.14.

Gel Breaking of Guar

Maximal well production can be achieved only when the solution viscosity and the molecular weight of the gelling agent are significantly reduced after the treatment. However, the reduction of the fracturing fluid viscosity, the traditional method of evaluating these materials, does not necessarily indicate that the gelling agent has also been thoroughly degraded.

The reaction between hydroxypropyl guar and ammonium peroxydisulfate in an aqueous potassium chloride solution was studied (Hawkins, 1986) under

TABLE 17.14 Membranes for Encapsulated Breakers

Membrane Material	References
Polyamide (PA)[a]	Satyanarayana Gupta and Cooney (1992)
Crosslinked elastomer	Manalastas et al. (1992)
Partially hydrolyzed acrylics crosslinked with aziridine prepolymer or carbodiimide[b]	Hunt et al. (1997), Norman and Laramay (1994), and Norman et al. (2001)
7% Asphalt and 93% neutralized sulfonated ionomer	Swarup et al. (1996)

a) For peroxide particle sizes 50–420 μ
b) Enzyme coated on cellulose derivative

controlled conditions to determine changes in solution viscosity and the weight average of the molecular mass of hydroxypropyl guar.

Bromine compositions used for gel breaking can be stabilized with sodium sulfamate (Carpenter, 2009). The sulfamate used in the production of such breakers stabilizes the active bromine species over long periods of time, especially at a pH of 13. For example, a WELLGUARD™ 7137 gel breaker is stable for over a year if protected from sunlight. The halogen source of the breaker is an interhalogen compound, bromine chloride, or mixtures of bromine and chlorine.

Unlike hypobromites ($^{-}$OBr), these breakers do not oxidize or otherwise destroy the organic phosphonates typically used as corrosion or scale inhibitors, and they exhibit a low corrosivity against metals, especially ferrous alloys because of their low oxidation-reduction potential (Carpenter, 2007, 2009). The effect of the breakers on guar is shown in Figure 17.21. The composition was prepared and studied at 50°C (120°F).

Borate-crosslinked guar polymer gels can be broken with EDTA compounds (Crews, 2007a). Examples are shown in Table 17.15. It is believed that these breakers act directly on the polymer itself and not on any crosslinker that may be present. Polyhydroxy compounds can also break guar gels, and these are formed by polysaccharides. They include mannitol and sorbitol, and can be used in combination with enzyme breakers (Crews, 2007b).

Gel Breaking of VES-gelled Fluids

The viscosity of fluids viscosified with VESs can be controlled by fatty acid salts. For example, a brine fluid gelled with an amine oxide surfactant may have its viscosity broken with a composition containing naturally occurring fatty acid salts from canola oil or corn oil (Crews, 2010).

The alteration of the fatty acid or the saponification reaction may occur during mixing and pumping of the fluid downhole. The method may also be used

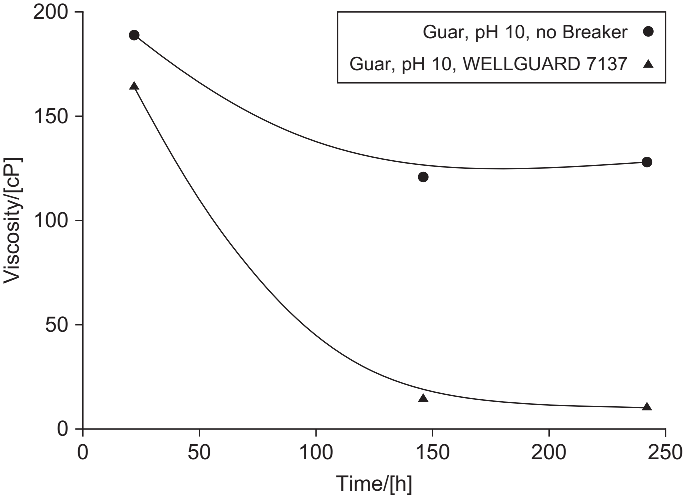


FIGURE 17.21 Effect of halogen-based breakers on guar (Carpenter, 2009).

TABLE 17.15 EDTA-related Gel Breakers (Crews, 2007a)

Complex Compound
Tetrasodium propylenediamine tetraacetic acid
Trisodium hydroxyethylene diamine tetraacetic acid
Trisodium nitrilo triacetic acid
Trisodium ethylene diaminetriacetic acid
Disodium ethylene diamine diacetic acid
Disodium calcium dihydrate ethylene diamine diacetic acid
Tetraammonium ethylene diamine tetraacetic acid

where most of the saponification occurs within the reservoir shortly after the treatment is over. Alternatively, the components may be preformed and added later as an external breaker solution to remove the VES-gelled fluids that have been already placed downhole.

It may be possible that the viscosity initially increases and then decreases. When canola oil is saponified with CaOH, initially a slight increase of the VES fluid is observed, followed by a breaking reaction (Crews, 2010). The increase in viscosity occurs because the saponified fatty acids may act as viscosity-enhancing cosurfactants for the fluid containing VESs.

Granules

Granules containing 40–90% of sodium or ammonium persulfate breaker and 10–60% of an inorganic powdered binder, such as clay, have been described (McDougall et al., 1993) as acting as a delayed breaker.

Controlled solubility compounds or clean-up additives, including polyphosphates, that slowly release certain salts act as delayed breakers (Mitchell et al., 2001).

Granules composed of a particulate breaker dispersed in a wax matrix are used in fracturing operations to break hydrocarbon liquids gelled with salts of alkyl phosphate esters. The wax granules are solid at surface temperatures, but melt or disperse in the hydrocarbon liquid at formation temperature, releasing the breaker to react with the gelling agent (Acker and Malekahmadi, 2001).

Scale Inhibitors

The formation of calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4$), and barium sulfate ($BaSO_4$) scales in brine may create permeability problems, so newly made fractures need a scale inhibitor in place. Formulations of hydraulic fracturing fluids containing a scale inhibitor have been described in the literature (Watkins et al., 1993).

Interference of Chelate Formers

Trace amounts of metal chelate-forming additives have been shown to have a debilitating effect on the performance of widely used barium sulfate scale inhibitors. Ethylene diamine tetraacetic acid, citric acid, and gluconic acid render some scale inhibitors, such as phosphonates, polycarboxylates, and phosphate esters, completely ineffective at concentrations as low as $0.1\,\mathrm{mg\,l^{-1}}$. Such low concentrations may be expected to return from formation stimulation treatments for many months and would appear to jeopardize any scale inhibitor program in place.

This conclusion follows from experiments with a simulated North Sea scaling system at pH 4 and 6. The scale inhibitor concentrations studied were 50 and $100\,\mathrm{mg\,l^{-1}}$. The large negative effect of the organic chelating agents was observed at pH 4 and 6. The only scale inhibitors studied that remained unaffected by these interferences were polyvinyl sulfonates (Barthorpe, 1993).

Encapsulated Scale Inhibitors

A solid, encapsulated scale inhibitor (calcium-magnesium polyphosphate) has been developed and extensively tested for use in fracturing treatments (Powell et al., 1995a,b, 1996). The inhibitor is compatible with borate and zirconium crosslinked fracturing fluids and foamed fluids because of its coating which exhibits a short-term effect on the release rate profile. The composition of the solid derivative has the greatest effect on its long-term release rate profile.

OIL-BASED SYSTEMS

One advantage of fracturing with hydrocarbon-based gels compared to their aqueous equivalents is that some formations may imbibe large quantities of water, whereas others are water sensitive and will swell if water is introduced.

Organic Gel Aluminum Phosphate Ester

A gel of diesel or crude oil can be produced using a phosphate diester or an aluminum compound with phosphate diester (Gross, 1987). The metal phosphate diester may be prepared by reacting a triester with phosphorous pentoxide to produce a polyphosphate, which is then reacted with hexanol to produce a phosphate diester (Huddleston, 1989).

The latter diester is then added to the organic liquid along with a nonaqueous source of aluminum, such as aluminum isopropoxide, c.f., Figure 17.22, in diesel oil, to produce the metal phosphate diester. The conditions in the previous reaction steps are controlled to provide a gel with good viscosity versus temperature and time characteristics. All the reagents are substantially free of water and will not affect the pH. The synthesis of phosphate diesters goes via. triethyl phosphate, using phosphorous pentoxide and the esterification reaction with hexanol. It is shown in Figure 17.23.

Amino compounds are enhancers for phosphate esters (Geib, 2002). The 2-ethylhexanoic acid trialuminum salt has been suggested with fatty acids as an activator (Subramanian et al., 2001).

Another method of producing oil-based hydrocarbon gels uses ferric salts (Smith and Persinski, 1995) rather than aluminum compounds for combination with orthophosphate esters. This can be done in the presence of large amounts of water, up to 20%. Ferric salts can be applied over wide pH ranges. The linkages that are formed can still be broken with conventional gel breaking additives.

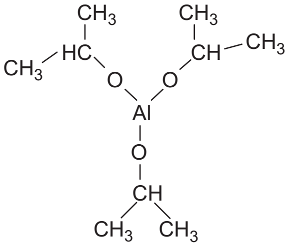


FIGURE 17.22 Aluminum isopropoxide.

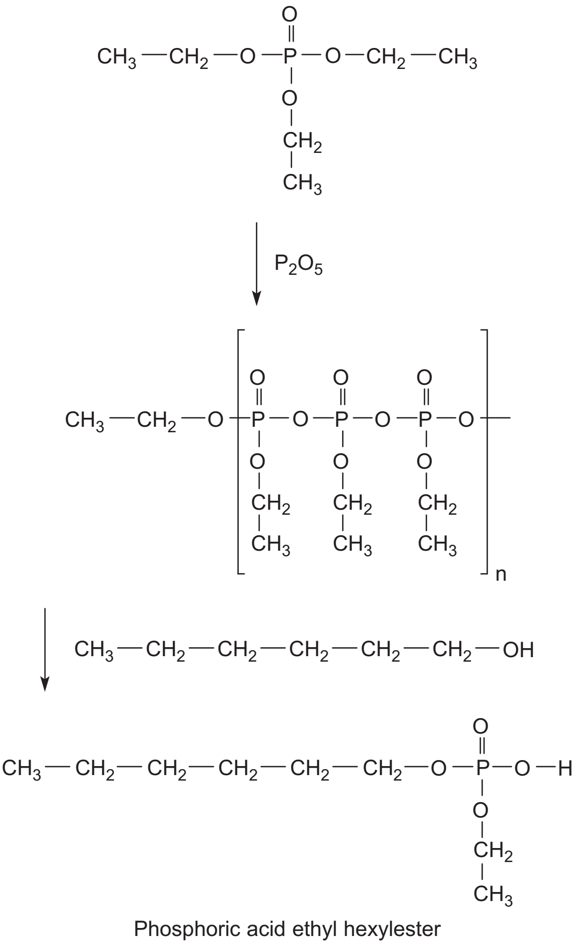


FIGURE 17.23 Synthesis of higher phosphoric esters.

Increasing the Viscosity of Diesel

A copolymer of *N*,*N*-dimethylacrylamide and *N*,*N*-dimethyl aminopropyl methacrylamide, a monocarboxylic acid, and ethanolamine increases the viscosity of diesel or kerosene (Holtmyer and Hunt, 1988). These compounds are shown in Figure 17.24.

Gel Breakers

Gel breakers used in nonaqueous systems have a completely different chemistry from those used in aqueous systems. A mixture of hydrated lime and sodium bicarbonate is useful in breaking nonaqueous gels (Syrinek and Lyon,

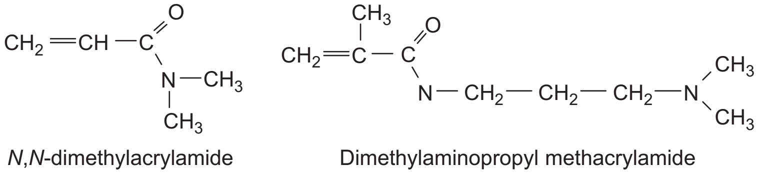


FIGURE 17.24 Monomers in a copolymer for viscosifying diesel.

1989). Sodium bicarbonate used by itself is totally ineffective for breaking the fracturing fluid for aluminum phosphate-based or aluminum phosphate ester-based gellants. Alternatively, sodium acetate can be used as a gel breaker for nonaqueous gels.

FOAM-BASED FRACTURING FLUIDS

Foam fluids can be used in many fracturing jobs, especially when environmental sensitivity is a concern (Stacy and Weber, 1995). Foam-fluid formulations are reusable, shear stable, and form stable foams over a wide temperature range, exhibiting high viscosities even at relatively high temperatures (Bonekamp et al., 1993).

A foamed fracturing fluid contains a relatively large volume of gas dispersed in a relatively small volume of liquid, and includes a surfactant for foaming, and stabilization of the foam produced when the gas is mixed with the liquid (Welton et al., 2010).

A coarse foamed fluid has a relatively nonuniform bubble size distribution, i.e., a combination of large and small gas bubbles, whereas a fine-textured foam has relatively uniform bubble size distribution and most of the bubbles are relatively small (Middaugh et al., 2007). In coarse foamed fracturing fluids, there may be regions of fine-textured foam. Such foams are able to support proppant in the fine textured regions even at very high foam quality levels.

The most commonly used gases for foam fluids are nitrogen and carbon dioxide, because they are noncombustible, readily available, and relatively cheap (Welton et al., 2010).

The content of the gas is called *quality*, therefore a 70 quality foam contains 70% gas. Recently, foams with 95% gas have been examined, but only foam prepared from 2% of an anionic surfactant with plain water had uniform, fine-bubble structure (Harris and Heath, 1996).

Surfactants are available that can change their power of foaming. For example, a tertiary alkyl amine ethoxylate can be changed from a foaming to a nonfoaming surfactant by lowering the pH of the environment. It can then be changed back to a foaming surfactant by the addition of a basic material, e.g., hydroxide ions. At low pH the amine group is quaternized, as shown in Figure 17.25.

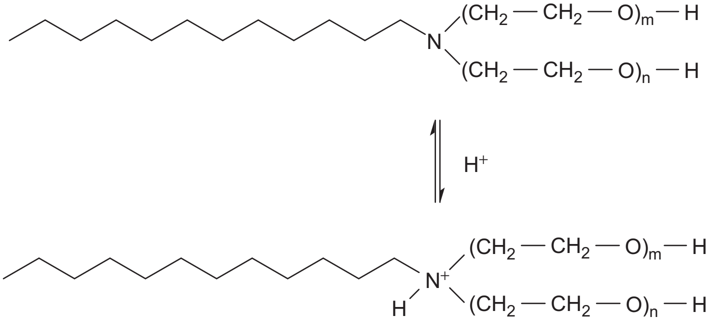


FIGURE 17.25 Changing the foaming ability by changing the pH. Top: Foaming modification. Bottom: Nonfoaming modification (Welton et al., 2010).

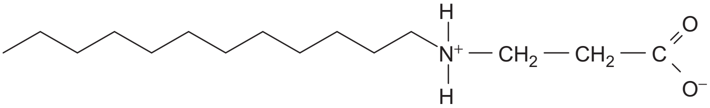


FIGURE 17.26 Lauryl betaine.

Cocobetaine and α-olefin sulfonate have also been proposed as foamers (Pakulski and Hlidek, 1992), and a mixture of laurylamine and myristylamine oxide performs well as a surfactant. Lauryl betaine is shown in Figure 17.26.

Recyclable foamed fracturing fluids are available (Chatterji et al., 2007). After use, the pH of the fracturing fluid is changed so that the foam is destroyed. At this stage, the fracturing fluid also releases its proppant. Afterwards, the fracturing fluid is allowed to flow back to the surface, where it can be recycled by restoring the initial pH and adding a gas to the fluid, causing it to foam again.

Defoamers

A defoamer and an antifoamer composition are described for defoaming aqueous fluid systems (Zychal, 1986). The composition of a typical defoamer for hydraulic fracturing fluids is shown in Table 17.16.

Orthoesters such as trimethyl orthoacetate, triethyl orthoacetate, and the corresponding orthoformates will generate acids in order to degrade the foam. Polyorthoesters are also important in medical applications (Heller et al., 2002). Some simple orthoesters are shown in Figure 17.27.

The synthesis of orthoesters may proceed either by a Williamson synthesis or by the addition of alcohols to a cyanide. The respective reactions are shown in Figure 17.28.

Orthoesters are stable to alkalis, but not to acids and water. The orthoester decreases the pH of the foamed fracturing fluid by enough to convert the foaming surfactant to a nonfoaming surfactant. To allow the orthoester to hydrolyze

TABLE 17.16 Composition of a Defoamer for Hydraulic Fracturing Fluids

Compound	Amount/[%]
C_6-C_{12} mixture of polar compounds	50 to 90
Sorbitan monooleate	10 to 50
Polyglycol M = 3.8 kDalton	10

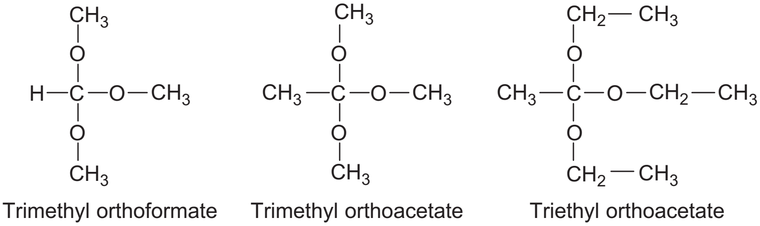


FIGURE 17.27 Orthoesters.

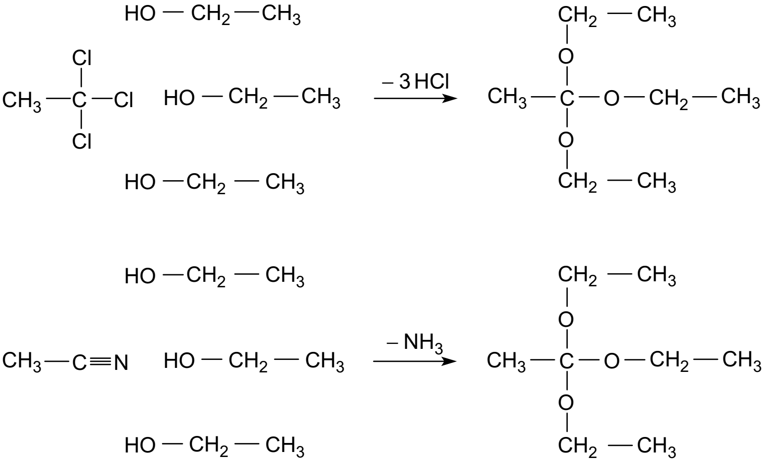


FIGURE 17.28 Synthesis of orthoesters.

and produce an acid, a source of water is needed, whether from the formation or introduced. The water should be present in an amount of 2 mol of water per mol of orthoester (Welton et al., 2010).

The orthoester compositions may also contain an inhibitor, to delay acid generation, and they may neutralize any generated acid during the delay period.

Suitable inhibitors include bases, e.g., alkali hydroxides, sodium carbonate, or hexamethylenetetramine.

Sometimes a small amount of a strong base as opposed to a large amount of a relatively weak base is preferred (Welton et al., 2010). A foamed fracturing composition may additionally contain other usual ingredients, such as (Welton et al., 2010).

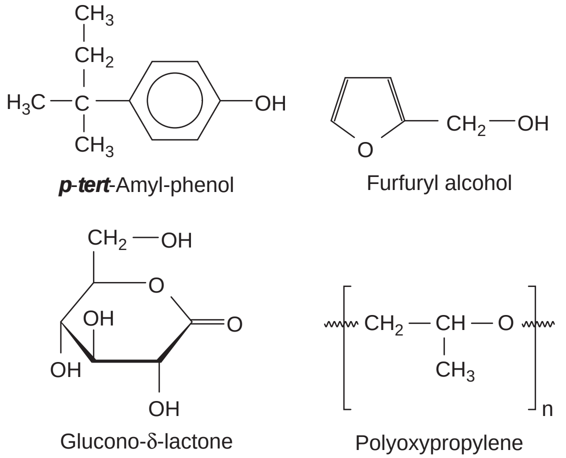
- Gelling agents,
- Bactericides, and
- Proppants.

FRACTURING IN COAL-BEDS

The production of natural gas from coal typically requires stimulation by hydraulic fracturing. Basic studies on the effectiveness of various treatment methods for coal-beds have been presented in the literature (Conway and Schraufnagel, 1995; Penny and Conway, 1995).

Treating a coal seam with a well treatment fluid containing a dewatering agent will enhance the methane production through a well. This additive enhances the permeability of the formation to water production and binds tenaciously to the coal surface, so that the permeability-enhancement benefits are realized over a long production term.

Polyoxyethylene, polyoxypropylene, and polyethylene carbonates (Nimerick and Hinkel, 1991), or *p*-*tert*-amylphenol condensed with formaldehyde, or copolymers of 80–100% alkyl methacrylate monomers and hydrophilic monomers have all been suggested as surfactants (Harms and Scott, 1993). Selected compounds for this purpose are shown in Figure 17.29.



p*-*tert-Amyl-phenol

Furfuryl alcohol

Glucono-δ-lactone

Polyoxypropylene

FIGURE 17.29 Monomers for dewatering.

Such a well treatment fluid may be used in both fracturing and competition operations to enhance and maintain fracture conductivity over an extended period.

PROPPING AGENTS

The best proppant and fluids have to be combined with a good design plan and the right equipment to give optimum performance. To select the best proppant for each well, a general understanding of available proppants is imperative.

They should have high permeability at the respective formation pressures, high resistance to compression, low density, and good resistance to acids. Some propping agents are listed in Table 17.17.

Sand

Sand is the simplest proppant material. It is cheap, but shows a comparatively strong reduction in permeability at higher stresses.

Ceramic Particles

Fired ceramic spheroids have been described for use as a well proppant (Laird and Beck, 1989). Each spheroid has a core made from mineral particulates, silicium carbide, and a binder. The mixture includes a mineral with chemically bound water or sulfur, which blows the mixture during firing, giving the core a number of closed air cells. Each spheroid has an outer shell of a metal oxide selected from aluminum oxide and magnesium oxide. The fired ceramic spheroids have a density of less than $2.2\,\mathrm{g\,cm^{-3}}$.

TABLE 17.17 Basic Propping Materials

Material	Description/Property	References
Bauxite	Standard	Andrews (1986), and Fitzgibbon (1986)
Bauxite + ZrO_2	Stress corrosion resistant	Khaund (1987a,c)
Sand	Low permeability at higher pressures	
Light weights	Specific gravity control	Bienvenu (1996a)
Ceramic		Gibb et al. (1988, 1990)
Clay		Fitzgibbon (1988, 1989), and Khaund (1987b)

Bauxite

Sintered bauxite spheres containing silica are standard proppant materials. The particles have a size range from 0.02–0.3 μ. They are enhanced to resist stress corrosion by inclusion of 2% zirconia in the mix before firing. A process for manufacturing a suitable material is characterized by the following steps (Andrews, 1988).

A fine fraction is separated from naturally occurring bauxite, which will contain mostly monomineralic particles of gibbsite, boehmite, and kaolinite. The kaolinite represents no more than 25% of the total. The separated fine fraction is pelletized in the presence of water, which are then treated to remove water.

Light-weight Proppants

Light-weight propping agents have a specific gravity of less than 2.60 $\mathrm{g\,cm^{-3}}$. They are made from kaolin clay and a light-weight aggregate. Special conditions of calcination are necessary (Lemieux and Rumpf, 1994). Their alumina content is between 25% and 40% (Sweet, 1993). A high-strength proppant has been described (Bienvenu, 1996b) with a specific gravity of less than 1.3 $\mathrm{g\,cm^{-3}}$.

Porous Pack with Fibers

It is possible to build a porous pack within the formation that is a mixture of fibers and the proppant. The fibrous material may be natural or synthetic organic fibers, glass fibers, ceramic fibers, or carbon fibers.

A porous pack filters out unwanted particles, proppant, and fines, while still allowing the production of oil. Using fibers to make a porous pack of fibers and a proppant within the formation reduces energy consumption by equipment. Pumping the fibers together with the proppant provides significant reductions in the frictional forces that otherwise limit the pumping of fluids containing a proppant (Card et al., 2001).

Coated Proppants

Typically, particulates, such as graded sand, suspended in a portion of the fracturing fluid are deposited in the fractures when the fracturing fluid is converted to a thin fluid to be returned to the surface. These particulate solids, or proppant particulates, serve to prevent the fractures from fully closing, and form conductive channels through which produced hydrocarbons can flow (Dusterhoft et al., 2008).

To prevent the subsequent flowback, the proppant may be coated with a curable resin or tackifying agent, which facilitates the consolidation of particles in the fracture. The partially closed fractures apply pressure to the coated proppant particulates, which forces them into contact with each other, at which point the resin or tackifying agent enhances the grain-to-grain contact between them. This ensures the consolidation of the proppant particles into a permeable mass with compressive and tensile strength, while still allowing small amounts of deformation at the surface of the proppant packs, to reduce the effects of point loading or to reduce proppant crushing (Dusterhoft et al., 2008).

An epoxy resin composition typically includes an oligomeric bisphenol-A epichlorohydrin resin, a 4,4′-diaminodiphenyl sulfone curing agent, a solvent, a silane coupling agent, and a surfactant (Nguyen et al., 2007).

In a series of experiments, three different types of proppant particulates were assessed using a two-component high-temperature epoxy resin system (Dusterhoft et al., 2008). In each experiment, 3% resin was used with bauxite, an intermediate strength proppant, and a lightweight proppant. These proppants are known to withstand pressures from 40 MPa to 80 MPa without substantial crushing. The test temperature was 120°C for all tests (Dusterhoft et al., 2008).

The stress was continuously increased from 14 MPa to 80 MPa over several days. Uncoated proppant particulates were also tested. The effects of the closure stresses and flow rates on resin-treated proppant were evaluated by using an API linear conductivity cell.

The conductivity and permeability of each proppant pack was continuously monitored at 14 MPa (2000 psi) and 120°C (250°F) for 25–30 h.

For all the three proppants, the fracture conductivity and proppant pack permeability were greater for the coated proppants than the uncoated proppants. The improvement was pronounced under lower stress conditions. There was an evidence for the coated proppants, that a much more stable interface was created between the proppant and the formation material.

The propping particles can be individually coated with a curable thermoset coating, which enhances the chemical resistance of the proppants. This modification is necessary if a proppant is not stable against the additives in the fracturing fluid, such as an acid gel breaker. Resole-type phenolic resins are recommended as coating materials in the presence of oxidative gel breakers (Dewprashad, 1995). Polymer coatings for propping agents are listed in Table 17.18.

Coating reduct also reduces friction between the proppant particles (de Grood and Baycroft, 2010). Coating materials are summarized in Table 17.19. Not all of these materials are economically viable. Multiple coatings of particulate material result in a final coated product that has a smooth, uniform surface.

Anti-settling Additives

Proppant transport inside a hydraulic fracture has two components when the fracture is being generated. The horizontal component is dictated by the fluid velocity and by the associated streamlines, which help to carry the proppant to the tip of the fracture. The vertical component is dictated by the terminal particle settling velocity, and is a function of proppant diameter and density and fluid viscosity and density (Watters et al., 2010).

TABLE 17.18 Polymer Coatings for Propping Agents

Material	References
Phenolic/furan resin or furan resin[a]	Armbruster (1987)
Novolak epoxide resin[a]	Gibb et al. (1989)
Pyrolytic carbon coating[a]	Hudson and Martin (1989)
Bisphenolic resin[b]	
Phenolic resin	Johnson et al. (1993a,b)
Furfuryl alcohol resin[b]	Ellis and Surles (1997)
Bisphenol-A resin (curable)[b]	Johnson and Tse (1996)
Epoxide resin with *N*-β-(aminoethyl)-δ-aminopropyltrimethoxysilane crosslinker	Nguyen et al. (2001)
PA and others	Nguyen and Weaver (2001)

a) Chemically resistant
b) Flowback prevention

An additive with a lower density than the fluid medium can be used to vary the density gradients inside the fracture. The upward movement of the low-density additive will interfere with the downward movement of high-density proppant and vice versa, and this mutual interference will significantly hinder the settling of the high-density proppant. This can be used to control the settling time of the proppant.

The low-density material should have a particle size distribution similar to that of a standard proppant. Examples of such materials are polylactic acid particles or glass beads. The influence of such a low density additive on the settling time is summarized in Table 17.20.

The tests were conduced in a 15 $\mathrm{lb\,Mgal^{-1}}$ (1.8 $\mathrm{g\,m^{-3}}$) guar-based linear gel with an apparent viscosity of 8 cP at 511 $\mathrm{s^{-1}}$. The gel contained a proppant concentration of 240 $\mathrm{kg\,m^{-3}}$ with a diameter of 30/50 mesh.

Proppant Flowback

The flowback of a proppant following fracture stimulation treatment is a major concern because of potential damage to equipment and loss in well production. The mechanisms involved and the methods to control it have been discussed in the literature (Nguyen et al., 1996a). A curable resin-coated proppant (Nimerick et al., 1990), which must be placed across the producing interval can be applied to prevent or reduce the proppant flowback.

TABLE 17.19 Friction Reducing Materials (de Grood and Baycroft, 2010)

Material
Antimony trioxide
Bismuth
Boric acid
Calcium barium fluoride
Copper
Graphite
Indium
Lead oxide
Lead sulfide
Molybdenum disulfide
Niobium diselenide
Fluoropolymers
Polytetrafluoroethylene
Silver
Tin
Tungsten disulfide
Zinc oxide

TABLE 17.20 Time of Settling in Presence of a Low-density Additive (Watters et al., 2010)

Distance/[ft]	Time to Settle/[s]	
Additive Added→	[0%]	[5%]
1	8	11
2	22	42
3	47	61
4	56	77

Thermoplastic Films

Thermoplastic film (Nguyen et al., 1996a,b) materials have been developed. A heat-shrinkable film cut into thin slivers provides flowback reduction over broad temperature ranges and closure stress ranges, and was found to cause little impairment to fracture conductivity with some dependency on use concentration, temperature, and closure stress.

Adhesive-coated Material

The addition of an adhesive-coated material to proppants decreases the flowback of the particulates (Caveny et al., 1996). The adhesive-coated material interacts mechanically with the proppant particles to prevent the flowback of particulates to the wellbore. The materials can be inorganic or organic fibers.

The consolidation of a proppant also may occur with a polyurethane coating, which will slowly polymerize after the fracturing treatment because of a polyaddition process (Wiser-Halladay, 1990).

Magnetized Material

Magnetized beads, fibers, strips, or particles can be placed with a proppant. The magnetized material moves to voids or channels where it forms clusters held together by magnetic attraction, which in turn facilitate the formation of permeable proppant bridges.

The magnetized material/proppant bridges retard and ultimately prevent the flowback of proppant and formation solids, but still allow production of oil and gas through the fracture at sufficiently high rates (Clark et al., 2000). In a similar way, fibrous bundles placed with the proppant may act in a fracture as a flowback preventer (Nguyen and Schreiner, 1999).

ACID FRACTURING

A difference exists between acid fracturing and matrix acidizing. Acid fracturing is used for low-permeability, acid-soluble rocks, whereas matrix acidizing is a technique used for high-permeability reservoirs. Formations such as limestones ($CaCO_3$) or dolomites ($CaCO_3 \times MgCO_3$) are candidates for acid fracturing. These materials react easily with hydrochloric acid to form chlorides and carbon dioxide, and this technique has the advantage that no problem with proppant clean-out will appear. The acid etches the fracture faces unevenly, which on closure forms a highly conductive channel for the reservoir fluid to flow into the wellbore (Mukherjee and Cudney, 1993).

On the other hand, shorter, fractures are formed, because the acid reacts with the formation and therefore is spent. Also, if traces of fluoride are present in the hydrochloric acid, then insoluble calcium fluoride precipitates out, and plugging by the precipitate can jeopardize the desired effect of stimulation.

Encapsulated Acids

Acids and etching agents in general, may be mixed with a gelling agent and encapsulated with oils and polymers (Gonzalez and Looney, 2000, 2001).

The In Situ Formation of Acids

The acid fracturing of sandstone formations has not been common practice due to the low rock solubility of mud acid, but useful methods and compositions have been developed. Such a method consists of (Qu and Wang, 2010):

1. Injecting an acid fracturing fluid into the formation at a pressure sufficient to form fractures within the formation. The fluid comprises a sulfonate ester, a fluoride salt, a proppant, and water; the sulfonate ester is hydrolyzed to produce sulfonic acid.
2. Producing hydrofluoric acid in situ in the formation by reacting the sulfonic acid with the fluoride salt after injection of the acid fracturing fluid into the formation.

Generating hydrofluoric acid in situ makes it possible to perform acid fracturing of sandstone formations with the assistance of partial monolayers of effectively placed propping agents and to create enlarged, propped fractures. Increased fracture width will lead to higher fracture conductivity and enhanced hydrocarbon production than is generally achievable by a conventional propped fracturing treatment.

Fluid Loss

Fluid loss limits the effectiveness of acid fracturing treatments, so formulations to control this have been developed and characterized (Sanford et al., 1992; White et al., 1992). It was discovered that viscosifying the acid improved acid fluid loss control. The enhancement was most pronounced in very low permeability limestone cores. The nature of the viscosifying agent also influenced the success, with polymeric materials being more effective than surfactant type viscosifiers (Gdanski, 1993).

A viscosity-controlled acid contains gels that break back to their original viscosity one day after being pumped. These acids have been used both for matrix acidizing and for fracture acidizing to obtain longer fractures. The pH of the fluid controls the gel formation and breaking. The gels are limited to formation temperatures of 50–135°C (Yeager and Shuchart, 1997).

Gel Breaker for Acid Fracturing

A particulate gel breaker for acid fracturing for gels crosslinked with titanium or zirconium compounds is composed of complexing materials such as fluoride, phosphate, sulfate anions, and multicarboxylated compounds. The particles are coated with a water-insoluble resin coating, which reduces the rate of release of the breaker materials of the particles so that the viscosity of the gel is reduced at a slower rate (Boles et al., 1996).

SPECIAL PROBLEMS

Corrosion Inhibitors

Water-soluble 1,2-dithiol-3-thiones for fracturing fluids and other workover fluids have been described as corrosion inhibitors for aqueous environments (Oude Alink, 1993). These compounds are prepared by reacting a PEO capped with isopropylphenol with elemental sulfur.

The compounds perform better in aqueous systems than their nonoxylated analogs. The concentration range is usually in the 10–500 ppm range, based on the weight of the water in the system.

The Problem of Iron Control in Fracturing

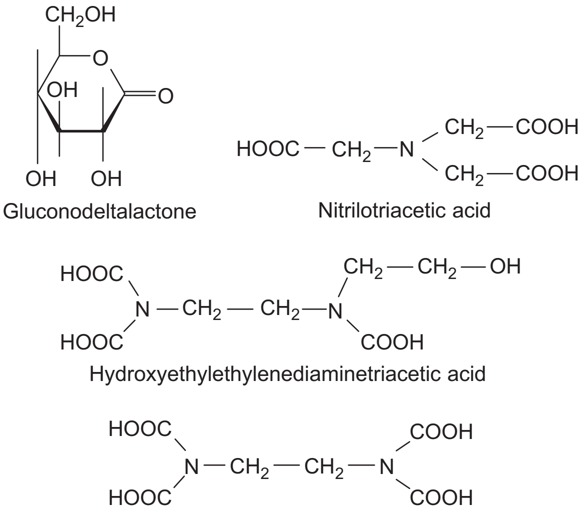
Results from laboratory tests and field work show that iron presents a significant and complex problem in stimulation operations (Smolarchuk and Dill, 1986). The problem differs with acidizing and nonacidic or weakly acidic fracturing fluids.

In acidic situations, the fluid dissolves iron compounds from the equipment and the flow lines as it is mixed and pumped into the formation.

The acid may dissolve additional iron as it reacts with the formation, which could precipitate if the fluid does not contain an effective iron control system. This precipitate may then accumulate as it is carried toward the wellbore during flowback, which could decrease the natural and created permeability and so have a detrimental effect on the recovery of the treating fluid and on production.

Iron can be controlled by complexing agents, such as glucono-δ-lactone, citric acid, ethylene diamine tetraacetic acid, nitrilo triacetic acid, hydroxyethylethylene diaminetriacetic acid, hydroxyethyliminodiacetic acid, and the salts of these compounds. They must be added together with nitrogen-containing compounds, such as hydroxylamine salts or hydrazine salts (Dill et al., 1988; Frenier, 2001; Walker et al., 1987). These complexing agents are shown in Figure 17.30. In general, chelating agents possess some unique chemical characteristics, the most significant of which is the high solubility of the free acids in aqueous solutions.

Linear coreflood tests were used to study the formation of wormholes. Both hydroxyethylethylene diaminetriacetic acid and hydroxyethyliminodiacetic acid produced wormholes in limestone cores when tested at 65°C (150°F), but their efficiency and capacities differ. Because these chemicals have high solubility in the acidic pH range, it was possible to test acidic formulations with pH of less than 3.5 (Frenier et al., 2001).



Gluconodeltalactone

Nitrilotriacetic acid

Hydroxyethylethylenediaminetriacetic acid

Ethylenediaminetetraacetic acid

FIGURE 17.30 Complexing agents for iron control.

To control the iron in an aqueous fracturing fluid with a pH below 7.5, a thioalkyl acid may be added (Brezinski et al., 1994). This is a reducing agent for ferric iron, in contrast to the complexants described in the previous paragraph.

Enhanced Temperature Stability

During the initial fracturing process, degradation resulting in a decrease of viscosity is undesirable. The polymer in fracturing fluids will degrade at elevated temperatures.

One method for preventing premature degradation is to cool down the formation with large volumes of pad solution before fracturing. The temperature stability of the fracturing fluid is extended by adding quantities of unhydrated, particulate guar or guar-derivative polymers before pumping it into the formation (Nimerick and Boney, 1992). Adjustment of the pH to moderate alkaline conditions can also improve stability.

The preferred crosslinkers for high-temperature applications are zirconium compounds. A formulation for a high-temperature guar-based fracturing fluid is given in Table 17.21. The fracturing fluid exhibits good viscosity and is stable at moderate to high temperatures, that is, 80–120°C.

Chemical Blowing

The efficiency of a fracturing fluid recovered from a formation can be increased by adding blowing agents (Abou-Sayed and Hazlett, 1989; Jennings, 1995).

TABLE 17.21 Formulation for a High-temperature Guar-Based Fracturing Fluid (Brannon et al., 1989)

Component	Action
Guar gum	Thickener
Zirconium or hafnium compound	Crosslinking agent
Bicarbonate salt	Buffer

TABLE 17.22 Frost-resistant Formulation for Hydraulic Fracturing Fluids (Barsukov et al., 1993)

Component	%
Hydrocarbon phase[a]	2 to 20
Surfactant	
Mineralized water	
Sludge from production of sulfonate additives (hydrocarbons 10–30%, calcium sulfonate 20–30%, calcium carbonate and hydroxide 18–40%)[b]	10 to 35
Emultal[c]	0.5 to 2.0

a) Gas condensate, oil, or benzene
b) Slows down filtration and increases sand-holding capability, frost resistance, and stability
c) Surfactant-emulsifier

After placing the blowing agent, for example, agglomerated particles and granules containing the blowing agent of dinitrosopentamethylenetetramine, sodium hydrogen carbonate and *p*-toluene sulfonyl hydrazide, azodicarbonamide, and *p*,*p*-oxybis(benzenesulfonyl hydrazide) and fracturing the formation, the blowing agent decomposes. The filter cake hence becomes more porous or provides a driving force for the removal of fluid load from the matrix.

Increased porosity enhances the communication between the formation and the fracture, thus increasing the efficiency of the production of the fracturing fluid. The gas liberation within the matrix establishes communication pathways between subsequent fractures and the well.

Frost-resistant Formulation

A frost-resistant formulation is given in Table 17.22, which is stable from −35 to −45°C (Barsukov et al., 1993).

Formation Damage in Gas Wells

Studies (Gall et al., 1988) on formation damage using artificially fractured, low permeability sandstone cores indicated that viscosified fracturing fluids can severely restrict the gas flow through narrow fractures. Polysaccharide polymers, such as hydroxypropyl guar, HEC, and xanthan gum caused a significant reduction in gas flow through the cracked cores, by up to 95%.

In contrast, PAM gels caused little or no reduction in the gas flow through cracked cores after a liquid clean-up. Other components of fracturing fluids, such as surfactants and breakers, caused less damage to gas flows.

CHARACTERIZATION OF FRACTURING FLUIDS

Historically, viscosity measurements have been the single most important method for characterizing fluids in petroleum-producing applications. The ability to measure a fluid's resistance to flow has been available in the laboratory for a long time, but the need to measure fluid properties at the well site has prompted the development of more portable and less sophisticated viscosity-measurement devices (Parks et al., 1986). These instruments must be durable and simple enough to be used by persons with a wide range of technical skills. As a result, the Marsh funnel and the Fann concentric cylinder, both variable-speed viscometers, have found wide use, and in some instances, the Brookfield viscometer has also been used.

It has been established that an intense control of certain variables may improve the execution of a hydraulic fracturing job and the success of a stimulation, meaning that intense quality control is recommended (Ely, 1996; Ely et al., 1990). This includes monitoring the breaker performance at low temperatures and measuring the sensitivity of fracturing fluids to variations in crosslinker loading, temperature stabilizers, and other additives at higher temperatures.

Rheological Characterization

To design a successful hydraulic fracturing treatment employing crosslinked gels, accurate measurements of rheological properties of these fluids are required. This turned out to be difficult with a rotational viscometer. In a laboratory apparatus, field pumping conditions (i.e., crosslinking the fluid on the fly) and fluid flow down tubing or casing and in the fracture could be simulated (Shah et al., 1988), and the effects of the pH and temperature of the fluid and the type and concentration of the gelling agent could be determined.

These parameters have a significant effect on the final viscosity of the gel in the fracture. Correlations to estimate friction pressures in field size tubulars have been developed from laboratory test data. In conjunction with field calibrations, these correlations can aid in the accurate prediction of the friction pressure of borate crosslinked fluids.

Zirconium-based Crosslinking Agent

The concentration of a crosslinking agent containing zirconium in a gel is determined by first adding an acid to break the gel, and convert the zirconium into the ionic, noncomplexed form (Chakrabarti and Marczewski, 1990). This is followed by the addition of Arsenazo (III) to produce a colored complex, which can be determined with standard colorimetric methods. Arsenic compounds are highly toxic. The colorimetric reagent to measure zirconium in gels is shown in Figure 17.31.

Oxidative Gel Breaker

The concentration of an oxidative gel breaker can be measured by colorimetric methods, by periodically or continuously sampling the gel (Chakrabarti et al., 1988). The colorimetric reagent is sensitive to oxidizing agents. It contains iron ions and thiocyanate. Thus the quantity of breaker added to the fracturing fluid can be controlled. The method is based on the oxidation of ferrous ions to ferric ions:

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

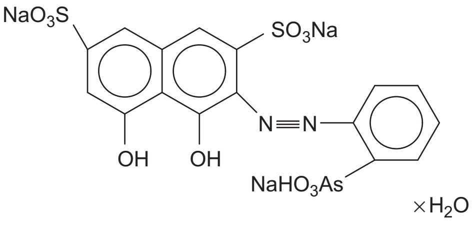
which form a deep red complex with thiocyanate.

Size Exclusion Chromatography

Size exclusion chromatography (Brannon and Tjon, 1995; Gall and Raible, 1986) has been used to monitor the degradation of the thickeners initiated by various oxidative and enzymatic breakers.

Assessment of Proppants

There are standardized methods for the characterization of the effect of proppants (API Standard API RP 19C, 2008; ISO Standard ISO-13503-5, 2006). The general methods of assessment have been exemplified (Wen et al., 2007).



Arsenazo I

FIGURE 17.31 Colorimetric reagent to measure zirconium in gels.

For some proppants, the experiments reveal polynomial relationships between the long-term fracture conductivity and the closure pressure (Wen et al., 2007)

$$F = A_1 + A_2 P + A_3 P^2 + A_4 P^3, \tag{17.2}$$

where F is the long-term fracture conductivity, P is the closure pressure, and A_i are constants. Similarly, an exponential relationship between fracture conductivity F and time t has been obtained for a certain closure pressure (Wen et al., 2007),

$$F = \exp(-A_5 t) + A_6. \tag{17.3}$$

REFERENCES

Abou-Sayed, I.S., Hazlett, R.D., 1989. Removing fracture fluid via chemical blowing agents. US Patent 4 832 123, assigned to Mobil Oil Corp., May 23, 1989.

Acker, D.B., Malekahmadi, F., 2001. Delayed release breakers in gelled hydrocarbons. US Patent 6 187 720, February 13, 2001.

Aften, C.W., Gabel, R.K., 1992. Clay stabilizing method for oil and gas well treatment. US Patent 5 099 923, assigned to Nalco Chemical Co., March 31, 1992.

Aggour, T.M., Economides, M.J., 1996. Impact of fluid selection on high-permeability fracturing. In: Proceedings Volume, Vol. 2, SPE Europe Petroleum Conference, Milan, Italy, October 22–24, 1996, pp. 281–287.

Ahlgren, J.A., 1993. Enzymatic hydrolysis of xanthan gum at elevated temperatures and salt concentrations. In: Proceedings Volume, 6th Institute of Gas Technology, Gas, Oil, & Environmental Biotechnology International Symposium, Colorado Springs, CO, November 29–December 1, 1993.

Ainley, B.R., McConnell, S.B., 1993. Delayed borate crosslinked fracturing fluid. EP Patent 528 461, assigned to Pumptech NV and Dowell Schlumberger SA, February 24, 1993.

Ainley, B.R., Nimerick, K.H., Card, R.J., 1993. High-temperature, borate-crosslinked fracturing fluids: A comparison of delay methodology. In: Proceedings Volume, SPE Production Operations Symposium, Oklahoma City, March 21–23, 1993, pp. 517–520.

Allan, T.L., Amin, J., Olson, A.K., Pierce, R.G., 2008. Fracturing fluid containing amphoteric glycinate surfactant. US Patent 7 399 732, assigned to Calfrac Well Services Ltd. (Calgary, Alberta, CA) Chemergy Ltd. (Calgary, Alberta, CA), July 15, 2008.

Andrews, W.H., 1986. Process for making a new type of propping agent derived from bauxite for use in hydraulic fracturing, and material for use as a propping agent (procede pour la production d'un nouveau type d'agent de soutenement derive de la bauxite pour l'utilisation dans la fracturation hydraulique, et matiere propre a etre utilisee comme agent de soutenement). FR Patent 2 582 346, November 28, 1986.

Andrews, W.H., 1988. Sintered bauxite pellets and their application as proppants in hydraulic fracturing. AU Patent 579 242, November 17, 1988.

Anonymous, 1999. Fracturing products and additives. World Oil 220 (8), 135,137,139–145.

API Standard API RP 19C, 2008. Recommended practice for measuring the long-term conductivity of proppants. American Petroleum Institute, Washington, DC.

Armbruster, D.R., 1987. Precured coated particulate material. US Patent 4 694 905, September 22, 1987.

Barkat, O., 1987. Rheology of flowing, reacting systems: The crosslinking reaction of hydroxypropyl guar with titanium chelates. Ph.D. thesis, Tulsa Univ.

Barsukov, K.A., Ismikhanov, V.Y., Akhmetov, A.A., Pop, G.S., Lanchakov, G.A., Sidorenko, V.M., 1993. Composition for hydro-bursting of oil and gas strata – consists of hydrocarbon phase, sludge from production of sulphonate additives to lubricating oils, surfactant-emulsifier and mineralised water. SU Patent 1 794 082, assigned to Urengoi Prod. Assoc., February 7, 1993.

Barthorpe, R.T., 1993. The impairment of scale inhibitor function by commonly used organic anions. In: Proceedings Volume, SPE Oilfield Chemistry International Symposium, New Orleans, March 2–5, 1993, pp. 69–76.

Bharat, P., 1990. Well treating fluids and additives therefor. EP Patent 372 469, June 13, 1990.

Bielewicz, V.D., Kraj, L., 1998. Laboratory data on the effectivity of chemical breakers in mud and filtercake (Untersuchungen zur Effektivität von Degradationsmitteln in Spülungen). Erdöl Erdgas Kohle 114 (2), 76–79.

Bienvenu Jr., R.L., 1996a. Lightweight proppants and their use in hydraulic fracturing. US Patent 5 531 274, July 2, 1996.

Bienvenu Jr., R.L., 1996b. Lightweight proppants and their use in hydraulic fracturing. WO Patent 9 604 464, February 15, 1996.

Boles, J.L., Metcalf, A.S., Dawson, J.C., 1996. Coated breaker for crosslinked acid. US Patent 5 497 830, assigned to BJ Services Co., March 12, 1996.

Bonekamp, J.E., Rose, G.D., Schmidt, D.L., Teot, A.S., Watkins, E.K., 1993. Viscoelastic surfactant based foam fluids. US Patent 5 258 137, assigned to Dow Chemical Co., November 2, 1993.

Brannon, H.D., 1988. Fracturing fluid slurry concentrate and method of use. EP Patent 280 341, August 31, 1988.

Brannon, H.D., Hodge, R.M., England, K.W., 1989. High temperature guar-based fracturing fluid. US Patent 4 801 389, assigned to Dowell Schlumberger Inc., January 31, 1989.

Brannon, H.D., Tjon-Joe-Pin, R.M., 1994. Biotechnological breakthrough improves performance of moderate to high-temperature fracturing applications. In: Proceedings Volume, Vol. 1, 69th Annual SPE Technical Conference, New Orleans, September 25–28, 1994, pp. 515–530.

Brannon, H.D., Tjon, J.P.R.M., 1995. Characterization of breaker efficiency based upon size distribution of polymeric fragments. In: Proceedings Volume, Annual SPE Technical Conference and Exhibition, Dallas, TX, October 22–25, 1995, pp. 415–429.

Brezinski, M., Gardner, T.R., Harms, W.M., Lane Jr., J.L., King, K.L., 1994. Controlling iron in aqueous well fracturing fluids. EP Patent 599 474, assigned to Halliburton Co., June 1, 1994.

Burdick, C.L., Pullig, J.N., 1993. Sodium formate fluidized polymer suspensions process. US Patent 5 228 908, assigned to Aqualon Co., July 20, 1993.

Cantu, L.A., Boyd, P.A., 1989. Laboratory and field evaluation of a combined fluid-loss control additive and gel breaker for fracturing fluids. In: Proceedings Volume, SPE Oilfield Chemistry International Symposium, Houston, TX, February 8–10, 1989, pp. 7–16.

Cantu, L.A., McBride, E.F., Osborne, M., 1990a. Formation fracturing process. EP Patent 401 431, assigned to Conoco Inc. and Du Pont De Nemours & Co., December 12, 1990.

Cantu, L.A., McBride, E.F., Osborne, M., 1990b. Well treatment process. EP Patent 404 489, assigned to Conoco Inc. and Du Pont De Nemours & Co., December 27, 1990.

Cantu, L.A., McBride, E.F., Osborne, M.W., 1993. Formation fracturing process. CA Patent 1 319 819, assigned to Conoco Inc., July 6, 1993.

Card, R.J., Howard, P.R., Feraud, J.P., Constien, V.G., 2001. Control of particulate flowback in subterranean wells. US Patent 6 172 011, assigned to Schlumberger Technol. Corp., January 9, 2001.

Carpenter, J.F., 2007. Breaker composition and process. US Patent 7 223 719, assigned to Albemarle Corporation, Richmond, VA, May 29, 2007.

Carpenter, J.F., 2009. Bromine-based sulfamate stabilized breaker composition and process. US Patent 7 576 041, assigned to Albemarle Corporation, Baton Rouge, LA, August 18, 2009.

Caveny, W.J., Weaver, J.D., Nguyen, P.D., 1996. Control of particulate flowback in subterranean wells. US Patent 5 582 249, December 10, 1996.

Cawiezel, K.E., Elbel, J.L., 1990. A new system for controlling the crosslinking rate of borate fracturing fluids. In: Proceedings Volume, 60th Annual SPE California Regional Meeting, Ventura, California, April 4–6, 1990, pp. 547–552.

Cawiezel, K.E., Navarrete, R.C., Constien, V.G., 1999. Fluid loss control. US Patent 5 948 733, assigned to Dowell Schlumberger Inc., September 7, 1999.

Chakrabarti, S., Marczewski, C.Z., 1990. Determining the concentration of a cross-linking agent containing zirconium. GB Patent 2 228 996, assigned to British Petroleum Co. Ltd., September 12, 1990.

Chakrabarti, S., Martins, J.P., Mealor, D., 1988. Method for controlling the viscosity of a fluid. GB Patent 2 199 408, assigned to British Petroleum Co. Ltd., July 6, 1988.

Chatterji, J., King, B.J., King, K.L., 2007. Recyclable foamed fracturing fluids and methods of using the same. US Patent 7 205 263, assigned to Halliburton energy Services, Inc., Duncan, OK, April 17, 2007.

Clark, M.D., Walker, P.L., Schreiner, K.L., Nguyen, P.D., 2000. Methods of preventing well fracture proppant flow-back. US Patent 6 116 342, assigned to Halliburton Energy Service, September 12, 2000.

Conway, M.W., Schraufnagel, R.A., 1995. The effect of fracturing fluid damage on production from hydraulically fractured wells. In: Proceedings Volume, Ala Univ. et al Int. Unconven. Gas Symposium, Intergas 95, Tuscaloosa, AL, May 14–20, 1995, pp. 229–236.

Cooke Jr., C.E., 2009. Method and materials for hydraulic fracturing of wells using a liquid degradable thermoplastic polymer. US Patent 7 569 523, August 4, 2009.

Cottrell, T.L., Spronz, W.D., Weeks III, W.C., 1988. Hugoton infill program uses optimum stimulation technique. Oil Gas J. 86 (28), 88–90.

Couillet, I., Hughes, T., 2008. Aqueous fracturing fluid. US Patent 7 427 583, assigned to Schlumberger Technology Corporation, Ridgefield, CT, September 23, 2008.

Craig, D.P., 1991. The degradation of hydroxypropyl guar fracturing fluids by enzyme, oxidative, and catalyzed oxidative breakers, Ph.D. thesis, Texas A & M Univ.

Craig, D., Holditch, S.A., 1993a. The degradation of hydroxypropyl guar fracturing fluids by enzyme, oxidative, and catalyzed oxidative breakers: Pt.1: Linear hydroxypropyl guar solutions: Topical report, February-December 1991, Gas Res Inst Rep GRI-93/04191, Gas Res Inst., December 1993.

Craig, D., Holditch, S.A., 1993b. The degradation of hydroxypropyl guar fracturing fluids by enzyme, oxidative, and catalyzed oxidative breakers: Pt.2: Crosslinked hydroxypropyl guar gels: Topical report, January-April 1992, Gas Res Inst Rep GRI-93/04192, Gas Res Inst, December 1993.

Craig, D., Holditch, S.A., Howard, B., 1992. The degradation of hydroxypropyl guar fracturing fluids by enzyme, oxidative, and catalyzed oxidative breakers. In: Proceedings Volume, 39th Annual Southwestern Petroleum Short Course Association, Inc. et al Mtg., Lubbock, TX, April 22–23, 1992, pp. 1–19.

Crews, J.B., 2006. Bacteria-based and enzyme-based mechanisms and products for viscosity reduction breaking of viscoelastic fluids. US Patent 7 052 901, assigned to Baker Hughes Incorporated, Houston, TX, May 30, 2006.

Crews, J.B., 2007a. Aminocarboxylic acid breaker compositions for fracturing fluids. US Patent 7 208 529, assigned to Baker Hughes Incorporated, Houston, TX, April 24, 2007.

Crews, J.B., 2007b. Polyols for breaking of fracturing fluid. US Patent 7 160 842, assigned to Baker Hughes Incorporated, Houston, TX, January 9, 2007.

Crews, J.B., 2010. Saponified fatty acids as breakers for viscoelastic surfactant-gelled fluids. US Patent 7 728 044, assigned to Baker Hughes Incorporated, Houston, TX, June 1, 2010.

Crews, J.B., Huang, T., Gabrysch, A.D., Treadway, J.H., Willingham, J.R., Kelly, P.A., Wood, W.R., 2010. Methods and compositions for fracturing subterranean formations. US Patent 7 723 272, assigned to Baker Hughes Incorporated, Houston, TX, May 25, 2010.

Dawson, J.C., 1992. Method for delaying the gellation of borated galactomannans with a delay additive such as glyoxal. US Patent 5 160 643, assigned to BJ Services Co., November 3, 1992.

Dawson, J.C., 1995. Method and composition for delaying the gellation of borated gallactomannans. GB Patent 2 253 868, assigned to BJ Services Co., April 5, 1995.

Dawson, J.C., Le, H.V., 1995. Controlled degradation of polymer based aqueous gels. US Patent 5 447 199, assigned to BJ Services Co., September 5, 1995.

Dawson, J.C., Le, H.V., 1998. Gelation additive for hydraulic fracturing fluids. US Patent 5 798 320, assigned to BJ Services Co., August 25, 1998.

de Grood, R.J.C., Baycroft, P.D., 2010. Use of coated proppant to minimize abrasive erosion in high rate fracturing operations. US Patent 7 730 948, assigned to Baker Hughes Incorporated, Houston, TX, June 8, 2010.

Dewprashad, B., 1995. Method of producing coated proppants compatible with oxidizing gel breakers. US Patent 5 420 174, assigned to Halliburton Co., May 30, 1995.

Dill, W.R., Ford, W.G.F., Walker, M.L., Gdanski, R.D., 1988. Treatment of iron-containing subterranean formations. EP Patent 258 968, March 9, 1988.

Doherty, D.H., Ferber, D.M., Marrelli, J.D., Vanderslice, R.W., Hassler, R.A., 1992. Genetic control of acetylation and pyruvylation of xanthan based polysaccharide polymers. WO Patent 9 219 753, assigned to Getty Scientific Dev Co., November 12, 1992.

Dusterhoft, R.G., Fitzpatrick, H.J., Adams, D., Glover, W.F., Nguyen, P.D., 2008. Methods of stabilizing surfaces of subterranean formations. US Patent 7 343 973, assigned to Halliburton Energy Services, Inc., Duncan, OK, March 18, 2008.

Ebinger, C.D., Hunt, E., 1989. Keys to good fracturing: Pt.6: New fluids help increase effectiveness of hydraulic fracturing. Oil Gas J. 87 (23), 52–55.

Elbel, J.L., Navarrete, R.C., Poe Jr., B.D., 1995. Production effects of fluid loss in fracturing high-permeability formations. In: Proceedings Volume, SPE Europe Formation Damage Control Conference, The Hague, Netherland, May 15–16, 1995, pp. 201–211.

Ellis, P.D., Surles, B.W., 1997. Chemically inert resin coated proppant system for control of proppant flowback in hydraulically fractured wells. US Patent 5 604 184, assigned to Texaco Inc., February 18, 1997.

Ely, J.W., 1989. Fracturing Fluids and Additives, Vol. 12 of Recent Advances in Hydraulic Fracturing (SPE Henry L Doherty Monogr Ser). SPE, Richardson, Texas.

Ely, J.W., 1996. How intense quality control improves hydraulic fracturing. World Oil 217 (11), 59–60, 62–65, 68.

Ely, J.W., Wolters, B.C., Holditch, S.A., 1990. Improved job execution and stimulation success using intense quality control. In: Proceedings Volume, 37th Annual Southwestern Petroleum Short Course Association, et al Mtg., Lubbock, Texas, April 18–19, 1990, pp. 101–114.

Fitzgibbon, J.J., 1986. Use of uncalcined/partially calcined ingredients in the manufacture of sintered pellets useful for gas and oil well proppants. US Patent 4 623 630, November 18, 1986.

Fitzgibbon, J.J., 1988. Sintered, spherical, composite pellets prepared from clay as a major ingredient useful for oil and gas well proppants. CA Patent 1 232 751, February 16, 1988.

Fitzgibbon, J.J., 1989. Sintered spherical pellets containing clay as a major component useful for gas and oil well proppants. US Patent 4 879 181, November 7, 1989.

Fodge, D.W., Anderson, D.M., Pettey, T.M., 1996. Hemicellulase active at extremes of pH and temperature and utilizing the enzyme in oil wells. US Patent 5 551 515, assigned to Chemgen Corp., September 3, 1996.

Frenier, W.W., 2001. Well treatment fluids comprising chelating agents. WO Patent 0 183 639, assigned to Sofitech NV, Schlumberger Serv. Petrol, Schlumberger Canada Ltd., Schlumberger Technol. BV, and Schlumberger Holdings Ltd., November 8, 2001.

Frenier, W.W., Fredd, C.N., Chang, F., 2001. Hydroxyaminocarboxylic acids produce superior formulations for matrix stimulation of carbonates. In: Proceedings Volume, SPE Europe Formation Damage Control Conference, The Hague, Netherlands, May 21–22, 2001.

Gadberry, J.F., Hoey, M.D., Franklin, R., Del Carmen Vale, G., Mozayeni, F., 1999. Surfactants for hydraulic fracturing compositions. US Patent 5 979 555, assigned to Akzo Nobel NV, November 9, 1999.

Gall, B.L., Maloney, D.R., Raible, C.J., Sattler, A.R., 1988. Permeability damage to natural fractures caused by fracturing fluid polymers. In: Proceedings Volume, SPE Rocky Mountain Regional Meeting, Casper, Wyoming, May 11–13, 1988, pp. 551–560.

Gall, B.L., Raible, C.J., 1986. The use of size exclusion chromatography to study the degradation of water-soluble polymers used in hydraulic fracturing fluids. In: Proceedings 192nd ACS Nat Mtg, Vol. 55, Amer. Chem. Soc. Polymeric Mater Sci Eng. Div Tech. Program, Anaheim, California, September 7–12, 1986, pp. 572–576.

Gdanski, R.D., 1993. Fluid properties and particle size requirements for effective acid fluid-loss control. In: Proceedings Volume, SPE Rocky Mountain Regional Meeting: Low Permeability Reservoirs Symposium, Denver, April 26–28, 1993, pp. 81–94.

Geib, G.G., 2002. Hydrocarbon gelling compositions useful in fracturing formations. US Patent 6 342 468, assigned to Ethox Chemicals LLC, January 29, 2002.

Gibb, J.L., Laird, J.A., Berntson, L.G., 1989. Novolac coated ceramic particulate. EP Patent 308 257, March 22, 1989.

Gibb, J.L., Laird, J.A., Lee, G.W., Whitcomb, W.C., 1988. Particulate ceramic useful as a proppant. CA Patent 1 232 921, February 16, 1988.

Gibb, J.L., Laird, J.A., Lee, G.W., Whitcomb, W.C., 1990. Particulate ceramic useful as a proppant. US Patent 4 944 905, July 31, 1990.

Gonzalez, M.E., Looney, M.D., 2000. The use of encapsulated acid in acid fracturing treatments. WO Patent 0 075 486, assigned to Texaco Development Corp., Gonzalez, Manuel E., and Looney, Mark D., December 14, 2000.

Gonzalez, M.E., Looney, M.D., 2001. Use of encapsulated acid in acid fracturing treatments. US Patent 6 207 620, assigned to Texaco Inc., March 27, 2001.

Gregory, G., Shuell, D., Thompson Sr., J.E., 1991. Overview of contemporary LFC (liquid frac concentrate) fracture treatment systems and techniques. In: Proceedings Volume, no. 91-01, 4th Cade/caodc Spring Drilling Conf., Calgary, Can, April 10–12, 1991.

Gross, J.M., 1987. Gelling organic liquids. EP Patent 225 661, assigned to Dowell Schlumberger Inc., June 16, 1987.

Gulbis, J., King, M.T., Hawkins, G.W., Brannon, H.D., 1990a. Encapsulated breaker for aqueous polymeric fluids. In: Proceedings Volume, 9th SPE Formation Damage Control Symposium, Lafayette, LA, February 22–23, 1990, pp. 245–254.

Gulbis, J., Williamson, T.D.A., King, M.T., Constien, V.G., 1990b. Method of controlling release of encapsulated breakers. EP Patent 404 211, assigned to Pumptech NV and Dowell Schlumberger SA, December 27, 1990.

Gulbis, J., King, M.T., Hawkins, G.W., Brannon, H.D., 1992. Encapsulated breaker for aqueous polymeric fluids. SPE Prod. Eng. 7 (1), 9–14.

Guo, D.R., Gao, J.P., Lu, K.H., Sun, M.B., Wang, W., 1996. Study on the biodegradability of mud additives. Drill. Fluid Completion Fluid 13 (1), 10–12.

Gupta, D.V.S., Prasek, B.B., 1995. Method for fracturing subterranean formations using controlled release breakers and compositions useful therein. US Patent 5 437 331, assigned to Western Co. North America, August 1, 1995.

Hall, B.E., Szememyei, C.A., 1992. Fluid additive and method for treatment of subterranean formations. US Patent 5 089 151, assigned to Western Co. North America, February 18, 1992.

Harris, P.C., 1988. Fracturing-fluid additives. J. Pet. Technol. 40 (10), 1277–1279.

Harris, P.C., Heath, S.J., 1994. Delayed release borate crosslinking agent. EP Patent 594 364, assigned to Halliburton Co., April 27, 1994.

Harris, P.C., Heath, S.J., 1996. High-quality foam fracturing fluids. In: Proceedings Volume, SPE Gas Technology Symposium, Calgary, Canada, April 28–May 1, 1996, pp. 265–273.

Harris, R.E., Hodgson, R.J., 1995. Delayed acid for gel breaking. WO Patent 9 533 914, December 14, 1995.

Harris, P.C., Norman, L.R., Hollenbeak, K.H., 1994. Borate crosslinked fracturing fluids. EP Patent 594 363, assigned to Halliburton Co., April 27, 1994.

Harms, W.M., 1992. Catalyst for breaker system for high viscosity fluids. US Patent 5 143 157, assigned to Halliburton Co., September 1, 1992.

Harms, W.M., Norman, L.R., 1988. Concentrated hydrophilic polymer suspensions. US Patent 4 772 646, September 20, 1988.

Harms, W.M., Scott, E., 1993. Method for stimulating methane production from coal seams. US Patent 5 249 627, assigned to Halliburton Co., October 5, 1993.

Harms, W.M., Watts, M., Venditto, J., Chisholm, P., 1988. Diesel-based HPG (hydroxypropyl guar) concentrate is product of evolution. Pet. Eng. Int. 60 (4), 51–54.

Hawkins, G.W., 1986. Molecular weight reduction and physical consequences of chemical degradation of hydroxypropylguar in aqueous brine solutions. In: Proceedings 192nd ACS Nat Mtg, Vol. 55, Amer. Chem. Soc. Polymeric Mater Sci Eng. Div Tech. Program, Anaheim, California, September 7–12, 1986, pp. 588–593.

Heller, J., Barr, J., Ng, S.Y., Abdellauoi, K.S., Gurny, R., 2002. Polyortho esters: Synthesis, characterization, properties and uses. Adv. Drug Deliv. Rev. 54 (7), 1015–1039.

Himes, R.E., 1992. Method for clay stabilization with quaternary amines. US Patent 5 097 904, assigned to Halliburton Co., March 24, 1992.

Himes, R.E., Parker, M.A., Schmelzl, E.G., 1990. Environmentally safe temporary clay stabilizer for use in well service fluids. In: Proceedings Volume, Vol. 3, CIM Petrol. Soc/SPE International Technical Meeting, Calgary, Canada, June 10–13, 1990.

Himes, R.E., Vinson, E.F., 1989. Fluid additive and method for treatment of subterranean formations. US Patent 4 842 073, June 27, 1989.

Himes, R.E., Vinson, E.F., 1991. Environmentally safe salt replacement for fracturing fluids. In: Proceedings Volume, SPE East Regional Conference, Lexington, KY, October 23–25, 1991, pp. 237–248.

Himes, R.E., Vinson, E.F., Simon, D.E., 1989. Clay stabilization in low-permeability formations. In: Proceedings Volume, SPE Production Operations Symposium, Oklahoma City, March 12–14, 1989, pp. 507–516.

Hodge, R.M., 1997. Particle transport fluids thickened with acetylate free xanthan heteropolysaccharide biopolymer plus guar gum. US Patent 5 591 699, assigned to Du Pont De Nemours & Co., January 7, 1997.

Holditch, S.A., Xiong, H., Rahim, Z., Rueda, J., 1993. Using an expert system to select the optimal fracturing fluid and treatment volume. In: Proceedings Volume, SPE Gas Technology Symposium, Calgary, Canada, June 28–30, 1993, pp. 515–527.

Holtmyer, M.D., Hunt, C.V., 1988. Method and composition for viscosifying hydrocarbons. US Patent 4 780 221, October 25, 1988.

Holtmyer, M.D., Hunt, C.V., 1992. Crosslinkable cellulose derivatives. EP Patent 479 606, assigned to Halliburton Co., April 8, 1992.

Hrachovy, M.J., 1994. Hydraulic fracturing technique employing in situ precipitation. US Patent 5 322 121, assigned to Union Oil Co. California, June 21, 1994.

Hubbert, M.K., Willis, D.G., 1957. Mechanics of hydraulic fracturing. Trans. AIME 210, 153–168.

Huddleston, D.A., 1989. Hydrocarbon geller and method for making the same. US Patent 4 877 894, assigned to Nalco Chemical Co., October 31, 1989.

Hudson, T.E., Martin, J.W., 1989. Pyrolytic carbon coating of media improves gravel packing and fracturing capabilities. US Patent 4 796 701, January 10, 1989.

Hunt, C.V., Powell, R.J., Carter, M.L., Pelley, S.D., Norman, L.R., 1997. Encapsulated enzyme breaker and method for use in treating subterranean formations. US Patent 5 604 186, assigned to Halliburton Co., February 18, 1997.

ISO Standard ISO-13503-5, 2006. Petroleum and natural gas industries – Completion fluids and materials – Part 5: Procedures for measuring the long-term conductivity of proppants. International Organization for Standardization, Geneva, Switzerland.

Jennings Jr., A.R., 1995. Method of enhancing stimulation load fluid recovery. US Patent 5 411 093, assigned to Mobil Oil Corp., May 2, 1995.

Johnson, M., 1996. Fluid systems for controlling fluid losses during hydrocarbon recovery operations. EP Patent 691 454, assigned to Baker Hughes Inc., January 10, 1996.

Johnson, M.H., Smejkal, K.D., 1993. Fluid system for controlling fluid losses during hydrocarbon recovery operations. US Patent 5 228 524, assigned to Baker Hughes Inc., July 20, 1993.

Johnson, C.K., Tse, K.T., 1996. Bisphenol-containing resin coating articles and methods of using same. EP Patent 735 234, assigned to Borden Inc., October 2, 1996.

Johnson, C.K., Tse, K.T., Korpics, C.J., 1993a. Improved phenolic resin coated proppants with reduced hydraulic fluid interaction. EP Patent 542 397, May 19, 1993.

Johnson, C.K., Tse, K.T., Korpics, C.J., 1993b. Phenolic coated proppants with reduced hydraulic fluid interaction. CA Patent 2 067 261, May 15, 1993.

Jones, T.G.J., Tustin, G.J., 2010. Process of hydraulic fracturing using a viscoelastic wellbore fluid. US Patent 7 655 604, assigned to Schlumberger Technology Corporation, Ridgefield, CT, February 2, 2010.

Kanda, S., Kawamura, Z., 1988. Stabilization of xanthan gum in aqueous solution. GB Patent 2 192 402, January 13, 1988.

Kanda, S., Kawamura, Z., 1989. Stabilization of xanthan gum in aqueous solution. US Patent 4 810 786, March 7, 1989.

Kanda, S., Yanagita, M., Sekimoto, Y., 1986. A method of stabilizing a fracturing fluid and a stabilized fracturing fluid. GB Patent 2 172 007, September 10, 1986.

Kanda, S., Yanagita, M., Sekimoto, Y., 1988. Stabilized fracturing fluid and method of stabilizing fracturing fluid. US Patent 4 721 577, January 26, 1988.

Kelly, P.A., Gabrysch, A.D., Horner, D.N., 2007. Stabilizing crosslinked polymer guars and modified guar derivatives. US Patent 7 195 065, assigned to Baker Hughes Incorporated, Houston, TX, March 27, 2007.

Khaund, A.K., 1987a. Improved stress-corrosion resistant proppant for oil and gas wells. EP Patent 207 427, January 7, 1987.

Khaund, A., 1987b. Sintered low density gas and oil well proppants from a low cost unblended clay material of selected composition. US Patent 4 668 645, May 26, 1987.

Khaund, A.K., 1987c. Stress-corrosion resistant proppant for oil and gas wells. US Patent 4 639 427, January 27, 1987.

King, M.T., Gulbis, J., Hawkins, G.W., Brannon, H.D., 1990. Encapsulated breaker for aqueous polymeric fluids. In: Proceedings Volume, Vol. 2, CIM Petrol. Soc/SPE International Technical Meeting., Calgary, Canada, June 10–13, 1990.

Laird, J.A., Beck, W.R., 1989. Ceramic spheroids having low density and high crush resistance. EP Patent 207 668, April 5, 1989.

Langemeier, P.W., Phelps, M.A., Morgan, M.E., 1989. Method for reducing the viscosity of aqueous fluids. EP Patent 330 489, August 30, 1989.

Laramay, S.B., Powell, R.J., Pelley, S.D., 1995. Perphosphate viscosity breakers in well fracture fluids. US Patent 5 386 874, assigned to Halliburton Co., February 7, 1995.

Lawrence, S., Warrender, N., 2010. Crosslinking composition for fracturing fluids. US Patent 7 749 946, assigned to Sanjel Corporation, Calgary, Alberta, CA, July 6, 2010.

Lemanczyk, Z.R., 1991. The use of polymers in well stimulation: Performance, availability and economics. In: Proceedings Volume, Plast Rubber Inst. Use of Polymers in Drilling & Oilfield Fluids Conference, London, England, December 9, 1991.

Lemanczyk, Z.R., 1992. The use of polymers in well stimulation: An overview of application, performance and economics. Oil Gas Europe Mag. 18 (3), 20–26.

Lemieux, P.R., Rumpf, D.S., 1994. Lightweight proppants for oil and gas wells and methods for making and using same. CA Patent 1 330 255, June 21, 1994.

Li, F., Dahanayake, M., Colaco, A., 2010. Multicomponent viscoelastic surfactant fluid and method of using as a fracturing fluid. US Patent 7 772 164, assigned to Rhodia, Inc., Cranbury, NJ, August 10, 2010.

Lukocs, B., Mesher, S., Wilson, T.P.J., Garza, T., Mueller, W., Zamora, F., Gatlin, L.W., 2007. Non-volatile phosphorus hydrocarbon gelling agent. US Patent Application 20070173413, assigned to Clearwater International, LLC, July 26, 2007.

Manalastas, P.V., Drake, E.N., Kresge, E.N., Thaler, W.A., McDougall, L.A., Newlove, J.C., Swarup, V., Geiger, A.J., 1992. Breaker chemical encapsulated with a crosslinked elastomer coating. US Patent 5 110 486, assigned to Exxon Research & Eng. Co., May 5, 1992.

McDougall, L.A., Malekahmadi, F., Williams, D.A., 1993. Method of fracturing formations. EP Patent 540 204, assigned to Exxon Chemical Patents In, May 5, 1993.

McElfresh, P.M., Williams, C.F., 2007. Hydraulic fracturing using non-ionic surfactant gelling agent. US Patent 7 216 709, assigned to Akzo Nobel NV, Arnhem, NL, May 15, 2007.

Middaugh, R.L., Harris, P.C., Heath, S.J., Taylor, R.S., Hoch, O.F., Phillippi, M.L., Slabaugh, B.F., Terracina, J.M., 2007. Coarse-foamed fracturing fluids and associated methods. US Patent 7 261 158, assigned to Halliburton Energy Services, Inc., Duncan, OK, August 28, 2007.

Mitchell, T.O., Card, R.J., Gomtsyan, A., 2001. Cleanup additive. US Patent 6 242 390, assigned to Schlumberger Technol. Corp., June 5, 2001.

Mondshine, T.C., 1987. Crosslinked fracturing fluids. WO Patent 8 700 236, assigned to Texas United Chemical Corp., January 15, 1987.

Mondshine, T.C., 1993. Process for decomposing polysaccharides in alkaline aqueous systems. EP Patent 559 418, assigned to Texas United Chemical Corp., September 8, 1993.

Muir, D.J., Irwin, M.J., 1999. Encapsulated breakers, compositions and methods of use. WO Patent 9 961 747, assigned to 3m Innovative Propertie C, December 2, 1999.

Mukherjee, H., Cudney, G., 1993. Extension of acid fracture penetration by drastic fluid-loss control. J. Pet. Tech. 45 (2), 102–105.

Navarrete, R.C., Brown, J.E., Marcinew, R.P., 1996. Application of new bridging technology and particulate chemistry for fluid-loss control during fracturing highly permeable formations. In: Proceedings Volume, Vol. 2, SPE Europe Petroleum Conference, Milan, Italy, October 22–24, 1996, pp. 321–325.

Navarrete, R.C., Mitchell, J.P., 1995. Fluid-loss control for high-permeability rocks in hydraulic fracturing under realistic shear conditions. In: Proceedings Volume, SPE Production Operations Symposium, Oklahoma City, April 2–4, 1995, pp. 579–591.

Nguyen, P.D., Barton, J.A., Isenberg, O.M., 2007. Methods and compositions for consolidating proppant in fractures. US Patent 7 264 052, assigned to Halliburton Energy Services, Inc., Duncan, OK, September 4, 2007.

Nguyen, P.D., Schreiner, K.L., 1999. Preventing well fracture proppant flow-back. US Patent 5 908 073, assigned to Halliburton Energy Serv., June 1, 1999.

Nguyen, P.D., Weaver, J.D., 2001. Method of controlling particulate flowback in subterranean wells and introducing treatment chemicals. US Patent 6 209 643, assigned to Halliburton Energy Serv., April 3, 2001.

Nguyen, P.D., Weaver, J.D., Brumley, J.L., 2001. Stimulating fluid production from unconsolidated formations. US Patent 6 257 335, assigned to Halliburton Energy Serv., July 10, 2001.

Nguyen, P.D., Weaver, J.D., Parker, M.A., King, D.G., 1996b. Thermoplastic film prevents proppant flowback. Oil Gas J. 94 (6), 60–62.

Nguyen, P.D., Weaver, J.D., Parker, M.A., King, D.G., Gillstrom, R.L., Van Batenburg, D.W., 1996a. Proppant flowback control additives. In: Proceedings Volume, Annual SPE Technical Conference, Denver, October 6–9, 1996, pp. 119–131.

Nimerick, K., 1996. Fracturing fluid and method. GB Patent 2 291 907, assigned to Sofitech NV, February 7, 1996.

Nimerick, K.H., Boney, C.L., 1992. Method of fracturing high temperature wells and fracturing fluid therefore. US Patent 5 103 913, assigned to Dowell Schlumberger Inc., April 14, 1992.

Nimerick, K.H., Crown, C.W., McConnell, S.B., Ainley, B., 1993. Method of using borate crosslinked fracturing fluid having increased temperature range. US Patent 5 259 455, November 9, 1993.

Nimerick, K.H., Hinkel, J.J., 1991. Enhanced methane production from coal seams by dewatering. EP Patent 444 760, assigned to Pumptech NV and Dowell Schlumberger SA, September 4, 1991.

Nimerick, K.H., McConnell, S.B., Samuelson, M.L., 1990. Compatibility of resin-coated proppants with crosslinked fracturing fluids. In: Proceedings Volume, 65th Annual SPE Technical Conference, New Orleans, September 23–26, 1990, pp. 245–250.

Noran, L., Vitthal, S., Terracina, J., 1995. New breaker technology for fracturing high-permeability formations. In: Proceedings Volume, SPE Europe Formation Damage Control Conference, The Hague, Netherland, May 15–16, 1995, pp. 187–199.

Norman, L.R., Laramay, S.B., 1994. Encapsulated breakers and method for use in treating subterranean formations. US Patent 5 373 901, assigned to Halliburton Co., December 20, 1994.

Norman, L.R., Turton, R., Bhatia, A.L., 2001. Breaking fracturing fluid in subterranean formation. EP Patent 1 152 121, assigned to Halliburton Energy Serv., November 7, 2001.

Oude Alink, B.A., 1993. Water soluble 1,2-dithio-3-thiones. US Patent 5 252 289, assigned to Petrolite Corp., October 12, 1993.

Pakulski, M.K., Hlidek, B.T., 1992. Slurried polymer foam system and method for the use thereof. WO Patent 9 214 907, assigned to Western Co. North America, September 3, 1992.

Parks, C.F., Clark, P.E., Barkat, O., Halvaci, J., 1986. Characterizing polymer solutions by viscosity and functional testing. In: Proceedings 192nd ACS Nat. Mtg., Vol. 55, Amer. Chem. Soc. Polymeric Mater Sci Eng. Div Tech. Program, Anaheim, California, September 7–12, 1986, pp. 880–888.

Pelissier, J.J.M., Biasini, S., 1991. Biodegradable drilling mud (boue de forage biodegradable). FR Patent 2 649 988, January 25, 1991.

Penny, G.S., 1987. Method of increasing hydrocarbon production from subterranean formations. US Patent 4 702 849, October 27, 1987.

Penny, G.S., Briscoe, J.E., 1987. Method of increasing hydrocarbon production by remedial well treatment. CA Patent 1 216 416, January 13, 1987.

Penny, G.S., Conway, M.W., 1989. Fluid Leakoff, Vol. 12 of Recent Advances in Hydraulic Fracturing (SPE Henry L. Doherty Monogr Ser). SPE, Richardson, Texas, pp. 147–176.

Penny, G.S., Conway, M.W., 1995. Coordinated studies in support of hydraulic fracturing of coalbed methane: Final report (July 1990–May 1995), Gas Res Inst Rep GRI-95/0283, Gas Res Inst, September 1995.

Penny, G.S., Stephens, R.S., Winslow, A.R., 1991. Method of supporting fractures in geologic formations and hydraulic fluid composition for same. US Patent 5 009 797, assigned to Weyerhaeuser Co., April 23, 1991.

Powell, R.J., Fischer, A.R., Gdanski, R.D., McCabe, M.A., Pelley, S.D., 1995a. Encapsulated scale inhibitor for use in fracturing treatments. In: Proceedings Volume, Annual SPE Technical Conference, Dallas, October 22–25, 1995, pp. 557–563.

Powell, R.J., Fischer, A.R., Gdanski, R.D., McCabe, M.A., Pelley, S.D., 1996. Encapsulated scale inhibitor for use in fracturing treatments. In: Proceedings Volume, SPE Permian Basin Oil & Gas Recovery Conference, Midland, TX, March 27–29, 1996, pp. 107–113.

Powell, P.J., Gdanski, R.D., McCabe, M.A., Buster, D.C., 1995b. Controlled-release scale inhibitor for use in fracturing treatments. In: Proceedings Volume, SPE Oilfield Chemistry International Symposium, San Antonio, February 14–17, 1995, pp. 571–579.

Prasek, B.B., 1996. Interactions between fracturing fluid additives and currently used enzyme breakers. In: Proceedings Volume, 43rd Annual Southwestern Petroleum Short Course Association, Inc. et al Mtg., Lubbock, Texas, April 17–18, 1996, pp. 265–279.

Putzig, D.E., 1988. Zirconium chelates and their use for cross-linking. EP Patent 278 684, assigned to Du Pont De Nemours & Co., August 17, 1988.

Putzig, D.E., 2010. Process to prepare borozirconate solution and use as cross-linker in hydraulic fracturing fluids. US Patent 7 683 011, March 23, 2010.

Putzig, D.E., Smeltz, K.C., 1986. Organic titanium compositions useful as cross-linkers. EP Patent 195 531, September 24, 1986.

Qu, Q., Wang, X., 2010. Method of acid fracturing a sandstone formation. US Patent 7 704 927, assigned to BJ Services Company, Houston, TX, April 27, 2010.

Ridland, J., Brown, D.A., 1990. Organo-metallic compounds. CA Patent 2 002 792, June 16, 1990.

Sanford, B.D., Dacar, C.R., Sears, S.M., 1992. Acid fracturing with new fluid-loss control mechanisms increases production, little knife field, north dakota. In: Proceedings Volume, SPE Rocky Mountain Regional Meeting, Casper, Wyoming, May 18–21, 1992, pp. 317–324.

Sanner, T., Kightlinger, A.P., Davis, J.R., 1996. Borate-starch compositions for use in oil field and other industrial applications. US Patent 5 559 082, assigned to Grain Processing Corp., September 24, 1996.

Satyanarayana Gupta, D.V., Cooney, A., 1992. Encapsulations for treating subterranean formations and methods for the use thereof. WO Patent 9 210 640, assigned to Western Co. North America, June 25, 1992.

Schield, J.A., Naiman, M.I., Scherubel, G.A., 1991. Polyimide quaternary salts as clay stabilization agents. GB Patent 2 244 270, assigned to Petrolite Corp., November 27, 1991.

Shah, S.N., Harris, P.C., Tan, H.C., 1988. Rheological characterization of borate crosslinked fracturing fluids employing a simulated field procedure. In: Proceedings Volume, SPE Production Technology Symposium, Hobbs, NM, November 7–8, 1988.

Sharif, S., 1993. Process for preparation and composition of stable aqueous solutions of boron zirconium chelates for high temperature frac fluids. US Patent 5 217 632, assigned to Zirconium Technology Corp., June 8, 1993.

Sharif, S., 1995. Process for preparation of stable aqueous solutions of zirconium chelates. US Patent 5 466 846, assigned to Benchmark Res. & Technl In, November 14, 1995.

Shuchart, C.E., Terracina, J.M., Slabaugh, B.F., McCabe, M.A., 1999. Method of treating subterranean formation. EP Patent 916 806, assigned to Halliburton Energy Serv., May 19, 1999.

Slodki, M.E., Cadmus, M.C., 1991. High-temperature, salt-tolerant enzymic breaker of xanthan gum viscosity. In: Donaldson, E.C. (Ed.), Microbial Enhancement of Oil Recovery: Recent Advances: Proceedings of the 1990 International Conference on Microbial Enhancement of Oil Recovery, Vol. 31 of Developments in Petroleum Science. Elsevier Science Ltd., pp. 247–255.

Smith, K.W., Persinski, L.J., 1995. Hydrocarbon gels useful in formation fracturing. US Patent 5 417 287, assigned to Clearwater Inc., May 23, 1995.

Smolarchuk, P., Dill, W., 1986. Iron control in fracturing and acidizing operations. In: Proceedings Volume, Vol. 1, 37th Annu. Cim. Petrol. Soc. Tech. Mtg., Calgary, Canada, June 8–11, 1986, pp. 391–397.

Stacy, A.L., Weber, R.B., 1995. Method for reducing deleterious environmental impact of subterranean fracturing processes. US Patent 5 424 285, assigned to Western Co. North America, June 13 1995.

Subramanian, S., Zhu, Y.P., Bunting, C.R., Stewart, R.E., 2001. Gelling system for hydrocarbon fluids. WO Patent 0 109 482, assigned to Crompton Corp., February 8, 2001.

Swarup, V., Peiffer, D.G., Gorbaty, M.L., 1996. Encapsulated breaker chemical. US Patent 5 580 844, assigned to Exxon Research & Eng. Co., December 3, 1996.

Sweet, L., 1993. Method of fracturing a subterranean formation with a lightweight propping agent. US Patent 5 188 175, February 23, 1993.

Syrinek, A.R., Lyon, L.B., 1989. Low temperature breakers for gelled fracturing fluids. US Patent 4 795 574, assigned to Nalco Chemical Co., January 3, 1989.

Thomas, T.R., Smith, K.W., 1993. Method of maintaining subterranean formation permeability and inhibiting clay swelling. US Patent 5 211 239, assigned to Clearwater Inc., May 18, 1993.

von Terzaghi, K., 1923. Die Berechnung der Durchlässigkeitsziffer des Tones aus dem Verlauf der hydrodynamischen Spannungserscheinungen, Sitzungsberichte der Akademie der Wissenschaften in Wien, Mathematisch-Naturwissenschaftliche Klasse, Abteilung 2a.

Walker, M.L., Ford, W.G.F., Dill, W.R., Gdanski, R.D., 1987. Composition and method of stimulating subterranean formations. US Patent 4 683 954, August 4, 1987.

Walker, M.L., Shuchart, C.E., 1995. Method for breaking stabilized viscosified fluids. US Patent 5 413 178, assigned to Halliburton Co., May 9, 1995.

Watkins, D.R., Clemens, J.J., Smith, J.C., Sharma, S.N., Edwards, H.G., 1993. Use of scale inhibitors in hydraulic fracture fluids to prevent scale build-up. US Patent 5 224 543, assigned to Union Oil Co. California, July 6, 1993.

Watters, J.T., Ammachathram, M., Watters, L.T., 2010. Method to enhance proppant conductivity from hydraulically fractured wells. US Patent 7 708 069, assigned to Superior Energy Services, LLC, New Orleans, LA, May 4, 2010.

Welton, T.D., Todd, B.L., McMechan, D., 2010. Methods for effecting controlled break in pH dependent foamed fracturing fluid. US Patent 7 662 756, assigned to Halliburton Energy Services, Inc., Duncan, OK, February 16, 2010.

Wen, Q., Zhang, S., Wang, L., Liu, Y., Li, X., 2007. The effect of proppant embedment upon the long-term conductivity of fractures. J. Pet. Sci. Eng. 55 (3–4), 221–227.

Westland, J.A., Lenk, D.A., Penny, G.S., 1993. Rheological characteristics of reticulated bacterial cellulose as a performance additive to fracturing and drilling fluids. In: Proceedings Volume, SPE Oilfield Chemistry International Symposium, New Orleans, March 2–5, 1993, pp. 501–514.

White, D.J., Holms, B.A., Hoover, R.S., 1992. Using a unique acid-fracturing fluid to control fluid loss improves stimulation results in carbonate formations. In: Proceedings Volume, SPE Permian Basin Oil & Gas Recovery Conference, Midland, Texas, March 18–20, 1992, pp. 601–610.

Williamson, C.D., Allenson, S.J., 1989. A new nondamaging particulate fluid-loss additive. In: Proceedings Volume, SPE Oilfield Chemistry International Symposium, Houston, TX, February 8–10, 1989, pp. 147–158.

Williamson, C.D., Allenson, S.J., Gabel, R.K., 1991a. Additive and method for temporarily reducing permeability of subterranean formations. US Patent 4 997 581, assigned to Nalco Chemical Co., March 5, 1991.

Williamson, C.D., Allenson, S.J., Gabel, R.K., Huddleston, D.A., 1991b. Enzymatically degradable fluid loss additive. US Patent 5 032 297, assigned to Nalco Chemical Co., July 16, 1991.

Williams, M.M., Phelps, M.A., Zody, G.M., 1987. Reduction of viscosity of aqueous fluids. EP Patent 222 615, May 20, 1987.

Wiser-Halladay, R., 1990. Polyurethane quasi prepolymer for proppant consolidation. US Patent 4 920 192, April 24, 1990.

Xiong, H., Davidson, B., Saunders, B., Holditch, S.A., 1996. A comprehensive approach to select fracturing fluids and additives for fracture treatments. In: Proceedings Volume, Annual SPE Technical Conference, Denver, October 6–9, 1996, pp. 293–301.

Yeager, R.R., Bailey, D.E., 1988. Diesel-based gel concentrate improves rocky mountain region fracture treatments. In: Proceedings Volume, SPE Rocky Mountain Regional Meeting, Casper, Wyoming, May 11–13, 1988, pp. 493–497.

Yeager, V., Shuchart, C., 1997. In situ gels improve formation acidizing. Oil Gas J. 95 (3), 70–72.

Yeh, M.H., 1995. Anionic sulfonated thickening compositions. EP Patent 632 057, assigned to Rhone Poulenc Spec. Chem. C, January 4, 1995.

Zeilinger, S.C., Mayerhofer, M.J., Economides, M.J., 1991. A comparison of the fluid-loss properties of borate-zirconate-crosslinked and noncrosslinked fracturing fluids. In: Proceedings Volume, SPE East Regional Conference, Lexington, KY, October 23–25, 1991, pp. 201–209.

Zychal, C., 1986. Defoamer and antifoamer composition and method for defoaming aqueous fluid systems. US Patent 4 631 145, assigned to Amoco Corp., December 23, 1986.

TRADENAMES

TABLE 17.23 Tradenames in References

Tradename Description	Supplier
ClearFRAC™ Stimulating fluid (Crews, 2010)	Schlumberger Technology Corp.
DiamondFRAQ™ VES System (Crews, 2010)	Baker Oil Tools
Injectrol® (Series) Selants (Dusterhoft et al., 2008)	Halliburton Energy Services, Inc.
Jordapon® ACl Sodium cocoyl isothionate surfactant (Crews, 2010)	BASF
Jordapon® Cl Ammonium cocoyl isothionate surfactant (Crews, 2010)	BASF
Microsponge™ Porous solid substrate (Crews, 2010)	Advanced Polymer Systems
Poly-S.RTM Polymer encapsulation coating (Crews, 2010)	Scotts Comp.
Wellguard™ 7137 Interhalogen gel breaker (Carpenter, 2007, 2009)	Albemarle Corp.
WS-44 Emulsifier (Welton et al., 2010)	Halliburton Energy Services, Inc.

Chapter 18

Water Shutoff

This chapter is closely related to the subject of gelling agents; see Chapter 8 for more information. Both gelling and plugging agents have similar aims—to minimize the permeability of a formation.

The idea of water shutoff treatments began in 1922 when the injection of silicate solutions into oil producing wells was patented, with the aim of gelation in situ to form a blocking phase.

The term gel can refer to a crosslinked polymer or to a polymer solution that is sufficiently viscous to appear as a gel. Although from the viewpoint of a polymer chemist, the hardening of cement is a polymerization resulting in an inorganic crosslinked polymer, we will not include cementing here, nor will we discuss fracturing fluids, even when gels are formed.

CLASSIFICATION OF METHODS

The formation of plugs can be achieved by using various chemical principles:

- Polymerization of vinyl monomers,
- Polyaddition of epoxies,
- Polycondensation of aminoplasts and phenoplasts,
- Crosslinking of polymers, and
- Cementing.

The methods can be classified in a number of ways, including by the job in which they are used, or the chemical process involved. Operations that include plugging or sealing are shown in Table 18.1, left column, where classification runs according to the particular job. A categorization by the type of molecular reaction taking place is shown in the right-hand column of the table (Kosztin et al., 2002).

Depending on the particular oil recovery technique in use, considerable quantities of water are produced in relation to crude oil produced, and this increases as the well becomes more and more exhausted. The ratio of water to oil is currently ca. three (Bailey et al., 2000). 55% of the water is reinjected, while

Petroleum Engineer's Guide to Oil Field Chemicals and Fluids. DOI: 10.1016/B978-0-12-383844-5.00018-0

TABLE 18.1 Classification of Gel Technology

According to Job	According to Technique
Conformance treatment	Mobility control by modification of rheological properties
Water shutoff	Injection of polymer solutions
Divertment control	In situ crosslinking of linear polymer
Oil recovery	In situ polymerization of monomers
Casing placing	Precipitation of gel like inorganic compounds
Cementing	Precipitation of crystalline inorganic compounds
Fracturing	Mobility control by the modification of the pore structure Combined, multifunctional methods

TABLE 18.2 Process Cost Distributions During Water Recycling

Operation	% Cost	Operation	% Cost
Pumping	28	Separation	15
Filtering	14	Lifting	17
De-Oiling	21	Injecting	5

the rest is discharged to open surface areas. Most discharged water requires treatment because of contamination with traces of oil, heavy metals, boron, and corrosive fluids like H_2S, CO_2, salt, and solids. The costs of water treatment vary between U.S. \$0.15/m^3 and U.S. \$15/m^3 depending on volumes and the location (Khatib and Verbeek, 2003). The typical process costs of the water life cycle are shown in Table 18.2.

IN SITU POLYMERIZATION

Vinyl monomers are allowed to polymerize in place to form a gel. The technique is used to enable a solution to gel slowly, even at high temperatures. An aqueous solution of a vinyl monomer is mixed with a radical-forming initiator and optionally with a dispersant. The initiator decomposes at elevated temperatures and initiates the polymerization process, so a gel is formed in place. For a more pronounced delay, polymerization inhibitors may be added to the solution in small amounts. The technique is used in the treatment of subterranean formations for plugging lost circulation in drilling operations, particularly at elevated temperatures.

ACRYLIC GELS

Water-soluble polymers in general are reviewed in the literature (Zahid, 1998). The use of polyacrylamide (PAM) gels in water shutoff treatments is common. PAM is prepared by radical polymerization of the monomer acrylamide (AAm). Charges along the main chain can be introduced by suitable comonomers or on the fly by alkaline treatment of the polymer.

N-methylol acrylamide and *N*-methylol methacrylamide (Figure 18.1), have been suggested as monomers (Leblanc et al., 1990), with phenol derivatives (Leblanc et al., 1988a), such as an *N*-nitrosophenylhydroxylamine salt, as inhibitors (Maurer and Landry, 1990).

In the latter case the amide group is hydrolyzed to a carboxyl group. Suitable comonomers are acrylyic acid or methacrylic acid, *N*-vinyl-2-pyrrolidone, and sodium-2-acrylamido-2-methylpropanesulfonate. A copolymer of AAm and *tert*-butyl acrylate can be crosslinked with polyethyleneimine.

The kinetics of the gelation reaction has been investigated. It was found that the addition of salts increases the gelation time, but this is reduced by higher content of copolymer and crosslinking agent (Al-Muntasheri et al., 2007). Recommendations for field application of this gelling composition have been worked out.

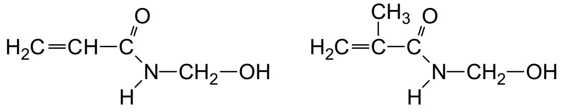
Treatment of acrylic polymers with ionizing radiation is reported to improve rheological properties and stability (Remnev et al., 2002). A number of nitrogen-containing vinyl compounds likely to withstand hostile environments have been disclosed (Ahmed et al., 2000a, 1997, 2000b), including *N*-acryloylmorpholine, *N*-acryloyl-*N*′-methyl piperazine, and various other acryloyl units with attached organic salts, c.f., Figure 18.2.

Crosslinkers

Crosslinkers are added to form intermolecular linkages in between the primary polymer chains to form a stable gel. There are various ways of crosslinking.

Physical Crosslinking

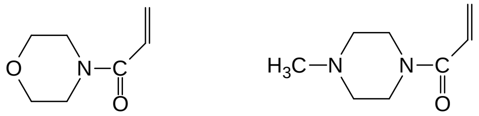
Modified PAMs that carry negative charges on their backbone can form gels by addition of multivalent positive ions, such as chromium salts. The gel consists of a physical network, similar to an ionomer. A single multivalent ion shares a salt with the charges of different polymer chains. The gelation time depends on the molecular weight of the primary polymer, the concentration of ions on the



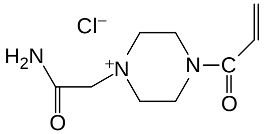
$H_2C{=}CH{-}C({=}O){-}N(H){-}CH_2{-}OH$ $\quad$ $H_2C{=}C(CH_3){-}C({=}O){-}N(H){-}CH_2{-}OH$

N-Methylol acrylamide *N*-Methylol methacrylamide

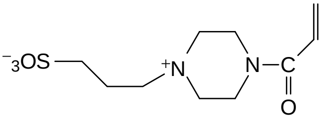
FIGURE 18.1 Amides.



N-Acryloylmorpholine *N*-Acryloyl-*N*′-methyl piperazine



N-Acryloyl-*N*′-(2-amino-2-oxoethyl)-*N*′-methyl piperazinium chloride



N-Acryloyl-*N*′-(3-sulfopropyl)-*N*′-methyl piperazinium inner salt

FIGURE 18.2 Monomers for acrylic gels (Ahmed et al., 2000a).

primary polymer chains, and the concentration of the multivalent cations in the solution.

Crosslinker formulations based on iron (III), such as ferric acetylacetonate or ammonium ferric oxalate (Moradi-Araghi et al., 2002) have been described. 2,4-Pentanedione can adjust the gel strength in such formulations. Zirconium acetylacetonate is also a suitable crosslinker (Fox et al., 1999). Table 18.3 gives a list of salts, which have been proposed for physical crosslinking.

Chromium (III) salts are used mainly for physical crosslinking. These are not as toxic as chromium(VI) salts, but they are not environmentally desirable compounds, and their use incurs additional costs to avoid the contamination of surface waters. Efforts to develop other methods of crosslinking have been therefore undertaken. Table 18.4 lists the characteristic pH range for crosslinking for some selected polymers (Lockhart, 2000).

Syneresis

Hydrolysis of mide groups takes place slowly in aqueous solutions at elevated temperatures. Bivalent ions such as Ca^{2+} are usually present in saline environments. The carboxyl groups formed from the polymer can react with these ions and thus form additional crosslinks (Moradi-Araghi, 2000). Thus, the number of crosslinks increases with time, altering the mechanical properties of the gel. As the crosslinking index of the gel increases, its equilibrium water content will decrease and it will shrink, losing some of its plugging properties. This phenomenon is known as syneresis.

TABLE 18.3 Commercially Available Salts for Physical Crosslinking

Crosslinking Agent
Chromium chloride
Chromium propionate
Chromium acetate
Zirconium lactate
Zirconium citrate
Tetrakis triethanol amine zirconate
Zirconium complex of hydroxyethyl glycine
Zirconium tartarate
Zirconium malonate
Zirconium propionate

TABLE 18.4 Characteristic pH Range for Crosslinking of Various Polymers

Hydroxypropyl Guar		Carboxymethylhydroxypropyl Guar		Polyacrylamides	
Ion	pH	Ion	pH	Ion	pH
Zr	7–10	Zr	3–6	Zr	4–6
Sb	3–6	Al	4–6	Al	4–6
Ti	7–9	Ti	7–9		
BO_4	8–12				

Chemical Crosslinking

Besides of physical crosslinking chemical crosslinking systems have been described. A combination of hydroquinone and hexamethylenetetramine can be used Hutchins et al. (1996). Sodium bicarbonate in a concentration of 2% serves as buffer and it softens the water by precipitating certain divalent cations present in the sea water.

Other chemical crosslinking systems include terephthalaldehyde, terephthalic acid, dihydroxynaphthalene, glutaric acid, gallic acid, and dibasic esters (Dovan et al., 1997). The authors identified both primary and secondary crosslinkers. Primary crosslinkers are those that produce gels with the polymer, although the gels may be unstable. Secondary crosslinkers stabilize the gels produced by primary crosslinking.

Phenol-formaldehyde Type Crosslinkers

The amide groups on PAM can be crosslinked with formaldehyde or a mixture of formaldehyde and phenol, but these small molecules are toxic, and hard to dispose of higher molecular weight reagents, such as hexanal and heptanal, which are not classed as toxic. These are suitable crosslinking agents but they are not sufficiently soluble in water to crosslink normal hydrophilic polymers such as the PAM/polyacrylate copolymer. They can, however, be readily solubilized in aqueous solutions by hydrophobically modified PAM polymers, and can then crosslink them (Jones and Tustin, 2001). Hexamethylenetetramine hydrolyzes slowly into ammonia and formaldehyde, and can be used in place of formaldehyde. Hexamethylenetetramine with an aminobenzoic acid compound produces better gels than those produced with phenol and formaldehyde (Moradi-Araghi, 1999), and this gelling system is more environmentally acceptable.

Polyethyleneimine Crosslinker

For copolymers of AAm, and of AAm and methyl acrylate (5%), polyethyleneimine (Reddy et al., 2001; Urlwin-Smith, 2001) can be used as crosslinker.

Aluminum Phosphate Ester Salts for Gelling Organic Liquids

Organic liquid gels are used for temporary plugging during fracturing operations. This type of gelling agent permits on-the-fly gelling of hydrocarbons, especially those used in this type of operation. A gel of an organic liquid, such as diesel or crude oil, can be formed using an aluminum phosphate diester in which all of the reagents are free of water and pH-affecting substances (Gross, 1987; Harris et al., 1986). The diester may be prepared by the reaction of a triester with phosphorous pentoxide to produce a polyphosphate, which is then reacted with an alcohol to produce a phosphate diester. The latter diester is then added to the organic liquid along with a nonaqueous source of aluminum, such as aluminum isopropoxide in diesel oil, to produce the metal phosphate diester. The conditions in the two preceding reaction steps are controlled, in order to provide a gel with good viscosity versus temperature and time characteristics.

A similar process involves the reaction of triethyl phosphate and phosphorous pentoxide to form a polyphosphate in an organic solvent (Huddleston, 1992). Aluminum sulfate is used as a crosslinker. Hexanol results in high-temperature viscosity of the gel, while maintaining a pumpable viscosity at ambient temperatures (Huddleston, 1989).

SPECIAL APPLICATIONS

Chromium acetate-partially hydrolyzed polyacrylamide (PHPA) gel systems have also been applied in fractured reservoirs for conformance control (Ganguly et al., 2002). A wide variety of polymers create flexible gels (James et al., 2002): polyvinyl alcohol or polyvinyl acetate, PAMs, AAm copolymers, acrylic acid methacrylamide copolymers, and PHPAs, as well as polymethacrylamides, several natural and modified polysaccharides, lignosulfonates, and polyalkylene oxides.

The crosslinking of polysodium 4-styrenesulfonate using Al^{3+} ions to form a gel is described by Keller and Narh (1994). The concentration of the high molecular weight hydrophilic polymers used to form hydrogels is typically in the range 3–10 $g\,l^{-1}$, and diverting agents can be added, to improve the penetration of a sand consolidating fluid into areas of lower permeability (Robert and Rosen, 2002).

Shear-Initiated Inversion of Emulsions

Some emulsions can be formulated to exhibit so-called *flow-initiated gelling*. Such liquids thicken when subjected to high shear stress or a pressure drop across a sudden constriction in the flow path; such as the nozzles of a drill bit. To effect gelling, the crosslinking agent and the polymer are dissolved in two separate aqueous solutions, which, when combined in the emulsion, are again separated by the continuous hydrophobic phase. Three types of emulsion system have been described for PAMs (Crawshaw and Nijs, 2002):

1. A water in oil-in-water emulsion system,
2. A dual water in oil emulsion system, and
3. A crosslinker in oil system.

THERMALLY STABLE GELS

It has been found that crosslinked gels can be ineffective at temperatures above about 80°C, because of the instability of the crosslinker or the polymer, which results in crosslinking rates that are too fast, crosslinker precipitation, polymer degradation, or inefficient solution propagation.

To correct these problems, the crosslinking metal ion can be coordinated with a ligand such as acetate or propionate to slow down the reaction of the metal ion with the polymer. While this and other techniques have been utilized successfully, the use of some metal ions, e.g., chromium, have adverse environmental effects. The metal ion can also be adsorbed by formation materials, preventing it from crosslinking the polymer (Hardy, 2001).

In general, to arrive at thermally stable gels, a thermally stable polymer must be utilized. Suitable polymers are shown in Table 18.5. An excellent review of thermally stable gels for fluid diversion in petroleum production has been presented by Moradi-Araghi (2000).

DISPROPORTIONATE PERMEABILITY REDUCTION

Many gels and some polymers without crosslinkers can reduce the permeability to water more than that to oil or gas (Seright et al., 2002), and references

TABLE 18.5 Thermally Stable Polymers

Polymer	Crosslinking
Alcaligenes biopolymer	Ionic Na^+
Polyacrylamides	Ionic Cr^{3+}
Scleroglucan	Ionic Cr^{3+}
Lignosulfonate	Ionic Cr^{3+}
Resorcinol	Formaldehyde
Polyvinyl alcohol/polyvinyl amide copolymer	Aldehydes
Polyvinyl alcohol	Phenol-formaldehyde
Acrylic esters	Polyethyleneimine

cited therein. This effect is known as selective permeability reduction, or disproportionate permeability reduction.

The use of chemicals to modify the water permeability in hydrocarbon and water-producing formations is considerably less expensive than other techniques, and does not require expensive zonal isolation techniques. However, these chemicals can often only give small reductions in water production, or lead to unacceptable reductions in the production of hydrocarbons (Hirasaki and Miller, 2003).

Field Experience

Details of extensive experience with the chromic-acetate-carboxylate/AAm-polymer gel technology for use in oil field conformance control, sweep improvement, and water and gas shutoff treatments have been compiled by Sydansk and Southwell (2000).

Chromic triacetate is often the preferred crosslinking agent used in conjunction with polymer gel technology. Many chromic salts cannot be used, because the kinetics of crosslinking is too fast. In high-temperature applications the gelation kinetics can still be slowed down by using complexed or chelated salts or the encapsulation techniques (Moradi-Araghi et al., 2002). Chromic acetate gels have a robust gel chemistry and are highly insensitive to petroleum reservoir environments and interferences. They are applicable over a broad range of temperature and pH range. Up to mid-1998 this procedure had been employed in over 1,400 conformance control treatments worldwide.

SILICATE-BASED AGENTS

The use of silicate-based agents has advantages and disadvantages (Lakatos et al., 1999b), as summarized in Table 18.6.

TABLE 18.6 Advantages and Disadvantages Using Silicates

Advantage	Disadvantage
Low viscosity of treating solutions, viz. good placement selectivity	The gel is rigid and prone to fracture
Short to moderate pumping time before onset of gelation	The gel shows syneresis, viz. it is prone to shrink
Simple and cost-effective surface technology	Alkaline silicates initiate intensive ion exchange, hence, precipitation of multivalent cations
Silicates are environmentally friendly materials	Silicates change the interfacial properties, thus they enhance in situ colloid chemical processes (emulsification, agglomeration, etc.)
Flexible chemical mechanism	Because of shrinking the blocking efficiency is changing in time, and it is never total
Good chemical and chemical stability	Penetration of the treating solutions is short if the buffer capacity of rock is high
Excellent thermal and mechanical resistivity	The setting time is usually short, namely, it is hard to control the gelation mechanism

Sodium silicate sealing compositions have been used successfully to control lost circulation, and to terminate undesirable fluid production and cross flows in subterranean zones.

The sodium silicate solution is polymerized or crosslinked in place, and a pliable gel is formed, which reduces or terminates lost circulation or undesirable fluid production. Gelation occurs by a change in the pH or the concentration of specific ions, such as copper sulfate (Kleshchenko et al., 2003).

Combined Polymer-Silicate Technology

The application of both PHPA and sodium orthosilicate or potassium orthosilicate has been extensively discussed by Lakatos et al. (1999a, 2001). Typically such plugging solution consists of a two-stage treatment. First PHPA, as an anionogenic polymer is injected, and then the second solution, which contains the cationogenic polymer, such as polydimethyl diallyl ammonium chloride and a multivalent metal cation in acidic medium follows it. The joint application of polymer and silicate reduces the consumption of chemicals (Dobroskok et al., 2002; Kan et al., 2002; Taziev et al., 2001).

Gel-Foam Technique

The restriction of gas coning is based on the simultaneous placement of a polymer/silicate gel at the gas/oil contact, and also placing a supporting foam pillow into the oil-bearing layer (Lakatos et al., 1998).

The effective restriction of gas flow requires a permanent barrier between the gas and oil-bearing zones, which may be provided by gels. The barrier should penetrate deeply, should be almost horizontal, and should be located close to gas/oil contact.

The extension of such a barrier interface at the gas oil is possible if a supporting foam pillow is simultaneously injected into the oil-bearing layer. The pillow must prevent the segregation by gravity of the gel-forming aqueous phases, its advancing front velocity should be similar to that of the barrier, and after placement of all treating fluids, the supporting media must not restrict the flow of oil in the zone previously invaded.

Gel System

The most specific feature of the gel used is a double network of anionic polymers, crosslinked by a multivalent cation and polysilicates formed from sodium orthosilicate in slightly acidic media (Lakatos et al., 1998, 1999b). The gel can be prepared by mixing two aqueous solutions, one containing PHPA and silicate, and the other alum ($KAl(SO_4)_2$), calcium chloride, and hydrochloric acid. The acidic milieu prevents the spontaneous hydrolysis of alum and thus controls the gelation of the silicates.

The solutions are injected sequentially into the reservoirs, or they can be mixed at the surface. The solutions form a multifunctional chemical system because both bulk phase and interfacial reactions take place, eventually leading to the gelation or to a resistivity enhancement in porous media:

- Crosslinking of polymers;
- Gelation of silicates;
- Precipitation of polymers, silicates, and metal hydroxides;
- Adsorption of all chemicals on rock surface; and
- Mechanical entrapment of the microgel and the hydroxides.

Foam System

A great variety of surfactants have been tested as foam-forming agents, including PAMs, polysaccharides, cationic tensides, and natural proteins (Lakatos et al., 1998). In all experiments the foam was generated by nitrogen. The composition of the foam-forming solution was usually 0.5–10.0 $g\,l^{-1}$ tenside and 0.5–2.0 $g\,l^{-1}$ additive. The best foam-forming system was selected by using the following screening criteria:

- Foamability,
- Foam stability,
- Rheological properties in bulk phase and in formation rocks,
- Adsorption and retention of chemicals, and
- Flow properties in porous media.

RESIN TYPES

Epoxide Resins

Epoxide resins have good adhesive properties. They can be cured at low temperatures with amine hardeners and at elevated temperatures with organic anhydrides. Formulations can be adjusted to give a long pot life and low exothermal reactions in the course of curing. The compositions are not miscible with well fluids. A disadvantage is the comparatively high price. Standard epoxide resins are based on bisphenol-A.

Wells can be selectively treated by using a low viscosity epoxide resin formulation (Dartez and Jones, 1994, 1995). A liquid bisphenol-A-based epoxide material and an amine hardener are used for curing at ambient temperature. The epoxide material has a very low viscosity at well surface temperatures and is immiscible with well fluids. The polyamine-curing agent is an amber-colored, mobile liquid having a low viscosity at ambient temperature, and a long pot life. It can be used for plugging permeable zones in a gravel-packed well, and may be used to repair leaks in well casing or production tubing, or in cementing to prevent communication between subterranean regions. Aliphatic epoxide resins are compatible with water, which is an advantage over the commonly used aromatic epoxide resins (Eoff et al., 2001).

A process has been disclosed for reacting polyurethanes with epoxy resins in the presence of aqueous, alkali metal, silicate solutions. The reactants are combined so that foaming of the reaction mixture is prevented, and an organic polymer structure containing oxazolidinone ring structures is formed, which bears adhesion-improving OH groups (Hilterhaus, 1992).

A similar system has been used as a sealing agent. The PU is based on diphenyl methane diisocyanate (Yoshida et al., 2002). Polyurethanes are used also in the absence of silicates for sealing operations (Cornely et al., 1984), and to support gel formation (Chatterji et al., 2000).

Urea-Formaldehyde Resins

Urea-formaldehyde resins can be cured with isopropylbenzene production wastes containing 200–300 $\mathrm{g\,l^{-1}}$ of aluminum trichloride ($AlCl_3$) as an acid hardener (Blazhevich et al., 1992). Isopropylbenzene is formed as an intermediate in the Hock process by a Friedel-Crafts reaction between propene and benzene. The mixture hardens in 45–90 min and develops an adhesion to rock and metal of 0.19–0.28 and 0.01–0.07 MPa, respectively. A particular advantage is the increased pot life of the formulation.

N-Methylol acrylamide or *N*-methylol methacrylamide can be polymerized with peroxides (Leblanc et al., 1988a,b). Suitable inhibitors may be used to retard the polymerization process to ensure sufficient pot life time. The components are present as a pre-emulsion.

The gelling of the vinyl monomers in an aqueous medium in the presence of an organic peroxide polymerization initiator is delayed by using an inhibitor consisting of an alkali metal or ammonium salt of the *N*-nitrosophenylhydroxylamine combined with an amino carboxylic acid (Maurer and Landry, 1990).

Curing of Urea-formaldehyde and Phenol-formaldehyde Resins

Urea-formaldehyde resins and phenol-formaldehyde resins can be cured by various mechanisms.

Acid Curing

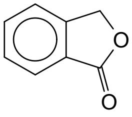
These resins can be acid-cured by using wastes from the production of maleic anhydride (MA) (Zhukhovitskij et al., 1992), which contains up to 50% MA, in addition to phthalic anhydride, citraconic anhydride, benzoic acid, *o*-tolulic acid, and phthalide, as shown in Figure 18.3. The plugging solution is prepared by mixing a urea-formaldehyde resin with a phenol-formaldehyde resin, adding the waste from production of MA, and mixing thoroughly.

Aluminum Trichloride

In an analogous way, an $AlCl_3$-containing waste of isopropylbenzene production (Blazhevich et al., 1992) can be used as an acid hardener for urea-formaldehyde resins. This waste contains approximately 200–300 $g\,l^{-1}$ of $AlCl_3$.

Alkaline Curing

A plugging solution based on phenol-formaldehyde resin, formaldehyde, and water has been described. To improve the plugging efficiency under conditions of low temperatures, the solution also contains a bituminous emulsion (Galchenko et al., 1993). Curing is achieved with free formaldehyde under alkaline conditions. The plugging solution is prepared by mixing an aqueous solution of a phenol-formaldehyde resin with a bituminous emulsion and adding the hardener (formaldehyde) directly, before pumping the solution into the stratum. Tests showed that the formulation has a low viscosity, a reduced hardening time, and an improved plugging capability at low (but above zero) temperatures.



Phthalide

FIGURE 18.3 Phthalide.

TABLE 18.7 Plugging Material with 2-Furaldehyde-Acetone Monomer and Silicone Oligomers

Components	%
2-Furaldehyde–acetone monomer	70–96
Silicoorganic compound	1–10
Acidic or alkali hardener	3–20

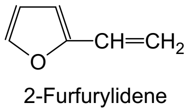


FIGURE 18.4 2-Furfurylidene.

Furan-Silicone Resins

A plugging material with a 2-furaldehyde-acetone monomer and silicone oligomers has been described (Leonov et al., 1993b). The components of this material are shown in Table 18.7.

The monomer can contain mono-furfurylidene-acetone and difurfurylidene-acetone. The hardener can be iron chloride, benzene sulfonic acid, hexamethylene diamine, or polyethylene amine. The plugging stone has improved strength, elastic deformation, and anticorrosion and adhesion properties. 2-Furfurylidene is shown in Figure 18.4.

CEMENT WITH ADDITIVES

Polymethyl Methacrylate Modified with Monoethanolamine

Polymethyl methacrylate (PMMA) can be modified with monoethanolamine to form a water-soluble polymer, which is used as a cement additive to increase strength in amounts less than 0.5% of the total weight of the composition (Sharipov et al., 1993). The plugging stone so produced has improved strength within a temperature range of $-30 - +300$°C.

Aluminum oxychloride and modified poly(methyl methacrylate) exhibit a reduction of the permeability of the stratum up to 99.69% (Sharipov et al., 1992b).

Crude Light Pyridine Bases

Small amounts of a pyridine base increases the corrosion resistance of cement without any associated loss of strength (Kudryashova et al., 1992). The use of nitrilo trimethyl phosphonic acid and an adduct between hexamethylenetetramine and chlorinated propene or butene improves adhesion to the metal, hardening times, mobility, and strength (Tsytsymushkin et al., 1992b). The latter adducts are further claimed to be useful as additives in cementing oil and gas wells in salt-bearing strata (Tsytsymushkin et al., 1993b).

Granulated Fly Ash

Granulated fly ash (Abramov et al., 1993) can substitute for Portland cement by up to 40–60%. Fly ash is used in granulated form and has a moisture content of around 10–20%. The formulation can be used for cementing oil and gas wells within a temperature range of 20–250°C. The solution has reduced water absorption and increased sedimentation stability. A formulation (Palij et al., 1993) is shown in Table 18.8. Hydrosil (Aerosil®) is used to increase the adhesion of the produced cement rock to the casing string. It also reduces the density and water absorption.

Phosphonic Acid Derivates

A corrosion-resistant formulation (Tsytsymushkin et al., 1993a) is achieved by adding phosphonic acid and hydrazine hydrochloride, as shown in Table 18.9.

TABLE 18.8 Portland Cement with Fly Ash as Active Constituent

Components	%
Portland cement	50–65
Fly ash	20–32
Sodium or calcium sulfate	2–8
Hydrosil	9–14

TABLE 18.9 Corrosion Resistant Formulation

Component	[%]
Plugging Portland cement	73.20–73.38
Nitrilo trimethyl phosphonic acid	0.02–0.04
Hydrazine hydrochloride	0.18–0.32
Water up to 100	

TABLE 18.10 Plugging Solution with Portland Cement and Phosphonium Complexone

Components	[%]
Portland cement	69–70
Calcium chloride	2.0–3.5
Phosphonium complexone	0.020–0.035
Water up to 100	

Hydrazine hydrochloride, combined with nitrilo trimethyl phosphonic acid, provides increased inhibition of the plugging solution.

The hydrazine hydrochloride can bind the free oxygen present in the plugging solution, and reduces the amount of sulfur oxides in the cement rock that is formed after hardening, thus preventing corrosion. The plugging rock has an increased corrosion stability in hydrogen sulfide-containing media. The final product has a high adhesion to metal. The recipe can be modified with polyoxyethylene and a water-soluble cationic polyelectrolyte to increase the sedimentation stability (Okishev et al., 1995).

Phosphonium Complexone

Small amounts of phosphonium complexone (Savenok et al., 1993) are sufficient to increase adhesion to the stratal rock. Table 18.10 illustrates an example plugging solution, containing Portland cement and phosphonium complexone. Calcium chloride regulates the setting time in the suggested composition. More precisely, phosphonium complexone is a name given to certain chelating phosphorous compounds (e.g., oxyethylidene diphosphonic acid, nitrilo trimethyl phosphonic acid, sodium tripolyphosphate, or amiphol) (Ryabova et al., 1993). The mixture is applicable at temperatures of 20–75°C.

Aerated Plugging Solution

An aerated plugging solution has been proposed that uses certain waste products from the chemical industry (Dulaev et al., 1992), as shown in Table 18.11. The water-glycol mixture contains ethylene glycol, ethylcellosolve, diethylene glycol, triethylene glycol, and ethyl carbitol. It is obtained as a waste from the production of oligomers as a result of washing the equipment with water.

The composition has an improved thermal stability, and when combined with a water-glycol mixture, it provides a high foam-forming ability and an increased degree of aeration of the plugging solution. It can be used as part of

TABLE 18.11 Composition for Preparation of Aerated Plugging Solution

Composition	[%]
Portland cement	100
Oxethylated monoalkyl phenols of propylene trimers	0.2–0.6
Water-glycol mixture	0.1–1.4
Air	0.01–0.02
Water	45–80

an aerated plugging solution that is suitable for wells under normal geologic conditions, and those having zones of abnormally low pressure.

Compressed Foam Mixture

Thread leaks, small holes, and leaks around packers in well casings and production tubing can be repaired by applying a compressed foam mixture (Hamilton, 1989). The mixture contains discrete solid particles of various sizes, to be forced into the opening to achieve a high friction seal. The foam mixture is moved along the inside of the conduit sandwiched between fluid bodies to keep it intact. A backpressure is applied to force the mixture through the openings.

Furfuramide

The addition of furfuramide to a plugging cement in portions of 1–10% produces a plugging rock of increased corrosion resistance and reduced water permeability (Leonov et al., 1993a).

Cellulosics and Polyacrylics

0.1% of modified methyl cellulose and mono-substituted sodium phosphate, respectively, may be added to plugging cement (Tsytsymushkin et al., 1992a). The latter weakens the effect of calcium ions on modified methyl cellulose and prevents its coagulation resulting in stabilization of the plugging solution and increased strength of the cement rock. Either PAM or cellulose esters, together with alkali silicate, are useful in enhanced oil recovery in front flooding techniques (Dobroskok et al., 2000). Injection in a wellbore forces the oil from adjacent interlayers. Similarly, PAM cellulose derivates in combination with silicates reduce the permeability (DiLullo Arias et al., 2001; Starshov et al., 2002).

TABLE 18.12 Acid Resistant Cement Formulation

Component	%
Slag-sand cement	100
Iron chloride	0.5–1.0
Polyacrylamide	0.05–0.10
Ethyl silicate	1–3
Water	48–51

A cement formulation, as indicated in Table 18.12, is useful as a plugging solution in deep and super-deep wells at temperatures of 100–160°C and in the presence of hydrogen sulfide (Alikin et al., 1992). The solution has a high resistance to hydrogen sulfide attack.

Trivalent iron chloride is used as the hexahydrate. The solution is prepared by first making a 1.5% aqueous solution of PAM by dissolving portions of dry PAM powder stepwise in water at temperatures of 40–60°C. A solution of iron chloride in water is prepared separately, and to this the required amount of ethyl silicate is added. Eventually the solution is mixed with slag-sand cement, and the prepared 1.5% PAM solution is added.

Smectite Clays

Smectite clays, e.g., hectorites, have been proposed as additives for Portland cement to obtain a thixotropic formulation. Good results have been obtained with the synthetic clay known as Laponite (Pafitis et al., 1996). The material is capable of gelling reversibly in less than 60 s. This thixotropic material generally finds use in oil well applications; for example, to plug lost circulation zones, as grouts to repair damaged or corroded casing, and to limit annular gas migration. The material also finds particular application in techniques for the completion of horizontal wells, which need slotted or predrilled liners.

Plasticizers

When drilling deep wells, successfully filling the annulus with cement slurry can be achieved by treating the slurry with plasticizers to increase its mobility. The plasticizer must liquefy the slurry, but should not adversely affect any other parameters. It should also be readily available and inexpensive.

These requirements have been met by caprolactam production wastes (Belov et al., 1989). The alkaline waste waters of caprolactam production (AWCP) are an aqueous solution of the sodium salts of mono- and dicarboxylic acids at a

TABLE 18.13 Formulation for a Plugging Slurry for Oil and Gas Well Drilling (Podgornov et al., 1992)

Compound	%
Portland cement	100
Bentonite clay powder	5–12
Water glass (calculated on the dry weight)	0.4–0.8
Sodium chloride	9.4–16.3
Water	52–63

concentration of 23–34%, with a solution density of 1.14–1.16 $\mathrm{g\,cm^{-3}}$, and a pH of 10.4. The AWCP agent increases the mobility of plugging agents prepared from Portland cement and gel-cement slurries with various bentonite contents. It is added to the mixing water of the cement slurry at a rate of 0.08–0.41%, with respect to the dry product, to the mass of mixing water. It plasticizes the plugging slurries but does not change the setting time or the strength of the hardened cement.

Water Glass

A plugging slurry for oil and gas well drilling is given in Table 18.13 (Podgornov et al., 1992). It is formed by adding water to a suspension containing the Portland cement and the other three constituents. The bentonite clay powder is premixed with water glass to form a paste, which is allowed to stand for at least 4 h. The composition is then mixed with the NaCl solution. Premixing the clay powder with the water glass adds a protective layer to the clay particles to hinder its hydration. The formulation is used as a plugging slurry for drilling oil and gas wells. The moisture-combining capacity of the solidified rock is increased, while its permeability is simultaneously reduced.

Organosilicones

Silicones may improve the properties of a Portland cement formulation when added in amounts of 0.2–2% (Moskvicheva et al., 1993). An example formulation of the additive is given in Table 18.14.

The presence of the additive results in the formation of a homogeneous structure of the plugging rock, with an improved uniformity of the phase composition of the system and a more compact distribution of the dispersed particles. An increased strength of the cement rock is also obtained.

TABLE 18.14 Composition of the Silicone Additive (Moskvicheva et al., 1993)

Components	%
Sodium organosilicone	25–30
Silicoorganic component	15–18
Sodium hydroxide	10–14
Ethanol	15

TABLE 18.15 Plugging Solution with Portland Cement, Expanding Additive, and Formaldehyde Resin

Components	[phr]
Portland cement	100
Expanding additive, based on caustic calcium oxide	2–10
Polymethylene urea, amino-formaldehyde resin	0.05–1.50
Water	45–55

Formaldehyde Resin

An expanding additive is based on calcium oxide (CaO) fired at high temperatures. The expansion takes place on the uptake of water. An example for a formulation containing an expanding additive is shown in Table 18.15 (Akhrimenko et al., 1992; Taradymenko et al., 1993).

An amino-formaldehyde or acetone-formaldehyde resin has the capability to harden in alkaline media, in contact with a cement solution with a pH of 11 to 12. The presence of sintered CaO provides the required conditions for hardening of the methylol groups of the formaldehyde resin with Ca^{2+} ions and a further simultaneous reaction of the methylol groups that formed hydrate compounds, resulting in an improved dispersion and plastification of the solution.

Liquid Metal Alloy

A liquid metal alloy containing gallium, indium, and tin has been proposed as an additive to Portland cement (Allakhverdiev et al., 1993). A formulation is shown in Table 18.16. The liquid metal alloy has a melting point of 11°C. Its

TABLE 18.16 Portland Cement with Liquid Metal Alloy

Components	%
Portland cement	63.4–65.0
Isobutyl alcohol	0.13–0.17
Liquid metal alloy of Ga, In, Sn	0.13–0.17
Water up to 100	

presence does not cause corrosion of stainless steel up to 250°C, but causes corrosion of steel alloys at temperature above 35°C. It dissolves aluminum at room temperature. The alloy is harmless to skin and to mucous membranes.

Isobutanol is used as an alcohol component to increase strength of produced cement stone. It should be noted that gallium and indium are precious metals, and better used in the nonferrous metal industries.

Bentonite

A composition of bentonite particles covered with a water-soluble coating of biodegradable natural resin is biodegradable and environmentally safe (Ryan, 1995). The bentonite may be used in the form of chips or compressed pellets, and when exposed to water, the soluble coating dissolves at a uniform rate, exposing it to water. The bentonite then expands to form a tough but flexible water-impermeable seal of a semisolid, gel-like mass. The well-plugging composition is non-toxic, nonpolluting, and non-hazardous. It will not become sticky or expand upon initial contact with water and thereby prevents binding, clumps, and faulty seals.

An aqueous suspension of bentonite clay powder (20–25%), ground chalk (7–8%), sulfanol (0.10–0.15%), and carboxymethyl cellulose (1.0–1.5%) forms the first component of (Trotskij et al., 1993) a two-component plugging material. This solution is pumped into the formation, and a gel is formed if diluted hydrochloric acid is then pumped down to mix with the first component. The hydrochloric acid is inhibited with a mixture of alkyl polybenzyl pyridinium chloride and urotropin.

Each of the individual reagents has a low viscosity and good pumping properties. After mixing in the stratum, they produce a highly viscous nonfiltering plug.

Blast Furnace Slag

Blast furnace slag is used successfully in mud-to-cement conversion worldwide because of its economic, technical, and environmental advantages (Pessier et al., 1994). Slag-mix slurries were used as primary, temporary abandonment and sidetrack plug cements during prospect predrilling in the Gulf of Mexico. However, the penetration rates were slower than expected when these plugs were drilled out, hence a basic study of its drilling properties was initiated.

Slag-mix, solidified mud, and conventional class H Portland cement were evaluated under controlled laboratory conditions to better understand and quantify differences in drillability between these two types of cement under realistic downhole conditions. The objectives of this study were to refine bit selection and drilling practices for more cost effective slag-mix plug drilling.

Fiber Reinforcement

Fibers can be added to a gelation solution (Merrill, 1994, 1995), but they must not interfere with the gelation process, must provide adequate reinforcement, and they should not adversely affect the ability of the solution to be pumped and injected. Glass and cellulosic fibers are preferred.

Mineral fibers that are highly soluble in acid can be used to control the permeability of formations (Montgomery et al., 1993, 1994). The fibers are 5–15 μ m in diameter and are formed into pellets of $\frac{1}{32}$ to $\frac{1}{2}$ in diameter. A fluid-blocking layer formed of semidispersed pellets can bridge the face pores of the formation. After well rework, the plugging layer is treated with an acid solution to quickly dissolve the mineral fibers to give the desired porosity.

The preferred fiber material typically consists of about 35.7% CaO, 9.6% MgO, 9.3% Al_2O_3, and 42.3% SiO_2. The composition of an example fiber material is shown in Table 18.17. This product is highly soluble in hydrochloric acid (HCl), forming a soluble silicic acid from the SiO_2, which is suspended in the HCl until, after a very long time, a residual silica gel may form and drop out of the solution. In a blend of 15% HCl and 10% acetic acid, the silica gel does not form or drop out of the solution. Thus, an acid wash scavenges as much of the fibrous network in the sealing mat as desired, resulting in a porous formation face of predetermined permeability.

Asbestos has been proposed as a reinforcing component (Fil et al., 1994), but it is a known carcinogen.

Glass and cellulose fibers are specifically disclosed as preferable reinforcing fibers for a gelling solution of PHPA with a crosslinking agent (Merrill, 1993). The fibers are added to a gelation solution, and the mixture is pumped to a subterranean injection site, where it gels in place. The fibers do not interfere with the gelation process and can provide adequate reinforcement without adversely affecting the ability of the solution to be pumped and injected.

Gels from Aluminum Hydroxychloride

Aluminum hydroxychloride is used as a plugging agent (Parker, 1988). A weak base activator such as sodium cyanate with an activator aid can establish delayed gelation.

TABLE 18.17 Composition of Raw Fiber Material (Montgomery et al., 1993, 1994)

Constituents	%
SiO_2	38–42
Al_2O_3	6–15
CaO	15–38
MgO	6–15
Fe_2O_3	0.2–15
Total alkalis such as Na_2O	1–3
SO_3	0.03–1
Loss on ignition	0.5
pH in water	<8.0
% Water-soluble	<0.2
Water-soluble sulfate	<0.05

ORGANOSILICONES

Silicones are frequently used compounds for hydrophobization in diverse industrial areas.

A silicone microemulsion was developed for restriction of water production in gas wells. The treating solution was a surfactant-stabilized siloxane emulsion, which was driven into the formation by water and nitrogen (Lakatos et al., 2002c). Various silanes, siloxanes, and silicone resins mostly in *i*-propanol or in *i*-octane solution were proposed for the restriction of water production in gas wells (Lakatos et al., 2002b). Both silicone fluids (microemulsion and solution in *i*-propanol) resulted in a significant mobility change in cores. The effect was strongest for the concentrated siloxane systems, due to their high viscosity.

A disproportional permeability modification was observed due to water retention by the microemulsions. This was attributed to the microemulsion inverting to a macroemulsion, initiated by the spontaneous dilution by water and then entrapping of formed siloxane droplets by the pores. The stock silicone emulsion was a water-external microemulsion with 30% siloxane content stabilized by a mixture of non-ionic surfactants. According to laser light scattering measurements, the siloxane droplet size was about 280 nm.

The silicone microemulsion is more effective in reducing mobility. The most extreme mobility reduction was obtained at a concentration of only $0.2\,\mathrm{g\,l^{-1}}$ siloxane. The experiments revealed that the mechanisms of silicone emulsion and solution type treatments are different (Lakatos et al., 2002c). The silicone emulsion makes the cores more water-wet and any negative effect of silicone on the wettability is completely absent. A shift in wettability toward the oil-wet character is imminent when an siloxane solution in *i*-propanol, is used as a treating agent. Any strong chemical interaction between the siloxane and the rock surface can be excluded in microemulsion-type treatments, where the formation of an adsorbed siloxane layer is probably responsible for changes in wettability, and hence in hydrodynamic properties of water/gas/rock systems.

NON-CROSSLINKED COPOLYMERS

Non-crosslinked polymers can also produce a disproportionate permeability reduction. Combinations of a hydrophilic-monomer and a hydrophobically-modified hydrophilic monomer were particularly effective in reducing permeability by adsorbing on to the surfaces within the porous formation.

Examples of hydrophilic comonomers are AAm, 2-acrylamido-2-methyl-1-propane sulfonic acid, acrylic acid (AA), dimethyl amino ethyl methacrylate, and vinylpyrrolidone (Eoff et al., 2002). Octadecyldimethyl ammonium ethyl methacrylate bromide, hexadecyldimethyl ammonium ethyl methacrylate bromide, hexadecyldimethyl ammonium propyl methacrylamide bromide, 2-ethylhexyl methacrylate, and hexadecyl methacrylamide are examples of hydrophobically modified hydrophilic comonomers. They are used at levels of 1–10 mol-%.

Anchoring

This type of disproportionate permeability reduction is known as anchoring (Dawson et al., 2001). The term *monomeric anchoring unit* refers to a component of a polymer that will preferentially adhere, by either a physical or a chemical process, to the subterranean formation. Anchoring groups are introduced to prevent a polymer from washing out of the formation in fluid flow.

Clay and feldspar surfaces existing in formation pores, channels, and pore throats are primary anchoring sites for the monomeric anchoring units. Anchoring units have polar functional groups, which can hydrolyze to form amine-based anchoring groups on the polymer. These types of monomers are known as first anchor units. Besides these, salt functional vinyl monomers that act as secondary anchor units may be present.

N-vinylformamide, *N*-methylacetamide, or *N*,*N*-diallylacetamide can be primary anchor monomers, and secondary anchor monomers can be acrylamidomethylpropanesulfonic acid ammonium or alkali metal salts, AA salts, dimethyl diallyl ammonium chloride.

INORGANIC COLLOIDS

Numerous inorganic compounds can form colloidal systems, particularly gel-like precipitates. This feature can be utilized for plugging purposes. The number of useful inorganic compounds is limited by the requirements of the sealing system. For instance, it is important that the chemical reaction should remain highly controllable.

These requirements are fulfilled, however, by the sulfur-ammonium group of multivalent cations. They hydrolyze easily in aqueous alkaline medias resulting in a gel-like precipitate. The hydroxides of such cations are practically insoluble in water, although some of them show amphoteric character. Experiments showed that Fe (III) compounds in particular give gel-like precipitates on in situ hydrolysis, which can then be immobilized by in situ flocculation or spontaneous aging (Lakatos et al., 2000).

The blocking agent proposed consists of two aqueous solutions. The first contains iron trichloride in hydrochloric acid, and a corrosion inhibitor, and the second contains sodium carbonate and a low molecular weight PAM or PHPA as flocculant. The technique has the following advantages (Kosztin et al., 2002):

1. Low viscosity of treating solutions, viz. good placement selectivity;
2. Short to moderate pumping time before onset of gelation, block/barrier formation;
3. Flexible chemical mechanism of gelation;
4. Good chemical and chemical stability of gel;
5. Effective immobilization of gel or barrier;
6. Excellent thermal, flow, and mechanical resistivity;
7. Easy gel breaking in case of technical failures; and
8. Simple and cost-effective surface technology.

WATER SWELLING ADDITIVES

Water-swelling Cellulose

In porous-fractured oil reservoirs, water shutoff can be achieved by the injection of a selective waterproofing polymer composition, followed by injection of a water-swelling hydroxyethyl cellulose (HEC) polymer, which has particles smaller than the transverse dimension of the fractures (Zakirov et al., 2002). The water shutoff takes place in the water-bearing part of formation, and the permeability of the oil formation is preserved.

Hydrolyzed Polyacrylonitrile

Hydrolyzed polyacrylonitrile (HPAN) exhibits the properties of a polyelectrolyte. A method of water shutoff utilizing HPAN consists of two steps (Latypov et al., 2002). The water-bearing part of the formation is first treated with a semi-concentrated solution of hydrochloric acid. Then HPAN is to be injected, further hydrolyzed in the formation.

Guar

Guar gum is a standard polymer for well-treating fluids. It develops a high viscosity via hydration are hydroxypropyl guar, carboxymethyl guar, and carboxymethyl hydroxypropyl guar. Fast-hydrating derivatives of guar, hydrating within only 30 s, while conventional materials need some 30 min.

Clays

Clays can swell when placed in the formation, when a clay dispersed in an organic medium comes into contact with water, or when the ionic strength of the aqueous medium changes.

High-permeability regions can be blocked with a reinforced, swelling clay gel. The slurry is prepared by mixing a swelling clay, such as bentonite, with an aqueous solution containing the salt of certain cations, which inhibit the clay swelling, and a reinforcing agent (Zhou et al., 2001). The reinforced clay slurry is introduced into high-permeability regions, where it is contacted with NaCl brine solution. The inhibitive cations bound to the clay particles are replaced by Na^+ ions, which attract water molecules and promote clay swelling. A similar procedure is suitable for blocking high-permeability channels (Zhou, 2000).

Organophilic Swelling Clay

Compositions for permanent plugging comprise an oil, a hydratable polymer, an organophilic clay, and a water-swellable clay. An oil-based sealing composition contains 43–53%, diesel oil 4–5%, HEC 0.4–0.5% an alkyl quaternary ammonium bentonite clay, and 42–53% water swellable bentonite clay (Sweatman, 2001). These compositions develop ultra-high viscosity in a few seconds or minutes, but they cannot easily be removed.

WASTES

Several industrial waste products may be used as ingredients for plugging solutions. Some examples are summarized in Table 18.18, and others are detailed elsewhere. The technique is regarded as a method of waste disposal and was originally proposed in the Eastern European countries. Waste from galvanizing processes is known to be active (Kosyak et al., 1993). Iron and chromic salts from lignosulfonate are used as a source of metal ions (Kotelnikov et al., 1992). Lignosulfonates are waste products from the paper industry.

Waste Oil Sludge

A mixture of approximately 85% oil sludge, 10% formaldehyde, and 2% sulfuric acid has been proposed as a plugging material (Kolesnikova et al., 1992).

TABLE 18.18 Industrial Waste Products as Ingredients for Plugging Solutions

Purpose	Waste	References
Clinker-less binder	Slag from melting of oxidized nickel ores	Rakhmatullin et al. (1992)
Hemi-hydrated gypsum	Waste obtained in production of nitrilo trimethyl phosphonic acid[a]	Sharipov et al. (1992a)
	Waste from formic acid production	Zeltser (1992)
Polyacrylamide	Manganese nitrate or waste from galvanizing, electronic works[b]	Kosyak et al. (1993)
Hydrolyzed polyacrylonitrile	Waste from lanolin production treated with triethanol amine and water[c]	Perejma and Pertseva (1994)
	Industrial waste from nitric industry	Burshtejn and Logvinenko (1995)
Mineral binder	Waste from production of epoxide resins	Leonov et al. (1995)
Portland cement	Sodium sulfate waste from sebacic acid production	Perejma et al. (1995)

a) Waste for setting time adjustment for gypsum
b) Two-component plugging solution
c) Waste-complexing reagent

The oil sludge was left behind during primary preparation of processing oil and contains 8–16% of oil. It is a paste-like mass containing finely crushed rock fractions and oil. The material is produced by direct mixing of the three components, and is pumped into the well followed by pressing-in air, which is preheated to 80–140°C.

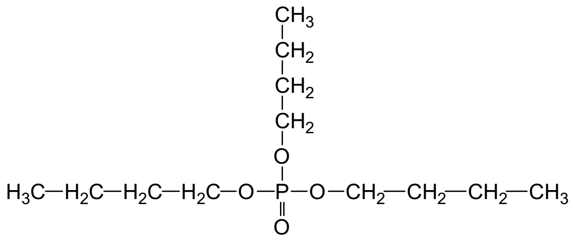
The compressive strength of the plugging rock so produced is shown in Table 18.19. The material is cheap because industrial waste is used, and it produces a plugging rock of increased strength.

Aluminum Trichloride

Aluminum trichloride, a cheap, abundant waste product of the chemical industry, forms a gel with carbonates and on mixing with alkalis. Laboratory and field tests showed that aluminum trichloride can be used as a gel-forming agent for reducing the permeability of water-conducting channels (Garifullin et al., 1996).

TABLE 18.19 Compressive Strength of the Produced Plugging Rock

Temperature [°C]	Compressive Strength [M Pa]	Water Absorption over 24 hr/[%]
80	1.40–1.46	2.3–2.5
110	1.44–1.45	2.3–2.6
140	0.54–0.59	2.4–2.7



$$H_3C{-}H_2C{-}H_2C{-}H_2C{-}O{-}\overset{\displaystyle O{-}CH_2{-}CH_2{-}CH_2{-}CH_3}{\underset{\displaystyle \| \atop O}{P}}{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_3$$

FIGURE 18.5 Tributyl phosphate

Antifoaming with Sulfite-waste Liquor

Sulfite-waste liquor (SWL) is an additive for plasticizing plugging agents, but its use is limited because of the pronounced foaming that occurs when SWL is added to the cement in amounts greater than 0.5%. To prevent this, a drilling mud antifoam agent should be added (Zobs et al., 1989).

A synergistic effect is served if polymethylsiloxane and tributyl phosphate are used. Polymethylsiloxane simultaneously displaces the adsorbed molecules of the foam stabilizer (i.e., lignosulfonate) from the foam film, and the tributyl phosphate, c.f., Figure 18.5, reduces the surface viscosity of the film.

SURFACTANTS

Polymeric Surfactants

Injecting a polymeric surfactant and an inert gas into the water producing zone reduces the water permeability of a water-producing zone.

There are a number of studies of the physical gels, which are formed by polymer-surfactant interactions. The gelation and viscoelastic behavior results from specific interactions between the polymer chains and the micelles formed from assembled surfactant monomers. Commonly, the polymers have some fraction of hydrophobic groups on their chains, which are associated with the surfactant micelle, or solubilized in the surfactant micelle (Loyen et al., 1995; Piculell et al., 1995; Sarrazin-Cartalas et al., 1994; Wang et al., 1997).

Viscoelastic Surfactant Solutions

The term *viscoelastic* refers to those viscous fluids having elastic properties, i.e., the liquid at least partially returns to its original form when an applied stress is released. Viscoelastic surfactant solutions have been described in detail by Hoffmann (1994); Hoffmann et al. (1992, 1994); and Hoffmann and Rauscher (1992). Viscoelasticity is caused by a different type of micelle formation than the spherical micelles formed by most surfactants. Viscoelastic surfactant fluids form worm-like, rod-like, or cylindrical micelles in solution. The formation of long, cylindrical micelles creates useful rheological properties.

A viscoelastic surfactant solution exhibits shear thinning behavior, and remains stable despite repeated high shear applications. By comparison, a typical polymeric thickener will irreversibly degrade when subjected to high shear (Dahayanake et al., 2002). However, viscoelastic surfactants usually require higher concentrations of surfactant than a polymeric gelling agent system to develop equivalent viscosity (Kubala, 1987).

Amphoteric and Zwitterionic Surfactants

An amphoteric surfactant contains both a positively and a negatively charged moieties over a certain pH range, only a negatively charged moiety over a certain pH range, and only a positively charged moiety at a different pH range. A zwitterionic surfactant has a permanently positively charged moiety in the molecule that remains regardless of pH, and a negatively charged moiety at alkaline pH (Dahayanake et al., 2002).

Ionic Strength

Two techniques have been proposed for the controlled gelation of surfactant solutions by using changes in their ionic environments. Firstly, it is proposed to exchange the anions in the surfactant solution by replacing an anion that inhibits gelation with one that promotes it.

This can be achieved by passing the surfactant solution through a pipe or tube, the walls of which consist of an anion exchange membrane, while a counter-flow of an electrolyte containing the exchange anion is passed across the other side of the membrane (Hughes et al., 2001).

Mixtures of a Surfactant with Polymers

Mixtures of a surfactant and a polymer can result in a rigid gel. Such compositions can undergo a two-stage gelation process (Jones and Tustin, 2001). In this context viscoelastic surfactants are also known as gel-promoting additives (Schwartz et al., 2009).

TABLE 18.20 Coacervate Gel Systems

Polymer	Surfactant
Polydimethyl diallyl ammonium chloride	Sodium lauryl sulfate
Polyacrylamidomethylpropyl sulfonic acid	Quaternary ammonium surfactants
Polyacrylic acid	Quaternary ammonium surfactants

In the first stage, the surfactant micelles in the solution aggregate and entangle to form a viscoelastic physical gel. The viscoelasticity of this gel can be rapidly destroyed by contact with hydrocarbons and other organic solvents, but is maintained for many hours in water (Jones and Tustin, 2001). In the second stage, the polymer can be crosslinked using a suitable chemical crosslinker. The crosslinked polymer gel forms within, and largely independently of, the surfactant gel. The final gel behaves as a chemical gel, which is significantly less responsive to its external physical and chemical environment. For example, the viscoelasticity of the final gel is not significantly affected by contact with a hydrocarbon.

Surfactant Polymer Compositions

An example of such an acrylic based composition is a solution of $30\,\mathrm{g\,l^{-1}}$ of the surfactant *N*-erucyl-*N*,*N*-bis2-hydroxyethyl-*N*-methyl ammonium chloride, and $7\,\mathrm{g\,l^{-1}}$ of hydrophobically modified PAM of molecular weight 2 MDalton with 3% of the hydrophobic *n*-nonyl acrylate monomer (Jones and Tustin, 2001).

A cationic colloidal coacervate includes both a cationic polymer and an anionic surfactant, e.g., polydiallyl dimethyl ammonium chloride. The viscosifying properties of a polymer coacervate are controlled by a long chain cationic or anionic polymer, and a smaller amount of an oppositely charged surfactant. A hydrophobic alcohol is also present to form a singular phase (Schwartz et al., 2009), e.g., lauryl alcohol. In Table 18.20 selected components for coacervate gel systems are summarized.

TAILORING THE HYDRODYNAMIC VOLUME

Gas production from gas fields and underground gas storage is usually accompanied by substantial water production, which often decreases the recovery efficiency and hampers environmentally friendly production. Because of the inverse mobility ratio of a gas/water system, conventional water shutoff or profile correction methods cannot be used successfully under field conditions.

A polymer solution containing a high salt concentration is injected into the wells. The reversible expansion and contraction, respectively, of polymer coils can be utilized for selective restriction of water flow and production in gas wells if special preconditions are fulfilled. The most important requirements are irreversible polymer adsorption at the rock surface, molecular size compatible with pore structure, and cyclic gas/water flow or change in salt content in the bulk aqueous phase.

An alternative approach is to use a poor solvent in preparation of the treating solution (Lakatos et al., 2002a). This concept is based on the fact that the solvent power worsens as the content of an at least partially water-soluble organic compound in an aqueous phase increases.

Short chain alcohols have drastic effects, both on the rheological properties and on the structure of aqueous polymer solutions, because of the substantial impact of a poor solvent on the coil size and hence, intermolecular and intramolecular interactions in different polymer solutions. There is also a remarkable effect on polymer adsorption and consequently, on flow phenomena of polymer solutions in porous media.

The change of coil density significantly depends on the type of alcohol and the ionization of the polymers. Partially hydrolyzed polymers show a much greater drop in size than only slightly or unhydrolyzed PAMs. The coil density increases with the alcohol content, and the specific polymer adsorption is gradually increased. Even at low alcohol content, the amount adsorbed might be an order of magnitude higher than in alcohol-free systems. At high alcohol content, the partial precipitation or the mechanical entrapment of the polymer in the porous medium cannot be excluded.

The permeability of polymer-treated cores can be completely reconstructed by removing all the solvents from the adsorbed layer by injecting dry gas into the polymer preflushed core. Evaporation of the bulk phase liquid from coils and adsorbed layers can be accelerated by using alcohols with a small enthalpy of vaporization. The specific enthalpy of vaporization of short chain alcohols decreases with the chain length, i.e., with the fraction of hydroxyl groups in the molecule that are capable of forming hydrogen bonds.

Alcohols also substantially decrease the surface tension, which allows more polymer to be absorbed and a more closely packed layer to form on the rock surface.

Temperature-Sensitive Latex Particles

Certain latex particles are temperature-sensitive and reversibly flocculate, shrink, and harden at higher temperatures and disperse, expand, and soften at lower temperatures. These particles can form effective blocking agents in the presence of an ionic compound.

The particle diameter of poly(*N*-isopropyl acrylamide) latex particles decreases on heating. This procedure was found to be fully reversible over a number of heating and cooling cycles, with no hysteresis taking place between the heating and cooling curves (Snowden et al., 1993).

REFERENCES

Abramov, S.A., Krezub, A.P., Mariampolskij, N.A., Bezrukova, E.S., Egorov, M.A., 1993. Plugging solution for cementing of oil and gas wells – contains plugging portland cement and granulated fly ash, of specified moisture content, as active additive. SU Patent 1 802 089, assigned to Borehole Consolidation Mu., March 15, 1993.

Ahmed, I., Moradi-Araghi, A., Hamouda, A.-A., Eriksen, O.I., 2000a. Compositions and processes for treating subterranean formations. US Patent 6 051 670, assigned to Phillips Petroleum Company (Bartlesville, OK), April 18, 2000.

Ahmed, I., Moradi-Araghi, A., Hamouda, A.-A., Eriksen, O.I., Patel, B.B., Stewart, W.S., 1997. Compositions and processes for treating subterranean formations. WO Patent 9 722 638, assigned to Phillips Petroleum Co., June 26, 1997.

Ahmed, I., Moradi-Araghi, A., Hamouda, A.-A., Eriksen, O.I., Patel, B.B., Stewart, W.S., 2000b. Compositions and processes for treating subterranean formations. GB Patent 2 340 832, assigned to Phillips Petroleum Co., March 01, 2000.

Akhrimenko, V.E., Levitin, V.B., Palij, L.V., Taradymenko, Y.Y., Timovskij, V.P., 1992. Plugging solution for cementing oil and gas wells – contains portland cement, expanding additive based on sintered calcium oxide, amino-formaldehyde or acetone-formaldehyde resin and water. SU Patent 1 776 765, assigned to Borehole Consolidation Mu., November 23, 1992.

Al-Muntasheri, G.A., Nasr-El-Din, H.A., Hussein, I.A., 2007. A rheological investigation of a high temperature organic gel used for water shut-off treatments. J. Pet. Sci. Eng. 59 (1–2), 73–83.

Alikin, P.A., Kasatkina, N.N., Makeev, N.M., Vantsev, V.Y., 1992. Plugging solution for deep wells – contains slag-sand cement, iron chloride, polyacrylamide, ethyl silicate and water, and has increased isolating efficiency. SU Patent 1 776 761, assigned to Kama Deep Extrem Borehole, November 23, 1992.

Allakhverdiev, R.A., Khydyrkuliev, B., Reznikov, N.V., 1993. Plugging solution for repairing oil and gas wells – contains plugging portland cement, isobutanol, water and liquid metal alloy of gallium, indium and tin, to increase strength of cement stone. SU Patent 1 802 082, assigned to Turkm Oil Ind. Res. Des. Inst., March 15, 1993.

Bailey, B., Crabtree, M., Tyrie, J., Elphick, J., Kuchuk, F., Romano, C., et al., 2000. Water control. Schlumberger's Oilfield Rev. 12, 30–51.

Belov, V.P., Zhivaeva, V.V., Egorov, K.K., 1989. Use of caprolactam production wastes as a plasticizer of plugging slurries. Izv Vyssh Ucheb Zavedenii, Neft Gaz (4), 15–18.

Blazhevich, V.A., Khisaeva, D.A., Umetbaev, V.G., Legostaeva, I.V., 1992. Polymer plugging solution for oil and gas wells – contains urea-formaldehyde resin, and aluminium chloride containing waste of isopropylbenzene production as acid hardener. SU Patent 1 763 638, assigned to Bashkir Oil Ind. Res. Inst., September 23, 1992.

Burshtejn, M.A., Logvinenko, S.V., 1995. Composition for temporary plugging of stratum during drilling process – comprises chemically precipitated chalk, or chalk-containing industrial waste e.g. from nitric industry, as plugging component (Eng). RU Patent 2 041 340, August 09, 1995.

Chatterji, J., Onan, D.D., King, B.J., Cromwell, R.S., 2000. Subterranean zone sealing methods and compositions. US Patent 6 059 035, assigned to Halliburton Energy Services, Inc. (Duncan, OK), May 9, 2000.

Cornely, W., Mehesch, H., Meyer, F., Kubens, R., Winkelmann, M., 1984. Process for consolidation and sealing of geological formations and artificial beds of rock, earth, and coal. US Patent 4 475 847, assigned to Bergwerksverband GmbH (Essen, DE) and Bayer Aktiengesellschaft (Leverkusen, DE), October 9, 1984.

Crawshaw, J.P., Nijs, O.C.J., 2002. Emulsion for well and formation treatment. US Patent 6 364 020, assigned to Schlumberger Technology Corporation (Sugar Land, TX), April 2, 2002.

Dahayanake, M.S., Yang, J., Niu, J.H.Y., Derian, P.-J., Li, R., Dino, D., 2002. Viscoelastic surfactant fluids and related methods of use. US Patent 6 482 866, assigned to Schlumberger Technology Corporation (Sugar Land, TX), November 19, 2002.

Dartez, T.R., Jones, R.K., 1994. Method for selectively treating wells with a low viscosity epoxy resin-forming composition. US Patent 5 314 023, May 24, 1994.

Dartez, T.R., Jones, R.K., 1995. Method for selectively treating wells with a low viscosity epoxy resin-forming composition. WO Patent 9 532 354, November 30, 1995.

Dawson, J.C., Le, H.V., Kesavan, S., 2001. Compositions and methods for selective modification of subterranean formation permeability. US Patent 6 228 812, assigned to BJ Services Company (Houston, TX), May 8, 2001.

DiLullo Arias, G.F., Rae, P.J., Mueller, D.T., 2001. Multi-functional additive for use in well cementing. US Patent 6 235 809, assigned to BJ Services Company (Houston, TX), May 22, 2001.

Dobroskok, B.E., Kubareva, N.N., Khisamov, R.S., Jakovlev, S.A., Ibragimov, N.G., Khannanov, R.G., et al., 2002. Oil-formation development. RU Patent 2 185 505, assigned to Oao Tatneft Neftekhim-servis, July 20, 2002.

Dobroskok, B.E., Kubareva, N.N., Musabirov, R.K., Ganeeva, Z.M., Abrosimova, N.N., Muslimov, R.K., et al., 2000. Method adjusting front of flooding of oil pools. RU Patent 2 146 002, assigned to Ooo Nau and Chno Proizv Pred Tatrojl, February 27, 2000.

Dovan, H.T., Hutchins, R.D., Sandiford, B.B., 1997. Delaying gelation of aqueous polymers at elevated temperatures. In: Proceedings Volume, no. SPE 37246, 1997 International Symposium on Oilfield Chemistry, February 18–21, 1997, Houston, Texas, p. 11.

Dulaev, V.K., Bondarets, N.M., Polukhina, N.A., Petresku, V.I., Galiev, R.G., Kapustin, P.P., et al., 1992. Composition for preparation of aerated plugging solution – contains portland cement, oxyethylated monoalkylphenol(s) of propylene trimers, glycol mixture, air, water, etc. SU Patent 1 745 893, July 07, 1992.

Eoff, L., Chatterji, J., Badalamenti, A., McMechan, D., 2001. Water-dispersible resin system for wellbore stabilization. In: Proceedings Volume, SPE Oilfield Chem. International Symposium, Houston, TX, February 13–16, 2001, p. 10.

Eoff, L.S., Reddy, R.B., Dalrymple, E.D., 2002. Reducing subterranean formation water permeability. EP Patent 1 193 365, assigned to Halliburton Energy Serv. Inc., April 03, 2002.

Fil, V.G., Ezlova, L.A., Kovalenko, V.D., Kostenko, D.A., Navrotskij, B.I., Koptenko, V.V., et al., 1994. Plugging solution for oil and gas wells – comprises portland cement, asbestos reinforcing component, mixture of sodium chloride and sulphate mineral component, fly ash and water. (rus). RU Patent 2 013 525, assigned to Ukr. Natural Gas Res. Inst., May 30, 1994.

Fox, K.B., Moradi-Araghi, A., Brunning, D.D., Zornes, D.R., 1999. Compositions and processes for oil field applications. WO Patent 9 947 624, assigned to Phillips Petroleum Co., September 23, 1999.

Galchenko, P.P., Titareva, A.P., Kalashnik, L.G., Krupenko, V.D., 1993. Plugging solution – contains phenol-formaldehyde resin, formaldehyde, water and additionally bituminous emulsion of specified composition. SU Patent 1 795 082, assigned to Mine Build Org Mech Res., February 15, 1993.

Ganguly, S., Willhite, G.P., Green, D.W., McCool, C.S., 2002. The effect of fluid leakoff on gel placement and gel stability in fractures. SPE J. 7 (3), 309–315.

Garifullin, S.S., Gallyamov, I.M., Plotnikov, I.G., Shuvalov, A.V., 1996. Aluminum chloride-based gel-forming technologies. Neft Khoz (2), 32–35.

Gross, J.M., 1987. Gelling organic liquids. EP Patent 225 661, assigned to Dowell Schlumberger Inc., June 16, 1987.

Hamilton, B.E., 1989. Method of plugging openings in well conduits. US Patent 4 869 321, September 26, 1989.

Hardy, M.A., 2001. Method and compositions for reducing the permeabilities of subterranean zones. US Patent 6 196 317, assigned to Halliburton Energy Services, Inc. (Duncan, OK), March 6, 2001.

Harris, L.E., Holtmyer, M.D., Pauls, R.W., 1986. Method for fracturing subterranean formations. US Patent 4 622 155, assigned to Halliburton Co., November 11, 1986.

Hilterhaus, K.-H., 1992. Organomineral products from aqueous alkali metal silicate, polyisocyanate and epoxy resin. US Patent 5 107 928, April 28, 1992.

Hirasaki, G.J., Miller, C.A., 2003. Reducing water permeability in subterranean formation. EP Patent 1 312 753, assigned to Univ. Wm Marsh Rice, May 21, 2003.

Hoffmann, H., 1994. Viscoelastic surfactant solutions. In: Herb, C.A., Prud'homme, R.K. (Eds.), Structure and Flow in Surfactant Solutions, vol. 578 of ACS-Symp. Ser., American Chemical Society, Washington, DC, pp. 1–31.

Hoffmann, H.R.H., Rauscher, A., 1992. Rheology of viscoelastic micellar solutions. In: Chen, S.H. (Ed.), Proceedings, Structure and Dynamics of Strongly Interacting Colloids and Supramolecular Aggregates in Solution. Kluwer Academic Publishers, Dordrecht, pp. 493–510.

Hoffmann, H., Schulz, S., Gradzielski, M., Rauscher, A., 1992. The influence of ionic surfactants on the viscoelastic properties of zwitterionic surfactant solutions. Langmuir 8, 2140–2146.

Hoffmann, H., Thunig, C., Schmiedel, P., Munkert, U., Ulbricht, W., 1994. The rheological behaviour of different viscoelastic surfactant solutions. Tenside Surf. Det. 31, 289–400.

Huddleston, D.A., 1989. Hydrocarbon geller and method for making the same. US Patent 4 877 894, assigned to Nalco Chemical Co., October 31, 1989.

Huddleston, D.A., 1992. Liquid aluminum phosphate salt gelling agent. US Patent 5 110 485, assigned to Nalco Chemical Co., May 05, 1992.

Hughes, T.L., Jones, T.G.J., Tustin, G.J., 2001. Viscoelastic surfactant based gelling composition for wellbore service fluids. US Patent 6 232 274, assigned to Schlumberger Technology Corporation (Sugar Land, TX), May 15, 2001.

Hutchins, R.D., Dovan, H.T., Sandiford, B.B., 1996. Field applications of high temperature organic gels for water control. In: Proceedings Volume, no. SPE/DOE 35444, 10th SPE/DOE Improved Oil Recovery Symposium, April 21–24, 1996, Tulsa, OK, p. 8.

James, S.G., Nelson, E.B., Guinot, F.J., 2002. Sand consolidation with flexible gel system. US Patent 6 450 260, assigned to Schlumberger Technology Corporation (Sugar Land, TX), September 17, 2002.

Jones, T.G.J., Tustin, G.J., 2001. Gelling composition for wellbore service fluids. US Patent 6 194 356, assigned to Schlumberger Technology Corporation (Sugar Land, TX), February 27, 2001.

Kan, V.A., Stupochenko, V.E., Sorkin, A.J., Djabin, A.G., Romashova, M.M., 2002. Method of isolation of formation high-permeability intervals. RU Patent 2 186 958, assigned to N Tekhnol Aoot and Auchno Tekhn Kompleks Nefteotd, August 10, 2002.

Keller, A., Narh, K.A., 1994. The effect of counterions on the chain conformation of polyelectrolytes, as assessed by extensibility in elongational flow: the influence of multiple valency. J. Polym. Sci., Part B: Polym. Phys. 32, 1697–1706.

Khatib, Z., Verbeek, P., 2003. Water to value-produced water management for sustainable field development of mature and green fields. J. Pet. Technol. 55 (1), 26–28.

Kleshchenko, I.I., Jagafarov, A.K., Panikarovskij, V.V., Efimov, A.D., Demichev, S.S., 2003. Composition for formation waters shutoff in oil and gas wells. RU Patent 2 196 877, assigned to Ooo Tju and Menniigiprogaz, January 20, 2003.

Kolesnikova, I.P., Sushkova, N.A., Ershov, B.N., 1992. Plugging material giving plugging rock of increased strength – contains oil sludge from primary oil processing, formaldehyde and sulphuric acid. SU Patent 1 781 415, assigned to Soyuztermneft Sci Prod. Assoc., December 15, 1992.

Kosyak, S.V., Danyushevskij, V.S., Pshebishevskij, M.E., Trapeznikov, A.A., 1993. Plugging formation fluid transmitting channel – by successive injection of aqueous solution of polyacrylamide and liquid glass, buffer liquid and aqueous solution of polyacrylamide and manganese nitrate. SU Patent 1 797 645, February 23, 1993.

Kosztin, B., Palasthy, G., Udvari, F., Benedek, L., Lakatos, I., Lakatos-Szabó, J., 2002. Field evaluation of iron hydroxide gel treatments. In: Proceedings Volume, no. SPE Number 78351, SPE 13th European Petroleum Conterence, Aberdeen, Scotland, UK, October 29–31, 2002, pp. 1–10.

Kotelnikov, V.S., Demochko, S.N., Fil, V.G., Rybchich, I.I., 1992. Polymeric composition for isolation of absorbing strata – contains ferrochromo-lignosulphonate, water-soluble acrylic polymer and water. SU Patent 1 730 435, assigned to Ukr. Natural Gas Res. Inst., April 30, 1992.

Kubala, G., 1987. Aqueous gelling and/or foaming agents for aqueous acids and methods of using the same. US Patent 4 695 389, assigned to Dowell Schlumberger Incorporated (Tulsa, OK), September 22, 1987.

Kudryashova, Z.N., Mikhajlov, B.V., Tarnavskij, A.P., Khajrullin, S.R., Mustafaev, V.M., Tsytsymushkin, P.F., 1992. Plugging solution for cementing oil and gas wells – contains plugging cement, ash, additional clay powder and crude light pyridine bases, and water. SU Patent 1 765 366, assigned to Volgo Urals Hydrocarbon, September 30, 1992.

Lakatos, I., Kosztin, B., Lakatosne, D.S.J., Palasthy, G., Bodola, M., Kristof, P., et al., 1999a. Layer-treating procedure basing upon of an "in situ" hydrolisation and flocculation of inorganic compounds for stream equalizing of porousous systems with heterogenous structural construction. HU Patent 9 701 455, assigned to Mol Magyar Olaj Es Gazipari Rt and Mta Banyaszati Kemiai Kutato L, July 28, 1999.

Lakatos, I., Lakatos-Szabó, J., Kosztin, B., Palasthy, G., 1998. Restriction of gas coning by a novel gel/foam technique. In: Proceedings Volume, no. SPE Number 39654, 1998 SPE/OOE Improved Oil Recovery Symposium, Tulsa, Oklahoma, April 19–22, 1998, pp. 1–10.

Lakatos, I., Lakatos-Szabó, J., Kosztin, B., Palasthy, G., 2000. Application of iron-hydroxide-based well treatment techniques at the hungarian gil fields. In: Proceedings Volume, no. SPE Number 59321, 2000 SPE/DOE Improved Oil Recovery Symposium, Tulsa, Oklahoma, April 3–5, 2000, pp. 1–10.

Lakatos, I., Lakatos-Szabó, J., Kosztin, B., Palasthy, G., 2002a. Disproportional permeability modification by alcohol-containing polymer solutions: laboratory studies and field experiences. In: Proceedings Volume, no. SPE Number 75185, SPE/OOE 13th Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA, April 13–17, 2002, pp. 1–7.

Lakatos, I., Lakatos-Szabó, J., Tiszai, G., Palasthy, G., Kosztin, B., Trömböczky, S., et al., 1999b. Application of silicate-based well treatment techniques at the hungarian oil fields. In: Proceedings Volume, no. SPE Number 56739, 1999 SPE Annual Technical Conference and Exhibition, Houston, Texas, October 3–6, 1999, pp. 1–11.

Lakatos, I., Lakatos-Szabó, J., Trömböczky, S., Munkácsi, I., Kosztin, B., Palasthy, G., 2001. Polymer/silicate well treatment technique: a potential alternative to gel treatments. In: Lakatos, I. (Ed.), Novelties in Enhanced Oil and Gas Recovery, Progress in Mining and Oilfield Chemistry. Akademiai Kiado, Budapest, pp. 137–150.

Lakatos, I., Tóth, J., Bauer, K., Lakatos-Szabó, J., Kosztin, B., Palásthy, G., et al., 2002b. Comparative study of different silicone compounds as candidates for restriction of water production in gas wells. In: Proceedings Volume, no. SPE Number 80204, SPE International Symposium on Oilfield Chemistry, Houston, TX, February 5–8, 2003, pp. 1–12.

Lakatos, I., Tóth, J., Lakatos-Szabó, J., Kosztin, B., Palasthy, G., Wöltje, H., 2002c. Application of silicone microemulsion for restriction of water production in gas wells. In: Proceedings Volume, no. SPE Number 78307, SPE 13th European Petroleum Conference, Aberdeen, Scotland, October 29–31, 2002, pp. 1–12.

Latypov, R.F., Mannanov, F.N., Kadyrov, R.R., Kalashnikov, B.M., Salimov, M.K., 2002. Method of shutoff of water inflow to well. RU Patent 2 186 941, assigned to Neft Aznakaevskoe Upnp I Krs and Ooo Tat, August 10, 2002.

Leblanc, M.C.P., Durrieu, J.A., Binon, J.P., Fery, J.J., Provin, G.G.L., 1988a. Process for treating an aqueous solution of acrylamide resin in order to enable it to gel slowly even at high temperature. GB Patent 2 197 655, May 25, 1988.

Leblanc, M.C.P., Durrieu, J.A., Binon, J.P., Provin, G.G.L., Fery, J.J., 1988b. Process for treating an aqueous solution of acrylamide resin in order to enable it to gel slowly even at high temperature (procede de traitement d'une solution aqueuse de resine acrylamide pour en permettre une gelification lente meme a temperature elevee). EP Patent 267 835, May 18, 1988.

Leblanc, M.C.P., Durrieu, J.A., Binon, J.P.P., Provin, G.G., Fery, J.J., 1990. Process for treating an aqueous solution of acrylamide resin in order to enable it to gel slowly even at high temperature. US Patent 4 975 483, December 04, 1990.

Leonov, Y.R., Lamosov, M.E., Ryabokon, S.A., Mosin, V.A., Dzetl, B.G., Mamulov, F.G., et al., 1995. Plugging material for wells in the oil and gas industry – contains mineral binder and powder waste from production of epoxide resins as epoxide resin- based additive. RU Patent 2 036 297, May 27, 1995.

Leonov, Y.R., Lamosov, M.E., Ryabokon, S.A., Mosin, V.A., Mamulov, F.G., Akhmadzhanov, A.R., et al., 1993a. Plugging material for oil and gas wells – contains portland cement and additive in form of product of reaction between furfurol and ammonia and has improved corrosion resistance. SU Patent 1 818 463, assigned to Borehole Consolidation Mu., May 30, 1993.

Leonov, Y.R., Mosin, V.A., Potapov, K.M., Lamosov, M.E., Ryzhov, V.N., 1993b. Plugging material – contains furfurol-acetone monomer, oligooxymethyl hydride silmethylenesiloxy- silane, and acidic or alkali hardener. SU Patent 1 821 550, June 15, 1993.

Lockhart, P.T., 2000. Process for the preparation of containment barriers impermeable to fluids. EP Patent 0 990 767, assigned to Enitecnologie SPA, April 05, 2000.

Loyen, K., Iliopoulos, I., Audebert, R., Olsson, U., 1995. Reversible thermal gelation in polymer/surfactant systems. control of gelation temperature. Langmuir 11, 1053–1056.

Maurer, R., Landry, M., 1990. Delayed-gelling compositions and their use for plugging subterranean formations. GB Patent 2 226 066, June 20, 1990.

Merrill, L.S., 1993. Fiber reinforced gel for use in subterranean treatment process. WO Patent 9 319 282, assigned to Marathon Oil Co., September 30, 1993.

Merrill, L.S., 1994. Fiber reinforced gel for use in subterranean treatment process. GB Patent 2 277 112, October 19, 1994.

Merrill, L.S., 1995. Fiber reinforced gel for use in subterranean treatment processes. US Patent 5 377 760, assigned to Marathon Oil Co., January 03, 1995.

Montgomery, F., Montgomery, S., Stephens, P., 1993. Method of controlling porosity of well fluid blocking layers and corresponding acid soluble mineral fiber well facing product. US Patent 5 222 558, June 29, 1993.

Montgomery, F., Montgomery, S., Stephens, P., 1994. Method of controlling porosity of well fluid blocking layers and corresponding acid soluble mineral fiber well facing product. US Patent 5 354 456, October 11, 1994.

Moradi-Araghi, A., 1999. Gelation of acrylamide-containing polymers with hexamethylenetetramine and an aminobenzoic acid compound or phenol. US Patent 5 905 100, assigned to Phillips Petroleum Company (Bartlesville, OK), May 18, 1999.

Moradi-Araghi, A., 2000. A review of thermally stable gels for fluid diversion in petroleum production. J. Pet. Sci. Eng. 26 (1–4), 1–10.

Moradi-Araghi, A., Daasvatn, K., Hamouda, A.A., 2002. Compositions and processes for oil field applications. US Patent 6 387 986, May 14, 2002.

Moskvicheva, N.T., Zhzhonov, V.G., Kateeva, R.I., 1993. Plugging mixture improving cement rock quality – contains plugging portland cement and aqueous alcoholic solution of sodium organosiliconate as modifying additive. RU Patent 2 002 040, assigned to Tartar Oil Inst., October 30, 1993.

Okishev, N.A., Ivanov, A.G., Karpenko, I.V., 1995. Plugging solution for oil and gas wells with increased sedimentation stability – containing portland cement, nitrile trimethyl phosphonic acid, polyoxyethylene, water-soluble cationic polyelectrolyte and water. RU Patent 2 039 207, assigned to Tomskneftegazgeol Enterp, July 09, 1995.

Pafitis, D.G., Maitland, G.C., Davies, S.N., 1996. Thixotropic materials for oilwell applications. GB Patent 2 296 713, assigned to Sofitech NV, July 10, 1996.

Palij, L.V., Akhrimenko, V.E., Kuksov, A.K., Medentsev, V.M., Panov, V.I., 1993. Plugging solution for oil and gas wells – contains portland cement, fly ash, sodium or calcium sulphate and additionally hydrosil, to increase adhesion of cement rock to casing string. SU Patent 1 802 087, assigned to Borehole Consolidation Mu., March 15, 1993.

Parker, A., 1988. Process for delaying and controlling the formation of gels or precipitates derived from aluminum and corresponding compositions together with its applications particularly those concerning the operation of oil wells. EP Patent 266 808, May 11, 1988.

Perejma, A.A., Pertseva, L.V., 1994. Complex reagent for treating plugging solutions – comprises hydrolysed polyacrylonitrile, ferrochromolignosulphonate Cr-containing additive, waste from lanolin production treated with triethanolamine and water. RU Patent 2 013 524, assigned to N Caucasus Nat Gaz Res., May 30, 1994.

Perejma, A.A., Tagirov, K.M., Ilyaev, V.I., Kovalev, A.A., 1995. Plugging solution for conducting well repair works, etc. – contains portland cement, polyacrylamide, specified stabilising additive, sodium sulphate waste from sebacic acid production and water. RU Patent 2 035 585, assigned to N Caucasus Nat Gaz Res., May 20, 1995.

Pessier, R.C., Javanmardi, K., Nahm, J.J., Leimkuhler, J.M., Dudley II., J.W., Moody, F.K., 1994. Evaluating slag solidified mud drillability and bit performance. World Oil 215 (10), 65, 67–68, 70, 72, 74.

Piculell, L., Thuresson, K., Ericsson, O., 1995. Surfactant binding and micellisation in polymer solutions and gels: binding isotherms and their consequences. Faraday Discuss. 101, 307–318.

Podgornov, V.M., Vedishchev, I.A., Mokhamad, M.A., 1992. Plugging slurry for oil and gas well drilling – contains cement, bentonite clay powder, water glass, sodium chloride and water. SU Patent 1 756 537, assigned to Moscow Gubkin Oil Gas Inst., August 23, 1992.

Rakhmatullin, T.K., Agzamov, F.A., Ivanov, V.V., Karimov, N.K., Tankibaev, M.A., Trenkenshu, N.V., 1992. Clinker-less binder composition – contains mixture of slag from melting of oxidised nickel ores and tails from enrichment of phosphorite ores. SU Patent 1 777 617, assigned to Kaza Oil Geolog. Survey, November 23, 1992.

Reddy, B.R., Eoff, L.S., Chatterji, J., Tran, S.T., Dalrymple, E.D., 2001. Preventing flow through subterranean zones. US Patent 6 176 315, assigned to Halliburton Energy Services, Inc. (Duncan, OK), January 23, 2001.

Remnev, G.E., Pushkarev, A.I., Kondrat, E.N.A., Telin, A.G., Svirskij, D.S., Ismagilov, T.A., et al., 2002. Gel-forming polymer material to equalize profile of acceptance and water insulation of wells, process and installation for its production. RU Patent 2 180 393, assigned to Inzhiniringovyj Aozt and Ts Jukos, March 10, 2002.

Robert, J.A., Rosen, J.W., 2002. Fluid placement and pumping strategy. In: Economides, M.J., Nolte, K.G. (Eds.), Reservoir Stimulation, chap. 19–3. John Wiley & Sons LTD, New York and Chichester, pp. 19–4, 19–9.

Ryabova, L.I., Savenok, N.B., Mariampolskij, N.A., Surova, L.M., Kovalev, D.F., 1993. Plugging solution – contains portland cement, aluminium oxychloride, water and phosphonium complexone in form of e.g. oxy-ethylidene diphosphonic acid. SU Patent 1 802 086, assigned to Borehole Consolidation Mu., March 15, 1993.

Ryan, R.G., 1995. Environmentally safe well plugging composition. US Patent 5 476 543, December 19, 1995.

Sarrazin-Cartalas, A., Iliopoulos, I., Audebert, R., Olsson, U., 1994. Association and thermal gelation in mixtures of hydrophobically modified polyelectrolytes and nonionic surfactants. Langmuir 10, 1421–1426.

Savenok, N.B., Mariampolskij, N.A., Mariampolskij, P.N., Loshmankina, L.A., 1993. Plugging solution – contains portland cement, calcium chloride, phosphonium complexone containing amine-group and water and has high adhesion to stratal rock. SU Patent 1 802 088, March 15, 1993.

Schwartz, K.N., Smith, K.W., Chen, S.-R.T., 2009. Polymeric gel system and use in hydrocarbon recovery. US Patent 7 575 057, assigned to Clearwater International, L.L.C. (Houston, TX), August 18, 2009.

Seright, R.S., Liang, J., Lindquist, W.B., Dunsmuir, J.H., 2002. Characterizing disproportionate permeability reduction using synchrotron X-ray computed microtomography. SPE Reserv. Eval. Eng. 5 (5), 355–364.

Sharipov, A.U., Dolganskaya, S.I., Rayanov, K.S., Rudomino, M.V., Kopejko, E.G., Krutikova, N.I., et al., 1992a. Composition for isolation of absorbing strata in oil and gas extraction contains hemi-hydrated gypsum and product obtained by reacting ammonia with waste obtained in production of nitrilo-trimethyl phosphonic acid. SU Patent 1 745 892, assigned to W Sibe Deep Surv Dril Inst. and Cheboksary Khimprom Prod., July 07, 1992.

Sharipov, A.U., Dolganskaya, S.I., Ryabova, L.I., Chumachenko, L.A., Petrukhin, G.I., 1993. Plugging solution for gas extraction wells – contains cement, polymethyl methacrylate modified with monoethanolamine, and water, and produces plugging stone of increased strength. SU Patent 1 818 464, assigned to W Sibe Deep Pros Dril Res., May 30, 1993.

Sharipov, A.U., Dolganskaya, S.I., Zajkovskaya, T.V., Ryabova, L.I., 1992b. Composition for isolation of oil stratum – contains plugging cement, aluminium oxychloride and polymethyl methacrylate modified with mono:ethanolamine. SU Patent 1 709 073, assigned to W Sibe Deep Pros Dril Res., January 30, 1992.

Snowden, M.J., Vincent, B., Morgan, J.C., 1993. Conformance control in underground reservoirs. GB Patent 2 262 117, assigned to British Petroleum Co. Ltd., June 09, 1993.

Starshov, M.I., Sitnikov, N.N., Khisamov, R.S., Volkov, J.V., Abdulkhairov, R.M., Salikhov, I.M., et al., 2002. Method of fresh water shutoff in wells of deposits of high viscosity oils and native bitumens. RU Patent 2 192 541, assigned to Tatneft Aoot, November 10, 2002.

Sweatman, R.E., 2001. Methods of sealing subterranean zones. US Patent 6 167 967, assigned to Halliburton Energy Services, Inc. (Duncan, OK), January 2, 2001.

Sydansk, R.D., Southwell, G.P., 2000. More than 12 years' experience with a successful conformance-control polymer-gel technology. SPE Prod. Facil. 15 (4), 270–278.

Taradymenko, Y.Y., Timovskij, V.P., Kushu, V.A., Akhrimenko, V.E., Karpenko, Y.G., 1993. Plugging solution – contains portland cement, calcium oxide-based expanding additive, water and additionally polymethylene-urea, to improve efficiency. SU Patent 1 799 999, assigned to Borehole Consolidation Mu., March 07, 1993.

Taziev, M.M., Fajzullin, I.N., Khlebnikov, V.N., Almaev, R.K., Bazekina, L.V., Bajdalin, V.S., 2001. Method of control of nonuniform oil pool development. RU Patent 2 168 005, assigned to Aktsionernaja Ne Aoot and Ftjanaja Kompanija Bashneft, May 27, 2001.

Trotskij, V.F., Banchuzhnyj, S.G., Zezekalo, I.G., Tishchenko, V.I., 1993. Blocking of absorbing strata – by pumping-in specified reagent followed by pumping-in of solution of hydrochloric acid and inhibitor, mixing and leaving for specified time. SU Patent 1 802 084, March 15, 1993.

Tsytsymushkin, P.F., Khajrullin, S.R., Tarnavskij, A.P., Glyantseva, G.S., Iskandarova, G.G., Mikhajlov, B.V., 1992a. Plugging solution for oil and gas wells – contains plugging cement, modified methylcellulose, mono-substituted sodium phosphate and water. SU Patent 1 740 627, assigned to Volgo Urals Hydrocarbon, June 15, 1992.

Tsytsymushkin, P.F., Khajrullin, S.R., Tarnavskij, A.P., Kovalenko, P.V., Kudryashova, Z.N., Iskhakov, R.M., et al., 1993a. Plugging solution for oil and gas wells – contains plugging portland cement, nitrilo-trimethyl phosphonic acid, hydrazine hydrochloride and water and has corrosion-protective properties. RU Patent 2 002 037, October 30, 1993.

Tsytsymushkin, P.F., Khajrullin, S.R., Tarnavskij, A.P., Kudryashova, Z.N., Levshin, V.N., Mikhajlov, B.V., et al., 1992b. Plugging solution for oil and gas wells – contains plugging cement, nitrilo-trimethyl-phosphonic acid, product of reacting hexamethylene tetramine with chloro-derivatives unsaturated hydrocarbon(s) and water. SU Patent 1 740 629, assigned to Volgo Urals Hydrocarbon, June 15, 1992.

Tsytsymushkin, P.F., Khajrullin, S.R., Tarnavskij, A.P., Kudryashova, Z.N., Kovalenko, P.V., Levshin, V.N., et al., 1993b. Plugging solution for cementing oil and gas wells in salt-bearing strata – contains plugging cement, sodium chloride, calcium chloride, additional preparate bakteritsid, and water. SU Patent 1 803 531, assigned to Volgo Urals Hydrocarbon, March 23, 1993.

Urlwin-Smith, P.L., 2001. Blocking composition for use in subterranean formation. US Patent 6 192 986, assigned to Halliburton Energy Services, Inc. (Duncan, OK), February 27, 2001.

Wang, G., Lindell, K., Olofsson, G., 1997. On the thermal gelling of ethyl (hydroxyethyl) cellulose and sodium dodecyl sulfate. phase behaviour and temperature scanning calorimetric response. Macromolecules 30, 105–112.

Yoshida, M., Tanaka, K., Saito, T., 2002. Injection chemical solution composition for filling in hole, and method for filling space with the same. JP Patent 2 002 194 354, assigned to Nippon Polyurethane Kogyo Kk, July 10, 2002.

Zahid, A. (Ed.), 1998. Water Soluble Polymers: Solution Properties and Applications, Plenum Press, New York.

Zakirov, A.F., Khaliullin, F.F., Sidorov, L.S., Valeeva, G.K., Takhautdinov, R.S., 2002. Method of water shut-off in porous-fractured oil reservoirs. RU Patent 2 187 620, assigned to Neftegazodobyvajushchee Upravl and Oao Tatneft, August 20, 2002.

Zeltser, P.Y., 1992. Plugging solution for oil and gas industry – contains plugging portland cement, lignosulphonate(s), waste from formic acid production obtained at stage of decomposition of sodium formate, and water. SU Patent 1 730 431, assigned to E Sibe Geolog. Geophy Min. Re, April 30, 1992.

Zhou, Z., 2000. Process for reducing permeability in a subterranean formation. US Patent 6 143 699, assigned to Alta Oil Sand Tech. Res. Auth, November 07, 2000.

Zhou, Z., Tremblay, B., Wiwchar, B.W., 2001. Reinforced clay gel. CA Patent 2 349 998, assigned to Alberta Oil Sands And Res. Auth, December 12, 2001.

Zhukhovitskij, V.B., Kolomoets, M.I., Zagrudnyj, A.M., 1992. Polymeric plugging solution contains urea-formaldehyde resin, expandable resol-phenol-formaldehyde resin containing surfactant and aluminium powder, and maleic anhydride production waste. SU Patent 1 728 473, assigned to Ukrgeologiya Min. Rscs Inst., April 23, 1992.

Zobs, V.Y., Belikov, G.V., Sheldybaev, B.F., Shaposhnikov, Y.I., Tikhonov, V.N., 1989. Regulating the density of plugging agents. Neft Khoz (5), 29–31.

TRADENAMES

TABLE 18.21 Tradenames in References

Tradename Description	Supplier
Avanel™ S150 Sulfonated ethylene oxide derivate (Sweatman, 2001)	PPG Industries, Inc., BASF
Ethomeen® T-12 *N*,*N*-bis(2-hydroxyethyl)tallowamine (Kubala, 1987)	Armak Industrial Chemicals
Heloxy® 107 Diglycidyl ether of cyclohexane dimethanol (Chatterji et al., 2000)	Shell Chemical Comp.
Hostamer® V2825 AMPS terpolymer (DiLullo Arias et al., 2001)	Clariant GmbH
Interdrill Emul HT® Emulgator (Crawshaw and Nijs, 2002)	Dowell Schlumberger
Isopar® (Series) Isoparaffinic solvent (Dawson et al., 2001)	Exxon
Isopar® L Isoparaffinic solvent (Dawson et al., 2001)	Exxon
Mirataine® BET-O Disodium oleamidopropyl betaine (Dahayanake et al., 2002)	Rhodia Inc. Corp.
Mirataine® T2C Disodium tallowiminodipropionate (Dahayanake et al., 2002)	Rhodia Inc. Corp.
Mirataine® TM Dihydroxyethyl tallow glycinate (Dahayanake et al., 2002)	Rhodia Inc. Corp.
PropNET™ Proppant-retention agent (James et al., 2002)	Schlumberger
Resomer® RG506 Polylactic acid-co-glycolic acid (Moradi-Araghi et al., 2002)	Boeringer Ingelheim
Sandlock® Consolidating fluid (James et al., 2002)	Dow
Teflon® Tetrafluoro polymer (Reddy et al., 2001)	DuPont

TABLE 18.21 Tradenames in References–Cont'd

Tradename Description	Supplier
Tegopren™ 7006 Siloxane emulsifier (Crawshaw and Nijs, 2002)	Evonik Goldschmidt GmbH
Truvis® Ester basestock lubricant (Crawshaw and Nijs, 2002)	Teknor Apex Comp.

Chapter 19

Oil Spill Treating Agents

The most devastating oil spills occur in coastal regions, so most of this chapter is devoted to this topic, and one section is devoted to subsurface and soil remediation jobs.

Chemical dispersants can be used to reduce the interfacial tension (IFT) of floating oil slicks, so that the oils disperse more rapidly into the water column and thus pose less of a threat to shorelines, birds, and marine mammals. The action of oil spill treating agents goes beyond simply dispersing the spilled oil, however.

Oil spill treating agents can be divided into four classes: solidifiers, demulsifying agents, surface-washing agents, and dispersants, which make up the majority. Oil spill treating agents can also be referred to as:

- Oil spill treating agents,
- Spill treating agents,
- Chemical shoreline cleaning agents,
- Shoreline cleaning agents,
- Chemical beach cleaners,
- Oil spill dispersants, and
- Oil spill clean-up agents.

HISTORY

Oil spill treating agents have been a subject of controversy since their introduction during the Torrey Canyon oil spill off the coast of the United Kingdom in 1967. The dispersant policies of several European nations and Canada have been reviewed and compared with those of the United States (Cunningham et al., 1991).

List of Major Oil Spills

The importance of spill treating agents is highlighted by a list of major oil spills, given in Table 19.1.

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TABLE 19.1 List of Major Oil Spills (Brown et al., 1992; List of oil spills, 2010)

Type	Name of Vessel/ Platform/Region	Date	Location	Barrels
Platform	Deepwater Horizon	04-20-10	Gulf of Mexico	4.9×10^9
Various	Kuwait	01-19-91	Persian Gulf, Iran	9,000,000
Platform	IXTOC I	06-03-79	Bahia de Campeche, Mexico	3,522,400
Platform	Nowruz Oil Field	02-10-83	Persian Gulf, Iran	1,904,700
Tank vessel	*Amoco Cadiz*	03-16-78	Brittany, France	1,619,000
Tank vessel	*Sea Star*	12-19-72	Gulf of Oman	937,000
Tank vessel	*Torrey Canyon*	03-18-67	Land's End, England	860,000
Tank vessel	*Urquiola*	05-12-76	La Coruña, Spain	733,000
Tank vessel	*Independenta*	11-15-79	Istanbul, Turkey	687,700
Tank vessel	*Jakob Maersk*	01-29-75	Leixoes, Portugal	637,500
Tank vessel	*Khark 55*	12-19-89	400 miles north of Las Palmas, Canary Islands	452,400
Tank vessel	*Metula*	08-09-74	Strait of Magellan	398,000
Tank vessel	*Assimi*	01-07-83	Oman	379,000
Tank vessel	*World Glory*	06-13-68	65 miles east northeast of Durban, South Africa	334,000
Tank vessel	*St. Peter*	02-05-76	Cabo Manglares, Colombia	279,000
Tank vessel	*Corinthos*	01-31-75	Delaware River, Marcus Hook, Pennsylvania	266,000
Tank vessel	*Burmah Agate*	11-01-79	Galveston Bay, Texas	254,761
Tank vessel	*Athenian Venture*	04-22-88	Canada, southeast of Cape Race, Newfoundland	252,400
Tank vessel	*Exxon Valdez*	03-24-89	Bligh Reef, Prince William Sound, Alaska	240,500
Facility	Texaco Storage Tank	04-27-86	Bahia Las Minas, Panama	240,000
Vessel	*Cosco Busan*	11-07-04	San Francisco	
Vessel	*Montara*	08-21-09	Timor sea	200

General Requirements

In particular, oil spill treating agents should have a long shelf life and should be:

- Ecologically friendly,
- Non-toxic,
- Nonpolluting,
- Biodegradable,
- Highly active,
- Noncorrosive, and
- Capable of being applied from boats, aircraft, and helicopters.

Special formulations that are suitable for various environments, such as marine, shoreline, fresh water and salt water, tropic, and arctic environments, have been developed.

Chemical dispersants are often used to disperse spilled oils that threaten to pollute shoreline areas. They increase the surface area of the oil, which accelerates the process of biodegradation, but their toxic properties limit their use.

Storage

Oil spill dispersant chemicals may need to be stored for long periods awaiting their use in an emergency. It is not uncommon to find stocks being stored for more than five years. Dispersants can lose much of their efficiency or deteriorate in other ways during storage so accelerated storage and corrosion tests have been performed (Albone et al., 1990), compiled background information which have about eight typical high-performance oil spill dispersants.

Mechanisms

Influence on the Dispersant Performance of the Crude Oil Type

Crude oils contain various amounts of indigenous surface active agents that stabilize water-in-oil emulsions. It has been shown that the effectiveness of a dispersant is dependent on both the dispersant type and the specific crude oil (Canevari, 1987), but there is no apparent correlation between the emulsion-forming tendency of the crude oil, which is a function of its indigenous surfactant content, and the effectiveness of the dispersant. In general, indigenous surfactants in crude oil reduce the effectiveness of the dispersant, but to an unpredictable level.

Surface Chemical Aspects of Oil Spill-dispersant Behavior

Dispersants are widely used in many parts of the world to deal with oil spills on the ocean. The objective of adding the dispersant is to emulsify the oil slick into the water column, which prevents wind forces from moving the slick to shore. This may also increase the bioavailability of the oil because of the large increase in surface area caused by emulsification. Dispersants are surface active agents whose behavior can be understood through the application of surface chemical principles (Christopher, 1993).

Modern oil spill-dispersant formulations are concentrated blends of surface active agents in a solvent carrier system. The solvent system has two key functions: (1) to reduce the viscosity of the surfactant blend in order to allow efficient dispersant application, and (2) to promote mixing and diffusion of the surfactant blend into the oil film (Fiocco et al., 1994).

Photocatalytic Oxidation of Organic Compounds on Water

A method for treating an oil film floating on water has two parts (Heller and Brock, 1995):

1. Dispersing a number of water-floatable particles on an oil film. They are composed of a material that accelerates the oxidation of organic compounds in the oil film under illumination and in the presence of air, and
2. Allowing the particles to be exposed to sunlight and ambient air.

The particles consist of a bead with an exterior surface that is at least partially coated with a material capable of accelerating the oxidation of organic compounds floating on water, under illumination, and in the presence of air. The coated bead floats in water and has a diameter of less than 2 mm. It has an intermediate layer of a material that prevents the oxidation of the plastic material.

Application

Oil spill treating agents may be applied from boats, hydrofoils, aircraft, or helicopters in the case of large-scale pollution. For minor incidents such as car accidents, the application is done by hand.

Boat

A dispersant fan sprayer has been built and tested statically on land and demonstrated offshore on a supply vessel while spraying water. Coverage rates of 4 $\mathrm{miles}^2\mathrm{d}^{-1}$ are possible, using high-speed fans that create a focused air stream with maximal velocities of 90 $\mathrm{miles\,h}^{-1}$ (Allen, 1985). The dispersant is injected into and propelled by the air stream, which acts as a carrier for the dispersant. This makes possible the spraying of smaller volumes of concentrated or dilute dispersant over a wide swath. The water surface is gently agitated by the air stream and liquid impact.

Corexit® 9527 is a dispersant, used in a solution of water and ethylene glycol monobutyl ether. The nature of the surface active agent has not been disclosed. Laboratory tests were conducted using 0.5 mm thick, fresh Alberta Sweet-Mixed Blend crude oil, treated with Corexit® 9527 dispersant applied from an overhead spray boom (Belore, 1987). The effects on dispersion efficiency of mixing jet pressure, mixing jet flow rate, jet standoff distance, and vessel speed were evaluated. The system operates with a nozzle pressure of 7000 kPa, a flow rate of 55 liter/min per nozzle, and nozzles positioned approximately 0.6 m from the water surface. In laboratory tests, such a system was shown to be capable of dispersing 80–100% of the surface slick.

Herding Effect

In a series of trials, three dispersants were sprayed from a boat. It was concluded that a high level of energy at the sea surface mitigates the discrepancies in the efficiencies of the dispersants as measured in laboratory tests. Better results were obtained in relatively thick oil slicks. The low efficiency measured when treating downwind was attributed to the already observed herding effect.

These complementary results reinforce the actions that have been developed to optimize the application of dispersants by ship. The equipment for neat dispersant spraying has been described. An operational treatment procedure has described how to map, mark out, prospect, and treat oil slicks according to the slick shape, estimated oil thickness, and wind direction (Merlin, 1989).

Hydrofoils

Ships are considered best for applying a dispersant with spray booms, because of their large carrying capacity, and their ability to navigate and operate under bad weather conditions and at night. Experiments have shown that clean-up at a speed greater than 10 knots is unadvisable, however, because the bow wave breaks up the oil film on the water. A high-speed craft such as a hydrofoil, when flying foilborne, solves this problem (Vacca-Torelli et al., 1987).

The hydrofoil has a special stability because it is kept above the water by the foil lift. This avoids creating a disturbing wave motion, and thus long spray booms can be used.

Aircraft

A portable spray unit has been developed for the application of dispersants by large airplanes, such as the Hercules C-130. This spray unit can be rapidly placed in the cargo aircraft without any mechanical alterations. Tests spraying a dispersant concentrate have been performed (Lindblom, 1987).

Campaigns of dispersant offshore trials were conducted from 1979 to 1985 off the French Mediterranean and Brittany coasts. Approximately 30 slicks were treated with several dispersants applied from ships, helicopters, and an aircraft by different spraying systems (Bocard et al., 1987). The experiments identified different effects of dispersants such as short-term dispersion of oil, delayed dissemination, and limiting parameters such as minimal energy of sea surface, ratio of dispersant to oil needed, and the negative herding effect. Various techniques were tested to optimize the application of dispersants in different situations, including the use of a variable flow rate system to spray neat concentrates from ships, and a range of ways of operating ships and aircraft to reach a selective distribution of dispersant and get good coverage of slicks.

A field test was conducted by spraying a commercial oil spill-dispersant (Corexit® 9527) from aircraft (Geyer et al., 1992). The objectives of the test were to determine the efficiency of delivering the dispersant to a selected target, and to compare various measurement systems for droplet size and spray pattern distribution. The results indicated that aerial flights up to 46 m can produce droplet sizes and swath widths that would be operationally effective for an oil spill.

Corexit® 9527, dyed with Rhodamine WT, was applied by aircrafts at a target dose rate of 5 gal/acre over a collection grid of metal trays, Kromekote cards, oil-sensitive cards, and a continuous trough (Fay et al., 1993). Analysis of the collected dispersant was done colorimetrically, fluorometrically, and by image analysis. Correlations of the different methodologies demonstrated that high-speed, moderate-altitude application of oil dispersant could deliver the dispersant to the surface at an effective concentration and appropriate drop size. Environmental studies of the test area showed no residual dispersant in the soil following cessation of spraying treatment.

Environmental Aspects

The rise in environmental concerns, coupled with the enormity of some oil spills in the recent past, has led to the development of new generations of oil spill dispersants.

Biodegradation

Biodegradable oil spill dispersants with high efficiency and low toxicity have been prepared and tested. They consist of non-ionic and surfactants with a low toxicity with different molecular weights (Abdel-Moghny and Gharieb, 1995). The relationship between IFT, efficiency, and chemical structure of the prepared oil spill dispersants was also studied.

A test to determine the biodegradation rate of the dispersant and the biodegradation rate of the dispersant-oil mixture has been proposed (Mulyono et al., 1993). It is intended to supplement the toxicity and effectiveness tests, which are currently used to evaluate the performance of oil spill dispersants.

Standardized Measurement of Ecological Effects

The number and variety of both toxicological and analytical methodologies that have generated the available data on this topic are numerous, making it virtually impossible to compare data sets and arrive at a coherent conclusion.

In 1994, the Chemical Response to Oil Spills Ecological Effects Research Forum (CROSERF) was formed. This is a working group composed of representatives from industry, academia, and government, whose goals are to standardize and improve the quality and usefulness of laboratory and mesocosmos research into the ecologic effects of oil spill treating agents (Aurand et al., 2001; Singer et al., 1995).

Toxicity

Seagrasses, Mangroves, and Corals

Jamaica's shoreline is at the intersection of five major petroleum tanker shipping routes, and is a cargo transshipment point for the Caribbean. The island of Jamaica experiences six small- to medium-sized oil spills per year. Major ports of petroleum entry are close to mangroves, seagrass, and coral resources. One of the most critical habitats throughout the Atlantic subtropics and tropics is seagrass. Seagrasses, mangrove, and coral habitats function as fish nursery habitats, as well as being important sources of food and erosion control. If the seagrasses were to disappear, hundreds of species of fish would disappear. Seven dispersants were tested for toxicity, over 100 h on three seagrasses (Thorhaug and Marcus, 1987).

The results showed that the mortality differed among seagrasses and among dispersants. Oil spill clean-up plans were recommended on the basis of these results that indicate exact dispersants and concentrations to be used in areas containing seagrasses.

In general, the response of coral parallels that of seagrass to the dispersants (Thorhaug et al., 1989). Recommended non-toxic dispersants, with respect primarily to coral reef and fish sensitivity, are Cold Clean, Corexit® 9550, and Finasol OSR7 (Thorhaug et al., 1991).

Response of *Daphnia magna*

The use of dispersants for petroleum is often recommended in accidental aquatic pollution situations where an oil layer is capable of reaching the banks of a river or water pond. The petroleum is then emulsified in the water, which makes it available to be biodegraded by organisms. However, this bioavailability causes an increase in the oil toxicity toward the organisms living in the water. In addition, the dispersant itself is potentially toxic and its release into the environment must be controlled.

In the case of rivers, the effect of dispersing the oil creates a strong peak of pollution running along the river flow, and the organisms are submitted to short-term but intense pollution, leading to acute effects.

The time dependence of the acute toxicity of oil and dispersants on a sensitive fresh water organism, namely, *D. magna*, was investigated (Vindimian et al., 1992). Two different oils were used: a crude oil from the southwest of France and a gas oil free from volatile substances. Two commercial dispersants were used: British Petroleum Enersperse 1037 and Basic Fresh water.

The response of marine macrophytes to oil dispersion is dependent on the type of both the oil and the dispersant (Burridge and Shir, 1995). Inhibition of the germination of the marine macrophyte *Phyllospora comosa* was used as a measure. The inhibition of germination by the water-soluble fraction of diesel fuel increased after adding all dispersants investigated, which contrasted with crude oil, where the addition of some dispersants resulted in an enhanced germination rate.

Implementation Application Programs

Guidelines

Ideally, decisions regarding the use of a dispersant use should take place before an emergency, to reach a timely decision (Cunningham et al., 1989). Several states and regional response teams have active programs that address the planning and technical and environmental considerations affecting dispersant use. In several states where the use of dispersants is an emerging issue, there appears to be a willingness to consider their use on a case-by-case basis and a genuine interest in learning more about their effectiveness and toxicity.

A decision concerning the use of a specific dispersant involves several components, including considerations of operational feasibility, regulatory policy, and environmental concerns. Eleven examples of major published procedures for making oil spill-response decisions, including decisions for or against the use of chemical dispersants, have been summarized and compared in a study (Fraser, 1989).

Several guidelines have been given for the use of oil spill dispersants, among them, ASTM guidelines (Corbin and Ott, 1985; Flaherty et al., 1987; Fraser, 1985; Fraser et al., 1989; Manen et al, 1987; Merlin et al., 1991; Wiechert et al., 1991). The guidelines cover a variety of environments such as fresh water ponds, lakes, and streams, as well as land. The laboratory tests to measure the effectiveness of the dispersant that are specified in federal regulations are not easy to perform, nor inexpensive, and generate a large quantity of oily waste water.

Computerized Model

A computerized model has been developed for planning and implementing an effective dispersant application program (Allen and Dale, 1995). This makes it possible to conduct a rapid assessment of specific oil-dispersant relationships, oil slick configurations, equipment types, and staging locations, as well as a broad range of dosages achievable within realistic operating constraints. Such constraints are provided for vessel, helicopter, and fixed-wing application systems. For a given spill scenario, the user can determine the amount of dispersant needed, the number of sorties required, the area and potential volume of oil treated per sortie, and the time required to treat a specified percentage of the slick.

Tests

Wave Basin

Many sea trials of dispersant chemicals have been undertaken to demonstrate the effectiveness of specific products, or to elucidate the processes of oil dispersion into the water column. Most have proved inconclusive, leading many to believe that dispersant chemicals are only marginally effective.

Tests in a wave basin have now been conducted to measure the effectiveness of the dispersant under closely controlled conditions (Brown et al., 1987). These tests show that dispersed oil plumes may be irregular and concentrated over small volumes, so extensive plume sampling was required to obtain accurate measurements. In large-scale sea trials, dispersants have been shown effective, but only when sufficient sampling of the water column was done to detect small concentrated dispersed oil plumes and when it was known that the dispersant was applied primarily to the thick floating oil.

Broken Ice

Experiments have been conducted in a wave basin to determine the effectiveness of dispersants when oil was spilled onto a mixture of broken ice and water. Forty-liter portions of a light crude oil were spilled into containment booms that had been frozen into ice in a salt water-filled wave tank (Brown and Goodman, 1996). The spills were treated with either Corexit® 9527 or Corexit® 9500, and then low-amplitude waves were generated for 2 h. In a short time, the spills were dispersed by 90% or better.

The oil-in-water dispersion was monitored by fluorometry, video, and still photography, and by measuring the oil remaining on the water and ice surface after the experiment. The size distribution of the ice floes had little effect on the amount of dispersion. The dispersion of oil spilled into a single straight lead in the ice sheet was also studied. It was found that oil spilled into a lead filled with slush ice and treated with dispersant rapidly dispersed into the water column.

Finite Difference Models

Finite difference models to simulate the diffusion and advection of oil in water have been developed and tested in wave basins (To et al., 1987).

Small Scale Testing

There are various testing procedures available, such as the Warren Spring Rotating Flask test (WSL test, Labofina test), Institute Francais du Petrole flow test (IFP test), Mackay-Nadeau-Steelman test (MNS test), EXDET, and other procedures.

Water Extraction Process

The traditional method of measuring the effectiveness of a dispersant under laboratory conditions is to take a small aliquot of the dispersion test water, extract the oil, usually with methylene chloride, and then measure the color at a specific wavelength. This value is compared with a standard curve from which the effectiveness can be calculated. An error was found in the traditional method for preparing standard curves, because adding water to the extraction process produced some coloration in the methylene chloride (Fingas et al., 1995).

Light oils have low absorbance at the wavelengths chosen and tests were found to be erroneous by as much as 300% when traditional methods of analysis were used. More typical medium oils showed errors of only a few percent, but heavy oils again showed significant error because of the different wavelengths at which they absorb. Several methods of compensating for this effect were tried and found to be inadequate. Gas chromatography is suggested to analyze the effectiveness of the dispersant in the laboratory.

Rotating Flask Test and Variants

Laboratory tests of the effectiveness of oil spill dispersants are used around the world to select those best applied to specific oils. The two most widely used tests are the Mackay test, otherwise known as the *Mackay-Nadeau-Steelman test*, and the Labofina test, otherwise known as the *Warren Spring* or *rotating flask test*. The Mackay test uses a high-velocity air stream to energize 6 liters of water, whereas the Labofina test uses rotation of a separatory funnel with 250 ml of water. Both tests apply a large amount of energy to the oil-water system.

Two lesser known devices are the oscillating hoop and the swirling flask (Fingas, 1995). The oscillating hoop apparatus uses a hoop moved up and down at the water surface. The concentric waves serve to energize the oil in the hoop and to contain it. Thirty-five liters of water are used in this test. The swirling flask test makes use of a 125 ml Erlenmeyer flask. The flask is rotated using a standard chemical/biologic shaker to swirl the contents. Results show that all high energy tests (the Mackay, the Labofina, and the oscillating hoop) produce unique dispersant effectiveness results that correlate poorly with the physical properties of the oil.

EXDET Test

The dispersant effectiveness test, EXDET, was developed to address concerns associated with available laboratory dispersant effectiveness test procedures (Becker et al., 1993). The EXDET procedure uses standard laboratory equipment (such as a Burrell Wrist-Action shaker) and small volumes of water, oil, and the chemical dispersant. Other features include the capability to mass-balance the dispersed and nondispersed oil, and to generate replicate data for statistical analysis.

Portable Equipment

Chemical shoreline cleaning agents enhance the removal of stranded oil from shoreline surfaces, but site-specific variables, physical and chemical properties of the oil, and variations in substrate types all influence their performance. It is difficult to predict the influence of site-specific variables, so on-site testing of shoreline cleaning agents with the contaminating oil and local substrates is needed.

A portable field kit, used to estimate quantitative and qualitative information for cleaning performance and dispersion of oil with shoreline cleaning agents, has been described in literature (Clayton et al., 1996). The methodology was tested with three substrate types (gravel, rip-rap, and eelgrass), two oils (Bunker C and Bonny Light), and two shoreline cleaning agents (Corexit® 9580 and PES-51). The results for cleaning performance and oil dispersion exhibit sufficient reproducibility to allow statistically significant differences to be identified in tests with and without shoreline cleaning agents or between shoreline cleaning agents.

Comparison of Effectiveness Tests

Three laboratory methods were compared: the revised standard dispersant effectiveness test used and required by regulation in the United States, the swirling flask test, and the IFP-dilution test (Sullivan et al., 1993). Six test oils and three dispersants were evaluated. It was concluded that the three tests gave results of similar precision, but that the swirling flask test was fastest, cheapest, simplest, and required the least operator skill.

Correlations Among the Different Test Methods

Comparative studies revealed that the test results from different apparatus are not highly correlated, and often even the rank is not correlated (Fingas et al., 1989). The effect of the settling time and oil/water ratio are important in determining the final effectiveness value. Energy is important only to the extent that, when high energy is applied to an oil-dispersant system, dispersion is increased by an amount related to the oil's natural dispersibility.

A study of the efficiency of dispersants by various testing methods showed that for some tests, for the same oil dispersant system produced no correlation (Moet et al., 1995). In another study, seven laboratory methods for testing dispersant effectiveness using commercial oil spill products and No. 2 and No. 6 fuel oils were evaluated (Rewick et al., 1988). The tests included the Environmental Protection Agency, Mackay, Russian, French, Warren Spring, and two IFT test methods (one based on the du Nouy ring principle and the other on drop weight).

These tests were reviewed in terms of type, scale, method of applying mixing energy, and the time required to conduct a product evaluation. The experimental results, compared in terms of test data precision and how effective the six nonionic dispersants were, demonstrate that the relative effectiveness found for the dispersants varies appreciably as a function of the testing method.

Effectiveness tests of dispersants have been performed according to two different methods (Gillot et al., 1986):

1. The WSL test and
2. The IFP test.

The WSL test is a rotating flask test and the IFP test is a lower energy test, with dilution by clean sea water. The results mainly show that there is no evident correlation between the methods, which may be because of their completely different designs. Another result is that the IFP test is much more selective than the WSL test.

It can be concluded that the nature of the oil is as important as the design of the method. As a global conclusion, dispersants should be tested under different conditions because their effectiveness varies significantly with the test design and the test oil.

Effectiveness of Chemical Dispersants Under Real Conditions

It is believed that the effectiveness of dispersants is influenced by a number of factors, including their chemical nature and the nature of the oil, their relative amounts, and the microscopic mixing processes occurring as the dispersant lands on the oil and penetrates it (Mackay and Chau, 1986). In addition, the oil to be treated can also partly evaporate, form mousses, and spread into thick and sheen patches.

There is no doubt that effective dispersion takes place in laboratory conditions and also under certain application conditions at sea. However, it is apparent that at sea, the effectiveness is often reduced by one or more factors:

- Underdosing and overdosing of the slick because of its variable thickness,
- Underestimation of the effect of weathering, and
- The character of the energy available at the sea surface.

Special Aspects

Arctic Conditions

The effectiveness of relevant dispersants for use under arctic conditions has been tested by a dilution test (Brandvik et al., 1992, 1994). Arctic conditions mean a temperature of 0°C and water salinities of 0.5–3.3%. The results showed that many dispersants that previously showed excellent effectiveness at high salinity (3.3%) may have low effectiveness at low-salinity conditions (0.5%). The study emphasizes the need for the development of dispersants with a high effectiveness both at low temperature and over a wide range of salinities.

Effectiveness in Salt Solutions

Dispersant effectiveness in calcium and magnesium salt solutions is different from that in sodium salt solutions (Belk et al., 1989). In general, the effectiveness is lower at zero salinity.

Effectiveness Testing

Initially, it was stated that oil spill treating agents can be divided into four classes: solidifiers, demulsifying agents, surface-washing agents, and dispersants.

Solidifiers, or gelling agents, solidify oil, requiring a large amount of agent, ranging from 16% to more than 200%. Emulsion breakers prevent or reverse the formation of water-in-oil emulsions.

The effectiveness of a dispersant can be defined as the percentage of oil in the water column. Emulsion breakers have been tested for their performance (Fingas et al., 1990b, 1991b). Among the tested products, only one highly effective formulation has been determined, but the conclusion is not too discouraging. Many products will work, but require large amounts of spill-treating agent.

Testing has shown that an agent that is a good dispersant is, conversely, a poor surface-washing agent, and vice versa. Tests of surface-washing agents show that only a few agents have an effectiveness of 25–40%, measured as the percentage of heavy oil removed from a test surface. The aquatic toxicity of these agents is an important factor and has been measured for many products (Fingas et al., 1994b).

Results using the swirling flask test for dispersant effectiveness have been reported. Heavy oils show effectiveness values of approximately 1%, medium crude oils of approximately 10%, light crude oils of approximately 30%, and very light oils of approximately 90%.

The effectiveness of a number of crude oil dispersants, measured using a variety of evaluation procedures, indicates that dispersants are most effective at a salinity of approximately 40 ppt (parts per thousand), and that the concentration of dispersant is critical to its effectiveness.

The mixing time has little effect on performance, and a calibration procedure for laboratory dispersant effectiveness must include contact with water in a manner analogous to the extraction procedure, otherwise, the effectiveness may be inflated (Fingas et al., 1990a). Compensation for the coloration produced by the dispersant alone is important only in some instances.

Natural Dispersion

In a study of the relationship of dispersant effectiveness to dispersant amount and mixing energy, the energy was varied by changing the rotational speed of a specially designed apparatus (Fingas et al., 1993b). The effectiveness goes up linearly with energy, expressed as flask rotational speed. Natural dispersion shows a behavior that is similar to the chemical dispersion, except that the thresholds occur at a higher energy and the effectiveness rises more slowly with increasing energy.

The effect of the amount of dispersant is the same at both low and high energies. The effectiveness increases exponentially with increasing dispersant amount. Although a trade-off exists between dispersant amount and energy required to achieve high effectiveness values, energy is considered to be the more important factor.

Each oil-dispersant combination shows a unique threshold or onset of dispersion (Fingas et al., 1993a). A statistical analysis showed that the principal factors involved are the oil composition, dispersant formulation, sea surface turbulence, and dispersant quantity (Fingas et al., 1994a). The composition of the oil is very important, since the effectiveness of the dispersant formulation correlates strongly with the amount of saturates present. The other components, i.e., asphaltenes, resins, polar substances, and aromatic fractions showed a negative correlation with dispersant effectiveness.

The viscosity of the oil is determined by its composition, so viscosity and composition are responsible for the effectiveness of a dispersant. The dispersant composition is significant and interacts with the oil composition. Sea turbulence positively affects dispersant effectiveness, rising with increasing turbulence to a maximal value. The effectiveness for commercial dispersants is a Gaussian distribution around a certain salinity value.

The effect of water temperature is logarithmically correlated with dispersant effectiveness (Fingas et al., 1991a). Dispersant/oil ratios greater than approximately 1:40 result in a low dispersant effectiveness.

Studies have been conducted concerning the variances among several standard regulatory tests. Three main causes of differences have been identified: oil/water ratio, settling time, and energy (Fingas et al., 1994c). The energy can be partially compensated for by correcting for the natural dispersion. With this correction and with high oil/water ratios and a settling time of at least 10 min, five test methods yield similar results for a variety of oils and dispersants. The repeatability of energy levels used in the instrumentation is largely responsible for the observed variation in the effectiveness values of the dispersant.

Analysis of Corexit 9527®

Corexit® 9527 in natural waters can be analyzed by the formation of a bis-(ethylene diamine) copper (II) complex, extraction of the complex into methylisobutylketone, and atomic absorption spectroscopy (Scelfo and Tjeerdema, 1991). The method is suitable for a concentration range of 2–100 $\mathrm{mg\,l^{-1}}$, with a precision as low as 5% relative to standard deviation for samples in the middle to high range. Only a small sample volume (10 ml) is required. The sensitivity may be substantially increased for trace analysis by increasing the sample volume.

Subsurface, Soil, and Ground Water

Subsurface contamination by organic chemicals is a widespread and serious problem, restricted not only to oil spills, but also pertinent in former and still-operating industrial sites. Remarkably, chemical-enhanced oil recovery technology can be used to remove oily contaminants from soil; see Chapter 16 for further explanation.

In Situ Chemical Oxidation

Chlorinated solvents, polyaromatic hydrocarbons, and other organics can be resistant to in situ biodegradation or may take very long periods of time to degrade in many subsurface settings.

Field experiences have demonstrated that the successful application of in situ chemical oxidation requires the consideration of several factors through an integrated evaluation and design practice. Matching the oxidant and in situ delivery system to the contaminants of concern and the site conditions is the key to the successful implementation of such techniques (Urynowicz et al., 2001).

Ground Water

Ground water contaminant plumes from accidental gasoline releases often contain methyl *tert*-butyl ether. Experiments with certain soil microorganisms showed that a culture able to degrade methyl *tert*-butyl ether did not degrade benzene and toluene. Further interactions were observed (Deeb et al., 2001).

Chemicals in Detail

Oxyethylated Alkyl Phenol

A solution of a surfactant mixture in liquid paraffin, containing an oil-soluble, oxyethylated alkyl phenol, with a C_8–C_{12} alkyl group, an alkyl phosphate of a higher fatty acid alcohol $(RO)_2{>}PO{-}OH$ where R is C_{10} to C_{20}, and a fatty acid amide of diethanol amine, was found to be suitable for removing oils and petroleum products from water surfaces (Chaplanov et al., 1992). The composition has low toxicity, is not inactivated by freezing, and has high biological activity, stimulating the growth of microflora and giving 80–83% dispersion in 5 min.

Sorbitan Oleates for Oil Slicks

Dispersant compositions for the treatment of oil spills at the surface of the water consist of a mixture of water, a hydrocarbon solvent, and a mixture of surfactants consisting of 55–65% of emulsifiers and 35–45% of dioctyl sodium sulfosuccinate. The emulsifying agents consist of a mixture of various sorbitan oleates (Charlier, 1988, 1989, 1990, 1991).

Fatty Alcohols

Petroleum spillages can be removed from water surfaces more efficiently with the following detergent mixture, which contains mainly oxyethylate fatty C_{10} to C_{20} alcohols and additional oxyethylated fatty C_{11} to C_{17} acids with an oxyethylene chain length of one to two units (Sulejmanov et al., 1993). It is used in the form of an aqueous 20–25% emulsion, which is sprayed onto a contaminated surface.

Proteins

A proteinaceous particulate material has been described, which is effective as an oil spill-dispersant composition (Potter, 1994). The material is a product of grain, such as oats, from which the lipids are removed through organic solvent extraction. When such compositions are applied to an oil spill, they will absorb oil, emulsify it, and finally, disperse it. The compositions are also substantially non-toxic.

Polymers

Functionalized copolymers of dienes and *p*-alkylstyrenes can serve as dispersants and viscosity index improvers. The functionalities are introduced via the aromatic units (Brandes and Loveless, 1996a,b). The polymers are selectively hydrogenated to produce polymers with highly controlled levels of unsaturation, permitting a highly selective functionalization. The dispersant substances may also include a carrier fluid to provide concentrates of the dispersant.

Cyclic Monoterpenes

The recovery of sludging oil crudes from hydrocarbon-bearing formations during acid stimulation treatments can be enhanced using an antisludging agent that is basically a dispersant. Such an antisludging agent consists of an admixture of dicyclopentadiene and a mixture of naturally occurring cyclic monoterpenes isolated from *Pinus* species (Ford and Hollenbeak, 1987, 1991). The agent is added to the acid used for the well stimulation treatment. Another dispersing agent that is active under these conditions is ethoxylated alkyl phenol dissolved in a mixture of ethylene glycol, methanol, and water (Ford, 1989, 1991, 1993).

Special Chemicals for Oiled Shorelines

The use of chemical dispersant for oiled shorelines is one of the most controversial, complex, and time-critical issues facing officials responsible for making decisions about the response methods used on coastal oil spills (Walker and Henne, 1991).

In general, the clean-up of oiled shorelines has been performed by mechanical, labor-intensive means. The use of surfactants to lift the oil from the surface results in more complete and rapid cleaning. Not only is this cleaning process more efficient, but it can also be less environmentally damaging, because potentially less human intrusion and stress on the biological community occurs, and also the chemicals can make the washing more effective at a lower temperature.

Chemical beach cleaners can facilitate the clean-up of oiled shorelines by improving the efficiency of washing with water. A dispersant has been developed that reduces the adhesion of the oil coating, which makes it easier to remove from shoreline surfaces, thereby reducing washing time and lowering the temperature of the wash water needed to clean a given area (Fiocco, 1991).

These experiences resulted in the development of Corexit® 9580 (Canevari et al., 1994a; Fiocco et al., 1996), which consists of two surfactants and a solvent. It exhibits low fish toxicity, low dispersiveness, and effective rock cleaning capability. Experiments on mangroves aimed at exploring the potential use of Corexit® 9580 to save and restore oiled vegetation have been considered.

Such a dispersant formulation contains a mixture of a sorbitan monoester of an aliphatic monocarboxylic acid, a polyoxyethylene adduct of a sorbitan monoester of an aliphatic monocarboxylic acid, a water-dispersible salt of a dialkyl sulfosuccinate, a polyoxyethylene adduct of a sorbitan triester or a sorbital hexaester of an aliphatic monocarboxylic acid, and propylene glycol ether as solvent (Canevari et al., 1994b, 1997).

Coagulants

Linseed oil, fatty acids, alkenes, and polyisobutylmethacrylate, are treated in a thermal process to prepare an oil coagulant, which floats on the water surface and coagulates oil independent of both agitation and temperature and can be used in both salt water and fresh water. After coagulation at least 99.9% of the floating coagulated oil can readily be removed from the water by mechanical methods.

REFERENCES

Abdel-Moghny, T., Gharieb, H.K., 1995. Biodegradable oil spill dispersants with high efficiency and low toxicity. In: Proceedings Volume, 1st Bahrain Soc. Eng. et al Environment Issues in the Petroleum and Petrochemical Industry Specifications Conference, Manama, Bahrain, December 4–6, 1995, pp. 184–195.

Albone, D.J., Kibblewhite, M.G., Sansom, L.E., Morris, P.R., 1990. The storage stability of oil spill dispersants, Quart. J. Tech. Pap. (Inst Petrol) 1–53, 1990.

Allen, A.A., Dale, D.H., 1995. Dispersant mission planner: A computerized model for the application of chemical dispersants on oil spills. In: Proceedings Volume, Vol. 1, 18th Environment Canada Arctic and Marine Oil Spill Program Technical Seminar, Edmonton, Canada, June 14–16, 1995, pp. 393–414.

Allen, T.E., 1985. New concepts in spraying dispersants from boats. In: Proceedings Volume, 9th Bien. API et al Oil Spill Conference Los Angeles, February 25–28, 1985, pp. 3–6.

Aurand, D.V., Jamail, R., Sowby, M., Lessard, R.R., Steen, A., Henderson, G., et al., 2001. Goals, objectives, and the sponsors perspective on the accomplishments of the chemical response to oil spills: Ecological effects research forum (croserf). In: Proceedings Volume, API et al International Oil Spill Conference, Tampa, FL, March 26–29, 2001.

Becker, K.W., Walsh, M.A., Fiocco, R.J., Curran, M.T., 1993. A new laboratory method for evaluating oil spill dispersants. In: Proceedings Volume, 13th Bien. API et al Oil Spill (Prev, Preparedness, Response & Coop) International Conference, Tampa, FL, March 29, 93–4, 1, 1993, pp. 507–510.

Belk, J.L., Elliott, D.J., Flaherty, L.M., 1989. The comparative effectiveness of dispersants in fresh and low salinity waters. In: Proceedings Volume, API et al Oil Spill 20th Anniversary Conference, San Antonio, February 13–16, 1989, pp. 333–336.

Belore, R., 1987. Use of high-pressure water mixing for ship-based oil spill dispersing. In: Proceedings Volume, 10th Bien. API et al Oil Spill Conference, Baltimore, April 6–9, 1987, pp. 297–302.

Bocard, C., Castaing, G., Ducreux, J., Gatellier, C., Croquette, J., Merlin, F., 1987. Protecmar: The french experience from a seven-year dispersant offshore trials program. In: Proceedings Volume, 10th Bien. API et al Oil Spill Conference, Baltimore, April 6–9, 1987, pp. 225–229.

Brandes, E.B., Loveless, F.C., 1996a. Dispersants and dispersant viscosity index improvers from selectively hydrogenated polymers. WO Patent 9 640 846, assigned to Mobil Oil Corp., December 19, 1996.

Brandes, E.B., Loveless, F.C., 1996b. Dispersants and dispersant viscosity index improvers from selectively hydrogenated polymers. WO Patent 9 640 845, assigned to Mobil Oil Corp., December 19, 1996.

Brandvik, P.J., Knudsen, O.O., Moldestad, M.O., Daling, P.S., 1994. Laboratory testing of dispersants under arctic conditions. In: Proceedings Volume, 2nd Astm Use of Chemicals in Oil Spill Response Symposium, Victoria, Canada, October 10–11, 1994, pp. 191–206.

Brandvik, P.J., Moldestad, M.O., Daling, P.S., 1992. Laboratory testing of dispersants under arctic conditions. In: Proceedings Volume, 15th Environment Canada Arctic and Marine Oil Spill Program Technical Seminar, Edmonton, Canada, June 10–12, 1992, pp. 123–134.

Brown, H.M., Goodman, R.H., 1996. The use of dispersants in broken ice. In: Proceedings Volume, Vol. 1, 19th Environment Canada Arctic and Marine Oil Spill Program Technical Seminar, Calgary, Canada, June 12–14, 1996, pp. 453–460.

Brown, H.M., Goodman, R.H., Canevari, G.P., 1987. Where has all the oil gone? dispersed oil detection in a wave basin and at sea. In: Proceedings Volume, 10th Bien. API et al Oil Spill Conference, Baltimore, April 6–9, 1987, pp. 307–312.

Brown, R.G.B., Curl, G., Curl Jr., H., Christopherson, S., Dale, D., Hall, C., et al., 1992. Oil spill case histories 1967–1991. Summaries of significant U.S. and international oil spills, National Oceanic and Atmospheric Administration HMRAD 92-11, NOAA Hazardous Material Response and Assessment Division, Seattle, Washington.

Burridge, T.R., Shir, M.A., 1995. The comparative effects of oil dispersants and oil/dispersant conjugates on germination of the marine macroalga phyllospora comosa (fucales: Phaeophyta). Mar. Pollut. Bull. 31 (4–12), 446–452.

Canevari, G.P., 1987. Basic study reveals how different crude oils influence dispersant performance. In: Proceedings Volume, 10th Bien. API et al Oil Spill Conference, Baltimore, April 6–9, 1987, pp. 293–296.

Canevari, G.P., Fingas, M., Fiocco, R.J., Lessard, R.R., 1994a. Corexit 9580 shoreline cleaner: Development, application, and status. In: Proceedings Volume, 2nd Astm Use of Chemicals in Oil Spill Response Symposium, Victoria, Canada, October 10–11, 1994, pp. 227–239.

Canevari, G.P., Fiocco, R.J., Becker, K.W., Lessard, R.R., 1994b. Chemical dispersant for oil spills. WO Patent 9 413 397, June 23, 1994.

Canevari, G.P., Fiocco, R.J., Becker, K.W., Lessard, R.R., 1997. Chemical dispersant for oil spills. US Patent 5 618 468, April 08, 1997.

Chaplanov, P.E., Chernikov, A.D., Mironov, O.G., Semanov, G.N., Svinukhov, A.G., Yaremenko, A.G., et al., 1992. Removing oils and petroleum products from water surfaces – using mixture of oxyethylated alkyl- phenol, alkyl-phosphate and fatty acid diethanolamine. SU Patent 1 325 816, October 15, 1992.

Charlier, A., 1988. Dispersant compositions for treating oil slicks on the surface of water (compositions dispersantes pour le traitement de nappes d’huile a la surface de l’eau). EP Patent 254 704, January 27, 1988.

Charlier, A.G.R., 1989. Dispersant compositions for treating oil slicks. US Patent 4 830 759, May 16, 1989.

Charlier, A., 1990. Dispersant compositions for treating oil slicks on cold water. EP Patent 398860, November 22, 1990.

Charlier, A.G.R., 1991. Dispersant compositions for treating oil slicks. US Patent 5 051 192, September 24, 1991.

Christopher, C.A., 1993. Surface chemical aspects of oil spill dispersant behavior. In: Proceedings Volume, 4th Annual Pennwell Conference & Exhibit. Co. Petro-Safe 93 Conference, Houston, January 26–28, 1993, pp. 375–389.

Clayton Jr., J.R., Stransky, B.C., Adkins, A.C., Lees, D.C., Schwartz, M.J., Snyder, B.J., et al., 1996. Methodology for estimating cleaning effectiveness and dispersion of oil with shoreline cleaning agents in the field. In: Proceedings Volume, Vol. 1, 19th Environment Canada Arctic and Marine Oil Spill Program Technical Seminar, Calgary, Canada, June 12–14, 1996, pp. 423–451.

Corbin, R.F., Ott, G.L., 1985. Federal region II regional contingency planning for a dispersant decision process. In: Proceedings Volume, 9th Bien. API et al Oil Spill Conference, Los Angeles, February 25–28, 1985, pp. 417–420.

Cunningham, J., Rojo, M., Kooyoomjian, K.J., Jordan, J.M., 1989. Decision-making on the use of dispersants: The role of the states. In: Proceedings Volume, API et al Oil Spill 20th Anniversary Conference, San Antonio, February 13–16, 1989, pp. 353–356.

Cunningham, J.M., Sahatjian, K.A., Meyers, C., Yoshioka, G., Jordan, J.M., 1991. Use of dispersants in the united states: Perception or reality?. In: Proceedings Volume, 12th Bien. API et al Oil Spill International Conference, San Diego, March 4–7, 1991, pp. 389–393.

Deeb, R.A., Hu, H.Y., Hanson, J.R., Scow, K.M., Alvarez-Cohen, L., 2001. Substrate inter-actions in btex [benzene, toluene, ethylbenzene, and xylene] and MTBE [methyl tert-butyl ether] mixtures by an mtbe-degrading isolate. Environ. Sci. Technol. 35 (2), 312–317.

Fay, R.R., Giammona, C.P., Binkley, K., Engelhardt, F.R., 1993. Measuring the aerial application of oil dispersant from very large aircraft at moderate altitude. In: Proceedings Volume, Vol. 2, 16th Environment Can. Arctic & Mar Oil Spill Program Tech. Seminar, Calgary, Canada, June 7–9, 1993, pp. 1057–1063.

Fingas, M., 1995. Water-in-oil emulsion formation: A review of physics and mathematical modelling. Spill Sci. Technol. Bull. 2 (1), 55–59.

Fingas, M., Bier, I., Bobra, M., Callaghan, S., 1991b. Studies on the physical and chemical behavior of oil and dispersant mixtures. In: Proceedings Volume, 12th Bien. API et al Oil Spill International Conference, San Diego, March, 4–7, 1991, pp. 419–426

Fingas, M.F., Kolokowski, B., Tennyson, E.J., 1990b. Study of oil spill dispersants effectiveness and physical studies. In: Proceedings Volume, 13th Environment Canada Arctic and Marine Oil Spill Program Technical Seminar, Edmonton, Canada, June 6–8, 1990, pp. 265–287.

Fingas, M.F., Kyle, D., Tennyson, E., 1994b. Dispersant effectiveness: Studies into the causes of effectiveness variations. In: Proceedings Volume, 2nd ASTM Use of Chemicals in Oil Spill Response Symposium, Victoria, Canada, October 10–11, 1994, pp. 92–132.

Fingas, M.F., Kyle, D.A., Holmes, J.B., Tennyson, E.J., 1993b. The effectiveness of dispersants: Variation with energy. In: Proceedings Volume, 13th Bien. API et al Oil Spill (Prev, Preparedness, Response & Coop) International Conference, Tampa, FL, March 29, 93–4, 1, 1993, pp. 567–574.

Fingas, M.F., Kyle, D.A., Lambert, P., Wang, Z., Mullin, J.V., 1995. Analytical procedures for measuring oil spill dispersant effectiveness in the laboratory. In: Proceedings Volume, Vol. 1, 18th Environment Canada Arctic and Marine Oil Spill Program Technical Seminar, Edmonton, Canada, June 14–16, 1995, pp. 339–354.

Fingas, M.F., Kyle, D.A., Laroche, N., Fieldhouse, B., Sergy, G., Stoodley, G., 1994a. The effectiveness testing of oil spill-treating agents. In: Proceedings Volume, 2nd ASTM Use of Chemicals in Oil Spill Response Symposium, Victoria, Canada, October 10–11, 1994, pp. 286–298.

Fingas, M.F., Kyle, D.A., Tennyson, E.J., 1993a. Physical and chemical studies on dispersants: The effect of dispersant amount and energy. In: Proceedings Volume, Vol. 2, 16th Environment Canada Arctic and Marine Oil Spill Program Technical Seminar, Calgary, Canada, June 7–9, 1993, pp. 861–876.

Fingas, M.F., Kyle, D.A., Wang, Z., Handfield, D., Ianuzzi, D., Ackerman, F., 1994c. Laboratory effectiveness testing of oil spill dispersants. In: Proceedings Volume, 2nd Astm Use of Chemicals in Oil Spill Response Symposium, Victoria, Canada, October 10–11, 1994, pp. 3–40.

Fingas, M.F., Munn, D.L., White, B., Stoodley, R.G., Crerar, I.D., 1989. Laboratory testing of dispersant effectiveness: The importance of oil-to-water ratio and settling time. In: Proceedings Volume, API et al Oil Spill 20th Anniversary Conference, San Antonio, February 13–16, 1989, pp. 365–373.

Fingas, M.F., Stoodley, R., Laroche, N., 1990a. Effectiveness testing of spill-treating agents. Oil. Chem. Pollut. 7 (4), 337–348.

Fingas, M.F., Stoodley, R., Stone, N., Hollins, R., Bier, I., 1991a. Testing the effectiveness of spill-treating agents: Laboratory test development and initial results. In: Proceedings Volume, 12th Bien. API et al Oil Spill International Conference, San Diego, March 4–7, 1991, pp. 411–414.

Fiocco, R.J., Canevari, G.P., Wilkinson, J.B., Bock, J., Robbins, M., Jahns, H.O., et al., 1991. Development of corexit 9580 – a chemical beach cleaner. In: Proceedings Volume, 12th Bien. API et al Oil Spill International Conference, San Diego, March 4–7, 1991, pp. 395–400.

Fiocco, R.J., Lessard, R.R., Canevari, G.P., 1996. Improving oiled shoreline cleanup with corexit 9580. In: Proceedings Volume, Asme/api Energy Week 96 Conference, Houston, January 29, 96–2, 2, 1996, pp. 276–280.

Fiocco, R.J., Lessard, R.R., Canevari, G.P., Becker, K.W., Daling, P.S., 1994. The impact of oil dispersant solvent on performance. In: Proceedings Volume, 2nd Astm Use of Chemicals in Oil Spill Response Symposium, Victoria, Canana, October 10–11, 1994, pp. 299–309.

Flaherty, L.M., Katz, W.B., Kaufmann, S., 1987. Dispersant use guidelines for freshwater and other inland environments. In: Proceedings Volume, Amer. Soc. Testing Mater Oil Dispersants: New Ecol Approaches Symposium, Williamsburg, VA, October 12–14, 1987, pp. 25–30.

Ford, W.C.F., 1991. Reducing sludging during oil well acidizing. US Patent 4 981 601, January 01, 1991.

Ford, W.G., Hollenbeak, K.H., 1987. Composition and method for reducing sludging during the acidizing of formations containing sludging crude oils. US Patent 4 663 059, May 05, 1987.

Ford, W.G., Hollenbeak, K.H., 1991. Composition and method for reducing sludging during the acidizing of formations containing sludging crude oils. CA Patent 1 280 585, February 26, 1991.

Ford, W.G.F., 1989. Reducing sludging during oil well acidizing. US Patent 4 823 874, April 25, 1989.

Ford, W.G.F., 1993. Reducing sludging during oil well acidizing. CA Patent 1 318 122, May 25, 1993.

Fraser, J.P., 1985. Advance planning for dispersant use/non-use. In: Proceedings Volume, 9th Bien. API et al Oil Spill Conference, Los Angeles, February 25–28, 1985, pp. 429–432.

Fraser, J.P., 1989. Methods for making dispersant use decisions. In: Proceedings Volume, API et al Oil Spill 20th Anniversary Conference, San Antonio, February 13–16, 1989, pp. 321–330.

Fraser, J.P., Horn, S.A., Kazmierczak, L.J., Kinworthy, M.L., Lasday, A.H., Lindstedt-Siva, J., 1989. Guidelines for use of dispersants on spilled oil – a model plan. In: Proceedings Volume, API et al Oil Spill 20th Anniversary Conference, San Antonio, February 13–16, 1989, pp. 331–332.

Geyer, R., Fay, R., Denoux, G., Giammona, C., Binkley, K., Jamail, R., 1992. Aerial dispersant application: Assessment of sampling methods and operational altitudes, Mar Spill Response Corp Tech. Rep Ser 93-0091, Marine Spill Response Corporation.

Gillot, A., Charlier, A., Van Elmbt, R., 1986. Correlation results between IFP (institute francais du petrole) and WSL (Warren Spring Laboratory) laboratory tests of dispersants. Oil. Chem. Pollut. 3 (6), 445–453.

Heller, A., Brock, J.R., 1995. Materials and methods for photocatalyzing oxidation of organic compounds on water. AU Patent 657 470, March 16, 1995.

Lindblom, G.P., 1987. Measurement and prediction of depositional accuracy in dispersant spraying from large airplanes. In: Proceedings Volume, 10th Bien. API et al Oil Spill Conference, Baltimore, April 6–9, 1987, pp. 325–328.

List of oil spills, [electronic:] http://en.wikipedia.org/wiki/List_of_oil_spills November (2010).

Mackay, D., Chau, A., 1986. The effectiveness of chemical dispersants: A discussion of laboratory and field test results. Oil. Chem. Pollut. 3 (6), 405–415.

Manen, C.A., Fox Jr., L.B., Getter, C., Whitney, J., Harris, L., O'Brien, P.S., et al., 1987. Oil dispersant guidelines: Alaska. In: Proceedings Volume, Amer. Soc. Testing Mater Oil Dispersants: New Ecol Approaches Symposium, Williamsburg, VA, October 12–14, 1987, pp. 141–151.

Merlin, F., 1989. Optimization of dispersant application, especially by ship. In: Proceedings Volume, API et al Oil Spill 20th Anniversary Conference, San Antonio, February 13–16, 1989, pp. 337–342.

Merlin, F., Bocard, C., Cabridenc, R., Oudot, J., Vindimian, E., 1991. Toward a french approval procedure for the use of dispersants in inland waters. In: Proceedings Volume, 12th Bien. API et al Oil Spill International Conference, San Diego, March 4–7, 1991, pp. 401–404.

Moet, A., Bakr, M.Y., Abdelmonim, M., Abdelwahab, O., 1995. Factors affecting measurements of the efficiency of spilled oil dispersion. ACS Pet. Chem. Div. Preprints 40 (4), 564–566.

Mulyono, M., Jasjfi, E., Maloringan, M., 1993. Biodegradation test for oil spill dispersant (osd) and osd-oil mixture. In: Proceedings Volume, 5th Asean Counc Petroleum Conference (Ascope 93), Bangkok, Thailand, November 2–6, 1993, pp. 355–363.

Potter, R., 1994. Proteinaceous oil spill dispersant. WO Patent 9 419 942, September 15, 1994.

Rewick, R.T., Sabo, K.A., Gates, J., Smith, J.H., McCarthy Jr., L.T., 1988. Project summary: Evaluation of oil spill dispersant testing requirements, US Environ. Protect Agency Rep EPA/600/S2-87/070, SRI International, EPA.

Scelfo, G.M., Tjeerdema, R.S., 1991. A simple method for determination of Corexit 9527 in natural waters. Mar. Environ. Res. 31 (1), 69–78.

Singer, M., Tjeerdema, R., Aurand, D., Clark, J., Sergy, G., Sowby, M., 1995. Croserf (chemical response to oil spills ecological effects research forum): Toward a standardization of oil spill cleanup agent ecological effects research. In: Proceedings Volume, Vol. 2, 18th Environment Canada Arctic and Marine Oil Spill Program Technical Seminar, Edmonton, Canada, June 14–16, 1995, pp. 1263–1270.

Sulejmanov, A.B., Geokchaev, T.B., Dashdiev, R.A., 1993. Removal of petroleum spillages from water surface - using a detergent mixture containing oxyethylated fatty 10-20c alcohols and additional oxyethylated fatty 11-17C acids to improve properties. SU Patent 1 803 418, March 23, 1993.

Sullivan, D., Farlow, J., Sahatjian, K.A., 1993. Evaluation of three oil spill laboratory dispersant effectiveness tests. In: Proceedings Volume, 13th Bien. API et al Oil Spill (Prev, Preparedness, Response & Coop) International Conference, Tampa, FL, March 29, 93–4, 1, 1993, pp. 515–520.

Thorhaug, A., Carby, B., Reese, R., Sidrak, G., Anderson, M., Aiken, K., et al., 1991. Dispersant use for tropical nearshore waters: Jamaica. In: Proceedings Volume, 12th Bien. API et al Oil Spill International Conference, San Diego, March 4–7, 1991, pp. 415–418.

Thorhaug, A., Marcus, J.H., 1987. Preliminary mortality effects of seven dispersants on subtropical/tropical seagrasses. In: Proceedings Volume, 10th Bien. API et al Oil Spill Conference, Baltimore, April 6–9, 1987, pp. 223–224.

Thorhaug, A., McFarlane, J., Carby, B., McDonald, F., Anderson, M., Miller, B., et al., 1989. Dispersed oil effects on tropical habitats: Preliminary laboratory results of dispersed oil testing on jamaica corals and seagrass. In: Proceedings Volume, API et al Oil Spill 20th Anniversary Conference, San Antonio, February 13–16, 1989, pp. 455–458.

To, N.M., Brown, H.M., Goodman, R.H., 1987. Data analysis and modeling of dispersant effectiveness in cold water. In: Proceedings Volume, 10th Bien. API et al Oil Spill Conference, Baltimore, April 6–9, 1987, pp. 303–306.

Urynowicz, M.A., Siegrist, R.L., Crimi, M.L., West, O.R., Lowe, K.S., Struse, A.M., 2001. Fundamentals and application of in situ chemical oxidation technologies. In: Abstracts Volume, Annual Aapg-Sepm Conv, Denver, CO, June 3–6, 2001, p. A205.

Vacca-Torelli, M., Geraci, A.L., Risitano, A., 1987. Dispersant application by hydrofoil: High speed control and cleanup of large oil spills. In: Proceedings Volume, 10th Bien. API et al Oil Spill Conference, Baltimore, April 6–9, 1987, pp. 75–79.

Vindimian, E., Vollat, B., Garric, J., 1992. Effect of the dispersion of oil in freshwater based on time-dependent daphnia magna toxicity tests. Bull. Environ. Contamination. Toxicol. 48 (2), 209–215.

Walker, A.H., Henne, D.R., 1991. The region III regional response team technical symposium on dispersants: An interactive, educational approach to enlightened decision making. In: Proceedings Volume, 12th Bien. API et al Oil Spill International Conference, San Diego, March 4–7, 1991, pp. 405–410.

Wiechert, J., Rideout, M.L., Little, D.I., McCormick, D.M., Owens, E.H., Trudel, B.K., 1991. Development of dispersant pre-approval for washington and oregon coastal waters. In: Proceedings Volume, 12th Bien. API et al Oil Spill International Conference, San Diego, March 4–7, 1991, pp. 435–438.

Chapter 20

Waste Disposal

There are monographs about environmental technology in the oil industry available in the literature (Orszulik, 2008), and cumulative data regarding disposed chemicals have been compiled (Environmental Report, 2008; Hudgins, 1994). They are shown in Table 20.1.

Waste disposal presents problems that are location-specific. For example, in Kuwait the problem of hydrocarbon waste management is complex because the country experienced a unique environmental catastrophe as a result of the 1991 Gulf War (Uddin et al., 2009).

DRILLING FLUIDS

The shale inhibition properties of polyol-containing water-based drilling mud (WBM) can be enhanced by the incorporation of potassium salts, e.g., potassium chloride, possibly in combination with gypsum.

The use of potassium can present waste disposal problems, however, and there are certain regions, e.g., The Gulf of Mexico, where the discharge of potassium into the environment is prohibited, or severely restricted. The use of a potassium-containing WBM can also present problems in land drilling due to contamination of ground water (Reid et al., 2003).

Bioremediation

The remediation of mud-polluted drilling sites is very important for the oil industry, and field trials have been undertaken in the Southeast of Mexico in order to find a technology to remediate such sites.

Polluted material was composted in biopiles, of one ton. Some nutrients and straw were added to these piles to establish the required ratio of carbon to nitrogen and phosphor. A control pile was also constructed and monitored. Compared to the control pile, after a period of 180 d the concentration of total petroleum hydrocarbon (TPH) in the test piles decreased by a much higher extent (Rojas-Avelizapa et al., 2007).

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TABLE 20.1 Total Consumption, Discharge and Injection of Chemicals by Application, Tonnes (Environmental Report, 2008)

Application	Year	1997	2002	2007
Drilling and well chemicals	Discharged	180,906	143,237	87,682
	Injected		89,406	78,166
	Consumption	350,782	533,410	352,533
Gas processing chemicals	Discharged	8,055	10,646	11,619
	Injected		411	757
	Consumption	12,314	14,796	18,804
Auxiliary chemicals	Discharged	835	2,566	3,622
	Injected	55	300	
	Consumption	1,861	4,161	6,269
Injection chemicals	Discharged	295	185	332
	Injected		3,332	1,464
	Consumption	7,487	13,441	15,361
Chemicals from other production locations	Discharged	3	9,913	697
	Injected			41
	Consumption	160	64	434
Chemicals added to the export flow	Discharged	293	9	311
	Injected			
	Consumption	3,797	14,616	5,180
Production chemicals	Discharged	4,398	8,582	15,317
	Injected	0	1,579	3,323
	Consumption	26,930	22,013	29,131
Pipeline chemicals	Discharged	910	1,259	2,015
	Injected	–	–	–
	Consumption	1,393	1,265	5,189

Gas chromatography studies indicated the presence of alkyl dibenzothiophenes. The highest bacterial populations were observed during the first 30 d. These correlated with highest rate TPH removal, whereas the number of fungi increased at the end of the experiment (Rojas-Avelizapa et al., 2007).

Assessment of Biodegradability

Biodegradability may be expressed in terms of Battersby (2005):

- Carbon dioxide evolution,
- Oxygen consumption, or
- Loss of parent material.

Test methods for assessing the biodegradability of environmentally acceptable lubricants have been critically reviewed and discussed. Examples are given, which show how confusion can arise through the use of different test methods.

It is recommended that the term "biodegradable" for an environmentally acceptable lubricant should only be used when the net amount of CO_2 production over 28 days, tested according to the OECD test Guideline 301 B, is at least 60% of the theoretical maximum (Battersby, 2005).

The CEC L-33-T-82 biodegradability oil CEC L-33-A-934 test is a widely recommended method for assessing the biodegradability of oil products (Battersby et al., 1994). This test applies to most organic compounds, and determines the overall biodegradability of hydrocarbons.

The ASTM D-5864 standard (ASTM, 2010) is similar to a modified Sturm test (Sturm, 1973), and measures the degree of aerobic aquatic biodegradation of fully formulated lubricants or their components, on exposure to an inoculum under laboratory conditions. A good positive relationship has been shown between biodegradation in the CEC L-33-T-82 standard and the mineralization to CO_2 in a modified Sturm test. A mathematical model describes these correlations (Battersby et al., 1992).

Supercritical Fluid Extraction

There are a number of options available to treat and dispose of oil-based drilling mud (OBM) drilling wastes, including land spreading and landfilling (Street and Guigard, 2009). Supercritical fluid extraction has also been used to treat this waste (Eppig et al., 1984). This is an extraction technique that uses substances at or above their critical pressure and temperature as solvents.

Supercritical carbon dioxide can remove the base oil from drilling waste, with extraction efficiencies of upto 98%. The hydrocarbons are unchanged by the extraction, meaning they may be recovered and potentially reused (Street and Guigard, 2009).

CUTTINGS

The contaminants present in drill cuttings vary with the nature of the drilling mud and the composition of the formation. Contaminants include petroleum hydrocarbons and heavy metals. OBMs are more harmful to the environment than synthetic drilling mud, but their biodegradation properties are quite similar (Leonard and Stegemann, 2010). Drill cuttings can be disposed of by several methods, including slurry reinjection, thermal desorption, incineration, or microwave treatment (Robinson et al., 2008; Shang et al., 2006).

Environmental Impact

Methods for monitoring the impact of drill cuttings contaminated with OBMs in marine environments have been developed. They are based on the analysis of benthic fauna, on chemical analysis of the sediments, or on ecotoxicological tests on the marine macrofauna (Jorissen et al., 2009). Benthos refers to all living organisms on the sea floor.

Pollution by oily drill cuttings has a range of impacts on the marine environment, in particular the benthic fauna (Jorissen et al., 2009). These are:

- Degradation of the oil in the benthic environment, giving an increased availability of organic compounds;
- Increase in the oxygen demand by the sediment, which can result in strongly hypoxic, or even anoxic conditions; and
- In the presence of sulfides, the combination of various stress factors may ultimately cause a total disappearance of the benthic fauna.

It has been found that benthic foraminifera are suitable bioindicators of the anthropogenic enrichment in open marine regions (Mojtahid et al., 2006). They respond by an increase in the density of a number of tolerant or opportunistic taxa, and a progressive disappearance of more sensitive taxa. Large-sized taxa appear to be more sensitive than smaller foraminiferal taxa (Jorissen et al., 2009).

Most of the cuttings discharged from well drilling contain WBMs rather than oil-based or synthetic muds, which are assumed to cause only marginal effects on the benthos. However, an experimental study revealed a significant reduction in the number of taxa, abundance, biomass, and diversity of macrofauna as the thickness of deposited drill cuttings increased. This phenomenon was not observed for natural sediment particles (Trannum et al., 2010). It is therefore recommended that the opinion that water-based drill cuttings only cause sedimentation, i.e., burial effects, be reconsidered as the cuttings initiate a typical eutrophication response in the sediment (Trannum et al., 2010).

The exploration and production of North Sea oil and gas reserves has caused the accumulation of large quantities of drill cuttings on the seabed around drill sites. This complex mixture contains higher concentrations of certain metals and hydrocarbons than are found in the natural sediments (Breuer et al., 2004).

It is known that the hydrocarbons within the cuttings piles remain relatively unchanged with time, and a considerable proportion of the associated contaminants are likely to remain within the cuttings pile unless they are disturbed. This increases the tendency to exchange porewater and solids back to the seabed surface resulting in the possibility of exposure to organisms (Breuer et al., 2004).

Modeling the Discharge

Models are available to predict the potential environmental impact of the drilling fluid components, based on estimates of the initial spatial extent and thickness of accumulations on the seabed. These models are a valuable tool for both the oil industry and regulatory agencies (Pivel et al., 2009).

Among the most widely used models are the Offshore Operators Committee (OOC) Mud and Produced Water Discharge Model (Brandsma and Smith, 1999). The use of the OOC model allows the estimation of the effect of discharges into the sea, i.e., of drilling fluids and cuttings, and also of produced water. An automated validation system based on this model has recently been developed (Brandsma, 2004). After setting up the validation system, only a small amount of additional work is needed for repeated validations to test the model, even after changes with respect to maintenance and development. The validation system provides a complete record of all validation methods, data, and results.

In a case study, the OOC model was used for modeling discharges in a deep-water environment from a well located offshore Brazil. Data were collected during the drilling and discharge activities, which enabled the researchers to carry out a study based on real data, i.e., hindcast modeling (Pivel et al., 2009).

Comparing the results obtained by modeling with real field observations gave satisfactory results, but the prediction of the affected area turned out to be more difficult, because the results are sensitive to small uncertainties, which are mainly attributed to the discharge activities. Nevertheless, in areas where there is knowledge of the hydrodynamics, the OOC model can be a valuable tool to determine the potential impact of drilling activities (Pivel et al., 2009).

Fuzzy Logics

A hierarchical model has been developed and evaluated to assess the aggregated environmental risk for various drilling waste discharge scenarios. These wastes are disposed into the marine environment. The technique incorporates the fuzzy set theory (Sadiq and Husain, 2005) and a sensitivity analysis has been performed to verify the effect of weighting schemes on the assessment of a final aggregative risk.

Weights to express the risk have been estimated through an analytical hierarchy process from priority vectors. These include the ecological risk and the human health risk at the upper levels, which are further specified as level two in health toxicological effects and safety related health dangers, and down to some more level three classes (Sadiq and Husain, 2005). These data are used in a rather complicated procedure to estimate the final risk.

The methodology outlined above has been used to evaluate various scenarios for discharging drilling waste into the marine environment. Three discharge scenarios were selected with various amounts of synthetic mud attached to dry drill cuttings. Sensitivity analysis showed that the aggregative environmental risks are not sensitive to the weighting schemes, but rather to the selection of the grade of risk and to grade of importance.

Microwave Treatment

Applications of microwaves are increasingly used in oil field technologies, at least on the laboratory scale (Mutyala et al., 2010). Of particular interest are the application of microwaves to bitumen extraction, upgrading of heavy oils, and removing heteroatoms. In addition, underground heating of oil sands to reduce bitumen viscosity is possible, which allows such materials to be pumped to the surface. Microwave energy provides a fundamentally different method of transferring energy from the source to the sample. By delivering energy directly to microwave-absorbing materials, conventional issues such as long heating periods and energy losses can be minimized.

In North America, the only allowed frequencies for industrial use are 915, 2450, 5800, and 22,000 MHz. For laboratory uses, 2450 MHz is preferred, since it has adequate penetration depth for most laboratory reaction conditions.

A patent was launched in 1983, that describes the recovery of shale oil and heavy oil using microwaves for heating (Bálint et al., 1983), which is still highly innovative (Cogliandro and Moses, 2009). Microwave energy has been shown to be effective in some applications, but it is not used commercially at present (Mutyala et al., 2010).

Oil-contaminated drill cuttings can be treated with microwaves. In contrast to conventional heating, the microwave energy is delivered directly to materials through molecular interactions with the electromagnetic field.

It was found that under favored operating conditions, the oil levels can be reduced to below 1%. Laboratory experiments revealed that 20 s of microwave treatment is sufficient to reduce the residual oil levels below 1%. A major drawback for the efficiency of this method is the moisture content, but increasing water content of the samples can potentially overcome such limitations (Shang et al., 2006). The effectiveness of microwaves for heating of a variety of materials are summarized in Table 20.2.

The penetration depth D_p is defined as the depth at which the intensity of the electric field drops to e^{-1} of its value at the surface. The penetration depth is approximately:

$$D_p = \frac{\lambda\sqrt{\varepsilon'}}{2\pi\varepsilon''} \tag{20.1}$$

TABLE 20.2 Dielectric Properties and Penetration Depths of Various Substances at 25°C and 2.45 GHz (Robinson et al., 2008)

Material	ε'	ε''	Penetration Depth/[cm]
Fuel oil	2.0	0.002	1378
Feldspar	2.6	0.02	157
Quartz	3.8	0.001	3799
Mica	1.6	0.005	493
Water	77	13	1.3

2.45 GHz at 10 kW cavity power and 22 s irradiation time was used. The effect of moisture content on residual oil levels at microwave heating is shown in Figure 20.1, and the energy consumption using various methods of stripping the organic material is shown in Figure 20.2.

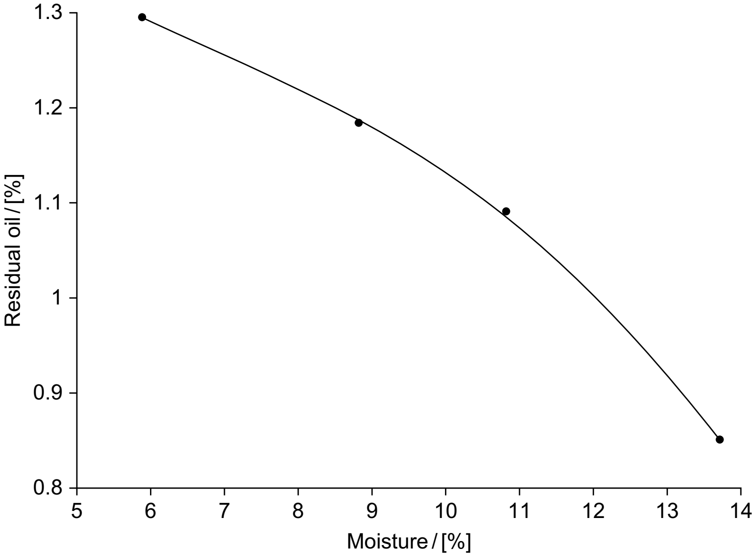

FIGURE 20.1 Initial moisture content viz. residual oil levels (Shang et al., 2006).

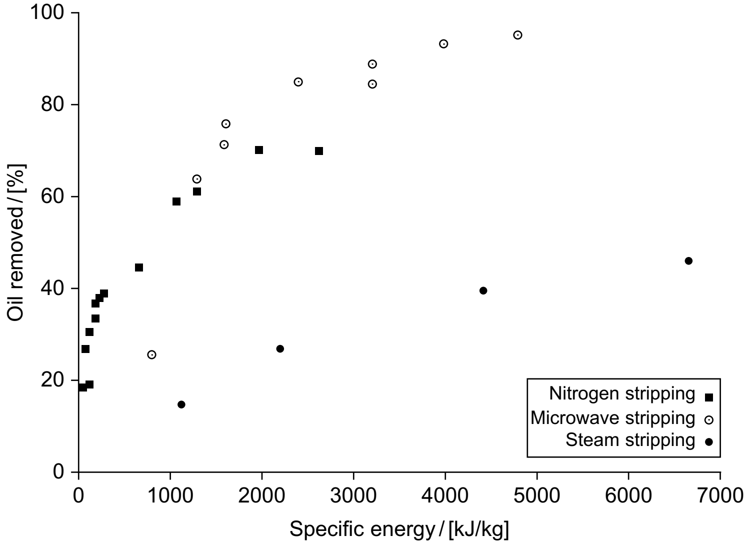

FIGURE 20.2 Specific energy needed for specific levels of oil removal (Robinson et al., 2008).

Based on previous research the authors have developed a continuous microwave treatment system for the remediation of contaminated drill cuttings on a semi-technical scale (Robinson et al., 2010). A system capable of treating $500\,\mathrm{kg\,h^{-1}}$ has been set up, which has demonstrated that the environmental discharge threshold of 1% oil can be achieved in continuous operation. The sensitivity of this pilot plant toward changes in the feedstock has been investigated. The system must process both slurries and granular solids. It has been found that when moisture content deviates from its nominal value of 6%, the system performance becomes lower, as the power to density ratio decreases.

Discharge in Cement

The inclusion into lime, pozzolanas, Portland, or slag cement forms a cost-effective and reliable technique for the immobilization of large amounts of drill cuttings. Unfortunately, chloride ions retard the setting of the cement and the mechanical strength of the end-product is reduced. For this reason, the disposal of sodium chloride-containing drill cuttings is still problematic.

The addition of orthophosphate seems to form a continuous and weakly soluble network in the cement matrix, which reduces the release of the salt. Actually, apatite and hydrocalumite are formed. These phases encapsulate the salt grains within a network, lowering its interaction with water or trapping the chloride (Filippov et al., 2009). Chloride trapping into hydrocalumite in ordinary Portland cement has been reported (Haque and Kayyali, 1995). At high pH, hydrocalumite precipitates according to:

$$2\mathrm{Ca(OH)_2} + \mathrm{Al(OH)_4^-} + \mathrm{Cl^-} + 2\mathrm{H^+} \rightarrow \mathrm{Ca_2(OH)_6Cl} \times 3\,\mathrm{H_2O} \tag{20.2}$$

Leaching experiments, where oil-based cuttings were embedded into cement matrices, have shown that treating the cuttings with potassium phosphate decreases the amount of dissolved salt from 41.3 to 19.1%. In contrast, aluminium phosphate is more efficient for the stabilization of water-based cuttings (Filippov et al., 2009).

Methods for treating synthetic drill cuttings intended for landfill or for potential reuse as construction products have been screened (Al-Ansary and Al-Tabbaa, 2007). Two synthetic mixes were used, based on average concentrations of specific contaminates present in typical drill cuttings from the North Sea and the Red Sea areas. They contained a chloride content of 2.03% and 2.13% and a hydrocarbon content of 4.20% and 10.95%, respectively, so the mixes were denoted as low and high oil content mixes.

A number of conventional binders for stabilization and solidification were screened, including Portland cement, lime, and blast furnace slag, alongside some novel binders, such as microsilica and magnesium oxide. Despite differences in the hydrocarbon content in the synthetic cuttings under investigation, the measured mechanical properties of the samples with the same binder type and content were similar. Tests of the leachability of the samples showed a reduction of the amount leached into a stable non-reactive hazardous waste. Leaching tests are standardized by a European standard (CEN, 2002), although there are alternatives (Al-Ansary and Al-Tabbaa, 2007).

Experiments of the leachability of paraffins showed that lime-Portland cement binders showed the best performance, even at levels of 10% (Al-Ansary and Al-Tabbaa, 2007).

Fillers in Bitumen

In offshore activities before 2000, the drill cuttings, are separated from other components of the drilling mud and then deposited in the vicinity of the platforms, but this has since been prohibited by legislation (OSPAR, 2006, 2007).

This states that the cuttings must be transported to the shore, hence a new waste stream was generated. For example, in the UK, $40\,\mathrm{kt\,a^{-1}}$ of drilling cuts have to be disposed of, which means that technologies for disposing of this kind of wastes have had to be developed.

Oil-drill cuttings contain typically 50% OBM. The hydrocarbon content of these materials must be reduced to less than 1% before being discharged to landfill sites. Cleaned oil-drill cuttings could be used as filler materials, in particular for bituminous mixtures (Dhir et al., 2010). Several samples from different locations in the North Sea, were tested and proved to be either readily suitable for inclusion in pavement asphalt, or for the fabrication of bituminous mixtures after a minor adjustment of the method. Their performance was similar to limestone, and a few products were found to be even more effective than the original (Dhir et al., 2010).

Chromium Removal

Flocculation effluents of liquid phase oil-based drill cuttings may contain comparatively high concentrations of heavy metals, such as Cr^{6+}. Environmental concerns can arise in the direct disposal of such liquids, so it is recommended that the flocculation effluent should be further treated before disposal.

Concentrations of Cr^{6+} of $5.26\,\mathrm{g\,m^{-3}}$ have been detected in representative untreated samples. Flocculation experiments using aluminum sulfate and sodium chloride as coagulant and flocculant, respectively, reduced this to $5.01\,\mathrm{g\,m^{-3}}$, which is highly unsatisfactory. Batch treatment with activated-carbon reduced the concentration of Cr^{6+} to $2.77\,\mathrm{g\,m^{-3}}$ (Ayotamuno et al., 2007).

INJECTION TECHNIQUES

Injection techniques are common in oil field operations. Besides their primary goal, such as fracturing, they may also be useful for waste disposal. Several applications in this field have been developed.

Acid Gas Injection

Acid gas injection is a practical method to dispose of undesirable H_2S and CO_2 produced from natural gas. This technology allows sour gas reservoirs to be economically viable and provides an environmentally friendly disposal option.

Suitable formations for disposal must first be selected, for which it is necessary to examine the properties of the minerals in the rock formation. Injection should cause no significant changes in permeability (Bennion et al., 2004). Geochemical analysis of carbonate cores, previously subjected to acid gas core displacement tests by X-ray tomography, revealed changes of the porosity, which may increase the permeability (Vickerd et al., 2005).

Storage of Carbon Dioxide

Since carbon dioxide is a greenhouse gas, its capture is considered to be an important technology. The assessment of possible storage sites is needed for the technique to work.

A methodology has been developed for screening CO_2 storage fields, which was tested with data available in The Netherlands (Ramírez et al., 2010). The CO_2 storage capacities used in that study were estimated on the basis of data and results of previous studies performed by TNO (Schuppers et al., 2003).

Risk factors associated with CO_2 storage influence the suitability of a reservoir. If risk aspects are taken into account, a more realistic idea of the total storage potential for CO_2 is obtained.

The evaluation starts with assessing the total storage potential in a certain region (The Netherlands), and the storage costs and the efforts needed to manage potential risk are taken into account. A spreadsheet tool enables assessment of the criteria by evaluating the fields present in the database. The data have been weighted with a set of scores (Ramírez et al., 2010).

The study showed that 25% of the theoretical potential storage capacity in The Netherlands falls under the category of having the lowest scores regarding the effort needed to manage risk.

Slurry Fracture Injection Technique

The slurry fracture injection (SFI) technique has been proposed as an alternative waste disposal method. This technique is environmentally secure and permanent, and does not leave any future liabilities that must be risk-evaluated or priced. An entire waste stream comprising the ground solids and the waste water can be injected into deep and hydraulically secure target strata. No contamination of drinking water formations should occur. The method could be used to clean and reclaim landfills, oil pits, and granular waste dumps (Uddin et al., 2009).

TABLE 20.3 Parameters for SFI

Parameter	Parameter
Thickness of target formation	Thickness of confining layer
Permeability	Porosity
Depth of formation	Structural complexity
Lithological sequence	Reservoir strength
Groundwater source distance	Economic value of formation
Urban distance	Industrial distance
Impact on vegetation	Micro-climatic impact
Topographic changes	Transportation distance

SFI feasibility can be measured by using a two-tier screening method to evaluate its feasibility and to identify suitable target zones. Parameters that have been used to decide about the feasibility of the method are summarized in Table 20.3.

Descriptive values are associated with these parameters, e.g., for impact on vegetation: reduction, unchanged, increase. Numerical scores are associated with the descriptions, and the scores flow into a decision tree.

This provides a simple and transparent decision aid for evaluating SFI sites. A multi-criterion evaluation is done, taking into account various engineering and environmental parameters.

A stringent environmental and process control monitoring program should accompany the period of planning and operation in order to ensure optimal environmental protection, waste containment, and regulatory health, safety, and environmental compliance. The necessary preconditions for the SFI technique are (Uddin et al., 2009):

- Formations at shallow to moderate depths of 350–2000 m, far below any useable aquifers;
- A structurally simple formation, with no tectonic structures that could impair the sealing properties;
- The formation should be embedded by impermeable, thick layers;
- The thickness of the confinement zone above the containment zone should be at least than 20–30 m; and
- The containment formation should be porous and permeable.

The injection of the slurry is carried out in three phases, over a period of up to 12 h. Initially, a solids-free waste water is pumped to initiate or to propagate fractures. In the second phase, solid wastes are added in increasing amounts to the water. The content of the solids may reach 30% by volume. The maximum amount, of course, depends on the size and the nature of the solids and the geological characteristics of the formation. In the final phase pure water is pumped again in order to clean up the regions, i.e., the injection system, and the well itself (Uddin et al., 2009).

Use as Sealants

Waste chemicals generated by, for example, industrial plants, are often disposed of by injecting into disposal wells that penetrate subterranean zones (Reddy and Nguyen, 2005). Suitable subterranean zones for receiving such waste are separated by natural barriers from other zones that contain oil, gas, or water.

Unfortunately, many such chemicals are corrosive to the hydraulic cement in the wellbore. Also, any hydrogen sulfide or carbon dioxide gases that are generated or injected will form additional sources of degradation for the hydraulic cement.

Hydrogen sulfide corrodes the cement, and carbon dioxide reacts with calcium present in the cement at temperatures above 95°C (200°F). The high downhole temperatures accelerate the degradation process, meaning that the waste chemicals can leak into subterranean zones containing drinking water.

Sealing compositions are used to prevent this. For example, epoxy-based compositions can resist chemical degradation, and can be used to replace conventional hydraulic cements (Reddy and Nguyen, 2010). Epoxy-based compositions are highly resistant to chemical and thermal degradation, but their curing times are relatively short at 150°C (300°F) or higher (Reddy and Nguyen, 2005).

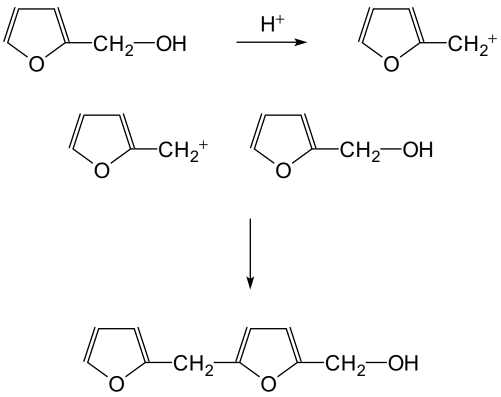

FIGURE 20.3 Acid catalyzed condensation of furfuryl alcohol.

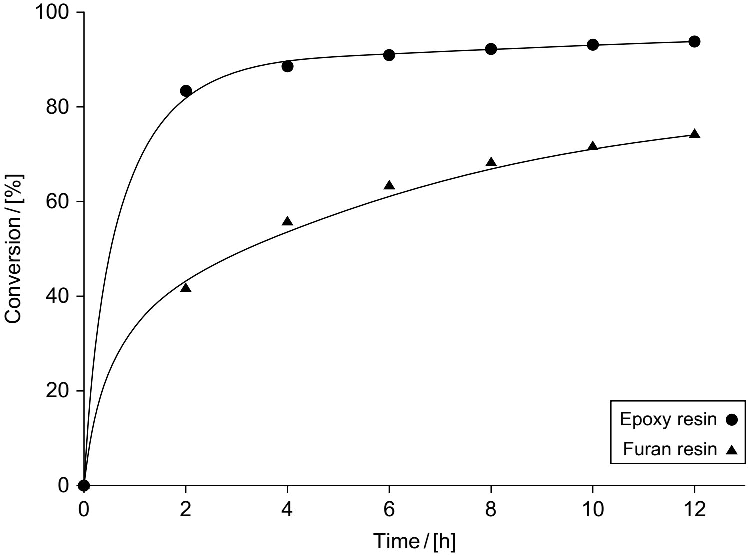

FIGURE 20.4 Curing behavior of compositions based on epoxy and furan (Reddy and Nguyen, 2005).

Alternative furan resins sealing compositions have therefore been developed. Furan resins in the so-called α-state are oligomers made from furfuryl alcohol and formaldehyde. When pumped down into the wellbore annulus, complete curing and crosslinking occurs.

The addition of a curing agent is necessary and a thinner or a diluent is added to adjust the viscosity. The curing of furan resins generally occurs by acid catalysis, c.f., Figure 20.3, so curing can be controlled via the adjustment of the pH of the system. For this reason, organic and inorganic acids are suitable curing agents, or for delayed curing, hydrolyzable esters additionally act as diluent. For pH adjustment, sodium bisulfate is used. Butyl acetate or furfuryl acetate are suitable hydrolyzable esters and diluents.

A coupling agent is added to enhance bonding to the interfaces, such as *N*-2-(aminoethyl)-3-aminopropyltrimethoxysilane, 3-glycidoxypropyltrimethoxysilane, and *N*-β-(aminoethyl)-γ-aminopropyl trimethoxysilane (Reddy and Nguyen, 2010).

The sealant compositions also need a filler, such as low-density microspheres, i.e., hollow spheres of glass. To adjust the mechanical properties, plasticizers can be added. These include diethyl phthalate, butyl benzyl phthalate, and di-(2-ethylhexyl) phthalate.

The curing behavior of compositions based on either epoxy or furan was tested at 163°C (325°F). The results are shown in Figure 20.4.

REFERENCES

Al-Ansary, M.S., Al-Tabbaa, A., 2007. Stabilisation/Solidification of synthetic petroleum drill cuttings. J. Hazard. Mater. 141 (2), 410–421.

ASTM (Standard test method for determining aerobic aquatic biodegradation of lubricants or their components), 2010. ASTM Standard, Book of Standards, Vol. 5.03 ASTM D 5864–05, ASTM International, West Conshohocken, PA.

Ayotamuno, M.J., Okparanma, R.N., Ogaji, S.O.T., Probert, S.D., 2007. Chromium removal from flocculation effluent of liquid-phase oil-based drill-cuttings using powdered activated carbon. Appl. Energy 84 (10), 1002–1011.

Bǻlint, V., Pinter, A., Mika, G., 1983. Process for the recovery of shale oil, heavy oil, kerogen or tar from their natural sources. US Patent 4 419 214, assigned to Orszagos Köolaj es Gǻzipari Troszt (Budapest, HU) and Budapesti Müszaki Egyetem (Budapest, HU), December 6, 1983.

Battersby, N.S., 2005. Biodegradable lubricants: What does *biodegradable* really mean? J. Synth. Lubr. 22 (1), 3–18.

Battersby, N.S., Fieldwick, P.A., Ablitt, T., Lee, S.A., Moys, G.R., 1994. The interpretation of CEC L-33-T-82 biodegradability test data. Chemosphere 28 (4), 787–800.

Battersby, N.S., Pack, S.E., Watkinson, R.J., 1992. A correlation between the biodegradability of oil products in the CEC L-33-T-82 and modified Sturm tests. Chemosphere 24 (12), 1989–2000.

Bennion, D.B., Thomas, F.B., Schulmeister, B.E., Imer, D., Shtepani, E., Becker, L., 2004. The phase behaviour of acid disposal gases and the potential adverse impact on injection or disposal operations. J. Can. Pet. Technol. 43 (5), 1–20. http://gisceu.net/PDF/U333.pdf.

Brandsma, M.G., 2004. Automatic validation of the offshore operators committee discharge model and application to predicting drilling solids accumulation on the sea floor. Environ. Model. Softw. 19 (7–8), 617–628.

Brandsma, M.G., Smith, J.P., 1999. Offshore operators committee mud and produced water discharge model–report and user guide, Production Research Report EPR.29PR.99. Exxon Production Research Company, Houston, TX.

Breuer, E., Stevenson, A.G., Howe, J.A., Carroll, J., Shimmield, G.B., 2004. Drill cutting accumulations in the Northern and Central North Sea: A review of environmental interactions and chemical fate. Mar. Pollut. Bull. 48 (1–2), 12–25.

CEN (European Standard EN 12457-1), 2002. Characterization of waste – leaching; compliance test for leaching of granular and sludges – part 1: One stage batch test at a liquid to solid ration of 2 l/kg with particle size below 4 mm (without or with size reduction). CEN – Committee for European Standardization, Brussels.

Cogliandro, J.A., Moses, J.M., 2009. Method and apparatus for capture and sequester of carbon dioxide and extraction of energy from large land masses during and after extraction of hydrocarbon fuels or contaminants using energy and critical fluids. US Patent 7 562 708, assigned to Raytheon Company, Waltham, MA, July 21, 2009.

Dhir, R.K., Csetenyi, L.J., Dyer, T.D., Smith, G.W., 2010. Cleaned oil-drill cuttings for use as filler in bituminous mixtures. Constr. Build. Mater. 24 (3), 322–325.

2007 Environmental Report, 2008. Environmental report. OLF The Norwegian Oil Industry Association, Stavanger. http://www.olf.no.

Eppig, C.P., Putnam, B.M., de Filippi, R.P., 1984. Apparatus for removing organic contaminants from inorganic-rich mineral solids. US Patent 4 434 028, assigned to Critical Fluid Systems, Inc., Cambridge, MA, February 28, 1984.

Filippov, L., Thomas, F., Filippova, I., Yvon, J., Morillon-Jeanmaire, A., 2009. Stabilization of NaCl-containing cuttings wastes in cement concrete by in situ formed mineral phases. J. Hazard. Mater. 171 (1–3), 731–738.

Haque, M.N., Kayyali, O.A., 1995. Free and water soluble chloride in concrete. Cem. Concr. Res. 25 (3), 531–542.

Hudgins, C., 1994. Chemical use in North Sea oil and gas E&P. J. Pet. Technol. 46 (1), 57–75.

Jorissen, F.J., Bicchi, E., Duchemin, G., Durrieu, J., Galgani, F., Cazes, L., et al., 2009. Impact of oil-based drill mud disposal on benthic foraminiferal assemblages on the continental margin off Angola. Deep Sea Res. Part II 56 (23), 2270–2291.

Leonard, S.A., Stegemann, J.A., 2010. Stabilization/Solidification of petroleum drill cuttings. J. Hazard. Mater. 174 (1–3), 463–472.

Mojtahid, M., Jorissen, F., Durrieu, J., Galgani, F., Howa, H., Redois, F., et al., 2006. Benthic foraminifera as bio-indicators of drill cutting disposal in tropical East Atlantic outer shelf environments. Mar. Micropaleontol. 61 (1–3), 58–75.

Mutyala, S., Fairbridge, C., Paré, J.R.J., Bélanger, J.M.R., Ng, S., Hawkins, R., 2010. Microwave applications to oil sands and petroleum: A review. Fuel Process. Technol. 91 (2), 127–135.

Orszulik, S.T. (Ed.), 2008. Environmental Technology in the Oil Industry. Springer Verlag, Dordrecht.

OSPAR, 2006. OSPAR report on discharges, spills and emissions from offshore oil and gas installations in 2004, Tech. Rep. 296, OSPAR Commission, London.

OSPAR, 2007. Convention for the protection of the marine environment of the north-east atlantic, Opar convention 1992, OSPAR Commission, London.

Pivel, M.A.G., Freitas, C.M.D.S., Comba, J.L.D., 2009. Modeling the discharge of cuttings and drilling fluids in a deep-water environment. Deep Sea Res. Part II 56 (1–2), 12–21.

Ramírez, A., Hagedoorn, S., Kramers, L., Wildenborg, T., Hendriks, C., 2010. Screening CO_2 storage options in The Netherlands. Int. J. Greenhouse Gas Contr. 4 (2), 367–380.

Reddy, B.R., Nguyen, P.D., 2005. Sealant compositions and methods of using the same to isolate a subterranean zone from a disposal well. US Patent 6 951 250, assigned to Halliburton Energy Services, Inc., Duncan, OK, October 4, 2005.

Reddy, B.R., Nguyen, P.D., 2010. Sealant compositions and methods of using the same to isolate a subterranean zone from a disposal well. US Patent 7 662 755, assigned to Halliburton Energy Services, Inc., Duncan, OK, February 16, 2010.

Reid, P.I., Craster, B., Crawshaw, J.P., Balson, T.G., 2003. Drilling fluid. US Patent 6 544 933, assigned to Schlumberger Technology Corporation, Sugar Land, TX, April 8, 2003.

Robinson, J.P., Kingman, S.W., Onobrakpeya, O., 2008. Microwave-assisted stripping of oil contaminated drill cuttings. J. Environ. Manage. 88 (2), 211–218.

Robinson, J.P., Kingman, S.W., Snape, C.E., Bradshaw, S.M., Bradley, M.S.A., Shang, H., et al., 2010. Scale-up and design of a continuous microwave treatment system for the processing of oil-contaminated drill cuttings. Chem. Eng. Res. Des. 88 (2), 146–154.

Rojas-Avelizapa, N.G., Roldán-Carrillo, T., Zegarra-Martínez, H., Muñoz-Colunga, A.M., Fernández-Linares, L.C., 2007. A field trial for an ex-situ bioremediation of a drilling mud-polluted site. Chemosphere 66 (9), 1595–1600.

Sadiq, R., Husain, T., 2005. A fuzzy-based methodology for an aggregative environmental risk assessment: A case study of drilling waste. Environ. Model. Softw. 20 (1), 33–46.

Schuppers, J.D., Holloway, S., May, F., Gerling, P., Bøe, R., Magnus, C., et al., 2003. Storage capacity and quality of hydrocarbon structures in the north sea and the aegean region, TNO Report NITG 02-020-B, Netherlands Institute of Applied Geoscience, Utrecht.

Shang, H., Snape, C.E., Kingman, S.W., Robinson, J.P., 2006. Microwave treatment of oil-contaminated north sea drill cuttings in a high power multimode cavity. Sep. Purif. Technol. 49 (1), 84–90.

Street, C.G., Guigard, S.E., 2009. Treatment of oil-based drilling waste using supercritical carbon dioxide. J. Can. Pet. Technol. 48 (6), 26–29.

Sturm, R.N., 1973. Biodegradability of nonionic surfactants: Screening test for predicting rate and ultimate biodegradation. J. Am. Oil Chem. Soc. 50 (5), 159–167.

Trannum, H.C., Nilsson, H.C., Schaanning, M.T., Øxnevad, S., 2010. Effects of sedimentation from water-based drill cuttings and natural sediment on benthic macrofaunal community structure and ecosystem processes. J. Exp. Mar. Biol. Ecol. 383 (2), 111–121.

Uddin, S., Oskui, R.P., Dusseault, M.B., Al Ghadban, A.N., 2009. Multi-criteria evaluation technique for SFI site identification of NORMS and oil industry waste disposal – Possibilities in Kuwait. J. Environ. Manage. 91 (1), 186–194.

Vickerd, M.A., Thring, R.W., Arocena, J.M., Heck, R.J., 2005. Identification of environmental effects of acid gas injection using X-Ray computed tomography. In: Canadian International Petroleum Conference. Petroleum Society of Canada, Calgary, Alberta, pp. 1–6.

TRADENAMES

TABLE 20.4 Tradenames in References

Tradename Description	Supplier
Sodasorb® Sodium calcium hydrate (Cogliandro and Moses, 2009)	W.R. Grace & Co.

Chapter 21

Dispersions, Emulsions, and Foams

There is no generic technical term common to these different subtopics. The admittedly clumsy term *small scale heterogenic materials* created by the author would not be adequate as a title for this chapter. Some authors use the term dispersion as a generic term that includes emulsions, c.f., Table 21.1. There is a difference between these three systems, however, depending on the size of the particle. If the particle size is in the range of one molecule, the dispersion is a solution. Between a nanometer and a micrometer, the particles are colloid-like, and above this range we are dealing with a suspension.

Emulsions, dispersions, and foams are related by their stability, preparation, and destruction. Monographs on the basic issues of these topics are available in the literature (Bibette et al., 2002; Ian D. Morrison, 2002; MacKay, 1994; Weaire and Hutzler, 1999).

TABLE 21.1 Examples for Dispersions [Dispersion (chemistry), 2010]

Dispersed	Continuous	Colloid	Suspension
Liquid	Gas	Fog	
Solid	Gas	Smoke	Dust
Gas	Liquid	Foam	Foam
Liquid	Liquid	Microemulsion	Emulsion
Solid	Liquid	Pigmented ink	Soil
Gas	Solid	Styrofoam	Sponge
Liquid	Solid	Gel	
Solid	Solid	Solid sol	Granite

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DISPERSIONS

In oil field applications, dispersions consist mostly of finely distributed solids in a liquid, but other physical states are sometimes encountered.

Dispersions have been reviewed in the literature (Bergenholtz et al., 2001; Endo and Kousaka, 1996; Tadros, 1993; Yaghmur and Glatter, 2009). Dispersants in oil field applications will be dealt with specifically in this section.

Dispersants

Also known as dispersing agents, dispersants are used to improve the separation of particles in order to prevent settling or clumping. Dispersants are used in many disciplines besides oil filed applications (Conley, 1996).

Dispersants usually contain surfactants, but the term *surfactant* is more general, since it also includes detergents, wetting agents, emulsifiers, and foaming agents. Let us say that dispersants are used to create slurries, whereas surfactants are used to create emulsions, but the border is blurred. In the oil industry, the term surfactant is used mostly for emulsifying agents for fluids, whereas dispersants are found in cement slurries, oil spill treating agents, and transport applications.

Aqueous Drilling Muds

Low Molecular Weight Dispersants

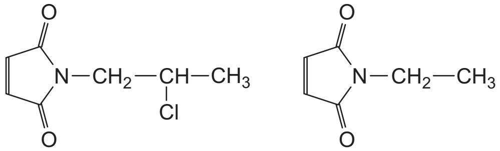
Complexes of tetravalent zirconium with ligands of organic acids such as citric, tartaric, malic, and lactic acid and a complex of aluminum and citric acid are suitable as dispersants (Burrafato and Carminati, 1994a,b, 1996; Burrafato et al., 1997), particularly for dispersing bentonite suspensions. The muds can be used at pH values ranging from slightly acidic to strongly basic.

Synthetic Polymers

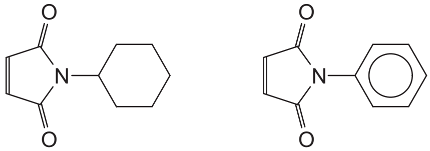
Polymers Containing Maleic Anhydride

A mixture of sulfonated styrene-maleic anhydride (MA) copolymer and polymers prepared from acrylic acid (AA) or acrylamide (AAm) and their derivatives (Hale and Lawson, 1988) act as dispersants for drilling fluids. The rheological characteristics of aqueous well drilling fluids are enhanced by incorporating small amounts of sulfonated styrene-itaconic acid copolymers (Hale and Rivers, 1988) and an AA or AAm polymer into the fluids (Hale, 1988).

Sulfonated styrene-maleimide copolymers are similarly active (Lawson and Hale, 1989). Maleimide, *N*-phenyl maleimide, *N*-ethyl maleimide, *N*-(2-chloropropyl) maleimide, and *N*-cyclohexyl maleimide, c.f., Figure 21.1 are used as monomers. *N*-aryl and substituted aryl maleimide monomers are preferred. The polymers are obtained by free radical polymerization in solution, in bulk, or by suspension.



N-(2-Chloropropyl) maleimide N-Ethyl maleimide



N-Cyclohexyl maleimide N-Phenyl maleimide

FIGURE 21.1 Imides.

In copolymers containing the styrene sulfonate moiety and MA units, the MA units can be functionalized with an alkyl amine (Peiffer et al., 1991, 1992a,b,c, 1993a,b). The water-soluble polymers impart enhanced deflocculation characteristics to the mud. Typically, the deflocculants are relatively low molecular weight polymers composed of styrene sodium sulfonate monomer, MA, as the anhydride or the diacid, and a zwitterionic functionalized MA. Typically the molar ratio of styrene sulfonate units to total MA units ranges from 3:1 to 1:1. The level of alkyl amine functionalization of the MA units is 75–100 mol-%. The molar concentrations of sulfonate and zwitterionic units are not necessarily equivalent, because the deflocculation properties of these water-soluble polymers can be controlled via changes in their ratio.

Alternating 1:1 copolymers of sodium methallylsulfonate and MA are useful as water-soluble dispersants (Grey, 1993). The copolymers are produced by free radical polymerization in acetic acid solution. Because of their high solubility in water and the high proportion of sulfonate salt functional groups, these alternating polymers are useful as dispersing agents in water-based drilling fluids.

Acrylics

Low molecular weight copolymers of AA and salts of vinyl sulfonic acid have been described as dispersants and high-temperature deflocculants for the stabilization of the rheological properties of aqueous, clay-based drilling fluids subjected to high levels of calcium ion contamination (Portnoy, 1986, 1987). Divalent ions, such as calcium or magnesium, can cause uncontrolled thickening of the mud and thus large increases in filtration times of fluids from the mud into permeable formations.

The mud can flocculate at high temperatures, which increases the thickening effects of certain chemical contaminants and deactivates or destroys many mud thinners.

Polyacrylic acid or its salt with a molecular weight of 1.5–5 kDalton, and a polydispersity of 1.05–1.45, has been described as a dispersant for a drilling or packer fluid (Farrar et al., 1992).

Copolymers or terpolymers of AA, which contain from 5–50 mol-% of sulfoethyl acrylamide, AAm and sulfoethyl acrylamide, ethyl acrylate and sulfoethyl acrylamide, AAm and sulfophenyl acrylamide, and AAm and sulfomethyl acrylamide, are claimed to be calcium-tolerant deflocculants for drilling fluids (Giddings and Fong, 1988). In general, 0.1–2 lb of polymer per barrel of drilling fluid is sufficient to prevent the flocculation of the additives.

A salt of a polymer or copolymer of acrylic or methacrylic acid, in which the acid is neutralized with alkanolamines, alkyl amines, or lithium salts (Garvey et al., 1987), is suitable as a dispersing agent.

Polymers with Amine Sulfide Terminal Moieties

Amine sulfide terminal moieties can be added to vinyl polymers by using aminethiols as chain transfer agents in aqueous radical polymerization (McCallum and Weinstein, 1994). The polymers are useful as mineral dispersants, or as water treatment additives for boiler waters, cooling towers, reverse osmosis applications, and geothermal processes in oil wells, as detergent additives acting as builders, antifilming agents, dispersants, sequestering agents, and encrustation inhibitors.

Polycarboxylates

Polycarboxylated polyalkoxylates and their sulfate derivatives may be prepared by reacting an ethoxylated or propoxylated alcohol with a water-soluble, alkali or earth alkali metal salt of an unsaturated carboxylic acid (Chadwick and Phillips, 1995). The reaction occurs in aqueous solution in the presence of a free radical initiator and gives products in enhanced yield and reduced impurity levels, compared with the essentially anhydrous reactions with free carboxylic acids. The method produces solutions that are clear on neutralization, remain clear and homogeneous on dilution, and are useful as cleaning agents in drilling and other oil field operations.

Modified Natural Polymers

Modified Polysaccharides

Phosphated, oxidized starch with a molecular weight of 1.5–40 kDalton, and a degree of carboxyl substitution of 0.30 to 0.96, is useful as a dispersant for drilling fluids (Just and Nickol, 1989).

Physical mixtures of reversibly crosslinked and uncrosslinked hydrocolloid compositions and hydrocolloids show improved dispersion properties (Szablikowski et al., 1995).

Sulfonated Asphalt

Sulfonated asphalt can be produced as follows (Rooney et al., 1988):

1. Heating an asphaltic material;
2. Mixing the asphalt with a solvent, such as hexane;
3. Sulfonating the asphalt with a liquid sulfonating agent, such as liquid sulfur trioxide;
4. Neutralizing the sulfonic acids with a basic neutralizing agent, such as sodium hydroxide;
5. Separating the solvent from the sulfonated asphalt;
6. Recovering the evaporated solvent for reuse; and
7. Drying the separated, sulfonated asphalt by passing it through a drum dryer.

This is a batch-type process in which the rates of flow of the solvent, the asphaltic material, the sulfonating agent, and the neutralizing agent and the periods of time before withdrawal of the sulfonic acids and the sulfonated asphalt are coordinated according to a pre-determined time cycle. The dried, sulfonated asphalt can then be used in the preparation of aqueous, oil-based, emulsion drilling fluids. These fluids have excellent rheological properties, such as viscosity and gel strength, and they exhibit a low rate of filtration or fluid loss.

Humic Acids

Coal with a mean particle size of less than 3 mm is slurried with water and then oxidized with oxygen or mixtures of oxygen and air at temperatures ranging from 100–300°C, at partial oxygen pressures ranging from 0.1–10 MPa, and reaction periods ranging from 5–600 min (Cronje, 1989). In the absence of catalysts, such as alkaline bases, the main products of oxidation are humic acids. These humic acids are not dissolved because the pH of this slurry is in the range of 4 to 9. Small amounts of fulvic acids are formed, and these are soluble in the water of the slurry. The coal-derived humic acids find applications as drilling fluid dispersants and viscosity control agents, whereas the fulvic acids may be used to produce plasticizers and petrochemicals.

Cement

Dispersants are used in well cement slurries to prevent high initial cement slurry viscosities and friction losses when the slurries are pumped. For this application, the dispersant should be water-soluble.

Polymelamine Sulfonate and Hydroxyethyl cellulose

Sodium polymelamine sulfonate and hydroxyethyl cellulose may be used as dispersing agents for oil field cement slurries containing microsilica (Baret and Drecq, 1989a,b, 1990). Melamine is shown in Figure 21.2. The cement slurries may contain up to 30% of microsilica (i.e., colloidal silica), silica

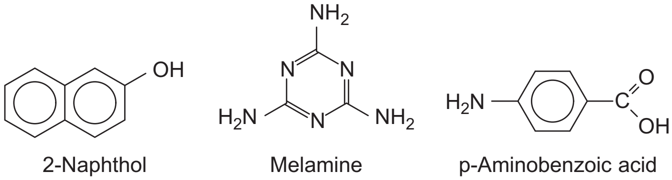


FIGURE 21.2 2-Naphthol, melamine, and *p*-aminobenzoic acid.

flour, diatomaceous earth, or fly ash with particle dimensions between 0.05 and 5 μ, together with conventional additives, such as antifoaming agents and set retarding agents, etc.

Polyethyleneimine Phosphonate Derivatives

In oil and gas well cementing operations, polyethyleneimine phosphonate-derivative dispersants enhance the flow behavior of the cement slurry (Crema et al., 1991). The slurry can be pumped in turbulent flow, thereby forming a bond between the well casing and the rock formation.

Acetone Formaldehyde Cyanide Resins

An aqueous solution of acetone and sodium cyanide is condensed by adding formaldehyde at 60°C. A resin with nitrile groups is obtained. A similar product can be obtained with sodium sulfite. These products are dispersants for cements (Eoff, 1994a,b). The dispersant properties of the composition can be enhanced by further reacting the composition with a hydroxide.

Napthalenosulfonic Acid Formaldehyde Condensates

The magnesium salt from the condensation of napthalenosulfonic acid and formaldehyde (Hendriks, 1989a,b) is yet another dispersing agent. The additive eliminates free water, even at low temperatures and in particular with those cements most susceptible to this phenomenon.

Sulfo-alkylated Naphthols

Sulfo-alkylated naphthol compounds are effective as dispersants in aqueous cement slurries. The compounds can also be applied in an admixture with water-soluble inorganic compounds of chromium to provide additives with increased overall effectiveness. Sodium chromate or ammonium dichromate are particularly suitable. α-Naphthol is reacted in an alkaline aqueous medium with formaldehyde to create condensation products. The aldehyde can be reacted with bisulfite to produce sulfoalkylated products (Patel and Stephens, 1991, 1990).

Azolignosulfonate

An azolignosulfonate formed from the coupling of a diazonium salt, made from sulfanilic acid or *p*-aminobenzoic acid, and a lignosulfonate has been reported as a cement dispersant (Detroit, 1989). The dispersant can reduce the aqueous cement slurry viscosity, or thin the cement composition to make it pumpable without significantly retarding the set time. The azo structure is formed by coupling lignosulfonate with diazonium salt. It masks the retardation effect of the phenolic group in the lignosulfonate molecule.

Polymers from Allyloxybenzenesulfonate

Water-soluble polymers of allyloxybenzenesulfonate monomers can be used as dispersants in drilling fluids, in treating boiler waters in steamflooding, and as plasticizers in cement slurries (Leighton and Sanders, 1988, 1990). The preferable molecular weight range is 1–500 kDalton.

Sulfonated Isobutylene Maleic Anhydride Copolymer

A dispersant controls the rheologic properties of and enhances the filtrate control of the fluids that contain it. The dispersant is a polymer, derived from monomeric residues, including low molecular weight olefins that may be sulfonated or phosphonated, unsaturated dicarboxylic acids, ethylenically unsaturated anhydrides, unsaturated aliphatic monocarboxylic acids, polyvinyl alcohols (PVAs) and diols, and sulfonated or phosphonated styrene. The sulfonic acid, phosphonic acid, and carboxylic acid groups on the polymers may be present in a neutralized form, as alkali metal or ammonium salts (Bloys et al., 1993, 1994).

Miscellaneous Dispersants

A nonpolluting dispersing agent for drilling fluids (Bouchut et al., 1989, 1990, 1992) has been described, based on polymers or copolymers of unsaturated acids, such as acrylic acid or methacrylic acid, with suitable counter ions.

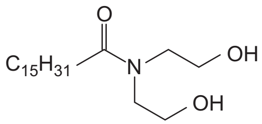
Sulfur

The deposition of elemental sulfur in conduits through which a sulfur-containing gas has flowed can be reduced by providing a sulfur dispersant. The dispersant is an adduct of a primary alcohol and epichlorohydrin, mixed with an aliphatic amine component (Emmons, 1993).

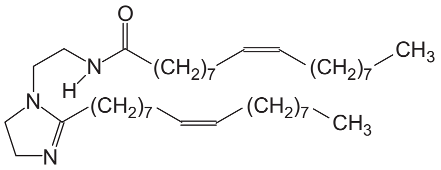
Asphalts

Certain petroleum products, including heavy crude and residual fuel oils, are rich in asphaltenes, whose presence can lead to various recovery and transportation problems. These are due to increased viscosity, formation of stable emulsions, fouling, and corrosion (Banavali et al., 2010).

Certain alkyl-substituted phenol-formaldehyde resins can act as dispersants for asphalts and asphaltenes in crude oils (Stephenson and Kaplan, 1991), keep asphalt and asphaltenes in dispersion, and so inhibit fouling, precipitation, and buildup in the equipment. Asphaltenes in petroleum products can be also stabilized with amine-chelate complexes. Ethylene diamine tetraacetic acid, a fatty



Fatty acid amide



Imidazoline amide

FIGURE 21.3 Asphaltene dispersants (Banavali et al., 2010).

acid amide, and an imidazoline amide compound (Banavali et al., 2010) is reported to do this. The compounds are shown in Figure 21.3.

Oil Spill

Dispersants are sprayed onto oil slicks in order to remove oil from the sea surface and disperse it into the aqueous phase. They can be used under harsh weather conditions, when mechanical collection may not be possible. The dispersion process accelerates the degradation of the oil by natural processes (Lessard and DeMarco, 2000), but consideration must be given to the impact of the dispersed oil on sub-surface ecosystems, such as fish stocks and coral. In addition, it is essential that the limitations of dispersants are recognized so that they will be used effectively (Chapman et al., 2007).

Ethoxylated sorbitol oleate and mixtures are suitable for emulsifying or dispersing spilled petroleum products in either terrestrial or marine environments (Riley, 1998).

A fully integrated and effective response to an oil or chemical spill at sea must include a well-planned and executed post-incident assessment of environmental contamination and damage. Case studies of the use of oil spill dispersants haves been reported (Kirby and Law, 2010; Lessard and DeMarco, 2000).

EMULSIONS

Emulsions play an important role in fluids used for oil field applications, particularly drilling and treatment fluids. Here the emulsions are known as oil-based drilling muds (OBMs) or water-based drilling muds, although these essentially are emulsions from the view of physics.

Oil field emulsions are sometimes classified based on their degree of kinetic stability (Kokal, 2006; Kokal and Wingrove, 2000):

- Loose emulsions: Those that will separate within a few minutes. The separated water is sometimes referred to as free water.

- Medium emulsions: They will separate in approximately ten minutes.
- Tight emulsions: They will separate within hours, days, or even weeks, and even then, not completely.

Emulsions are also classified by droplet size. When the dispersed droplets are larger than 0.1 μ, the emulsion is a macroemulsion (Kokal, 2006).

Thermodynamically an emulsion is an unstable system, because there is a natural tendency for a liquid-liquid system to separate, and reduce its interfacial area and thus its interfacial energy (Kokal and Wingrove, 2000).

A second class of emulsions is known as a microemulsion. These are formed spontaneously when two immiscible phases with extremely low interfacial energy are brought together. Microemulsions have droplet sizes of less than 10 nm, and are thermodynamically stable. They differ fundamentally from macroemulsions in their formation and stability.

Oil-in-water Emulsions – Invert Emulsions

Invert emulsions have an oleaginous continuous phase, and a discontinuous phase that is a fluid, which is at least partially immiscible in the oleaginous fluid.

Invert emulsions may have desirable suspension properties for particulates like drill cuttings. As such, they can easily be weighted if desired. They can be reversed to regular emulsions by changing the pH or by protonating the surfactant (Taylor et al., 2009).

If a residual amount of an invert emulsion remains in a wellbore, it can be reversed to a regular emulsion to clean it from the wellbore. Invert emulsions can be also used, where the organic phase is gelled. For example, diesel can be gelled with decanephosphonic acid monoethyl ester and a Fe^{3+} activator (Taylor et al., 2009).

Polymers are often used to increase the viscosity of an aqueous fluid. The polymer should interact with this fluid as it should show a tendency to hydrate. Microemulsions may be helpful to achieve this objective (Jones and Wentzler, 2008).

Breakers

Polymerized linseed oil reacted with diethanolamine has been proposed as a breaker for invert emulsions (Audibert-Hayet et al., 2007). Breakers are described in more detail in Chapter 17.

Drilling Fluid systems

Invert emulsion fluid systems tend to perform well in shale inhibition, borehole stability, and lubricity, but they have a high risk of loss of circulation (Xiang, 2010). Latex additives can counterbalance this drawback, but since water must be added, an oil base drilling fluid system becomes an unbalanced invert emulsion system with different rheological properties. They can be rebalanced, either in the field or offsite.

Some special formulations avoid this drawback, in which the latex particles are dispersed in the emulsified aqueous phase as opposed to the oil base continuous phase. In fact, one of the advantages of invert emulsion fluids is that they have at least some of the benefits of having an aqueous phase without requiring it to be in direct contact with the borehole wall (Xiang, 2010).

Drill Cuttings Removal

It is often necessary to drill a wellbore through geological formations whose constituent materials swell or disintegrate on contact with water. In such cases an OBM is used, that is, a fluid in which the liquid phase consists of oil, or of water-in-oil emulsions, which are known in the art as invert emulsion fluids (Sawdon and Ballard, 1997).

Invert emulsions of mud have many advantages, but these must be weighed against the environmental problems they incur, in particular for offshore drilling. The mud itself is always recycled, but the cuttings have to be removed after separating them on the surface. This is done using mechanical separators (Monfreux-Gaillard et al., 2007), such as vibratory screens, hydrocyclones, and centrifuges.

Regulations permit the discharge of cuttings into the sea only if they contain less than 1% of organic substances. Invert emulsion contain much more than this because the film of the mud which contaminates the cuttings cannot be removed by using mechanical techniques. It has been proposed to wash the cuttings before discharging them to the sea. However, the surfactants added to stabilize the invert emulsion are so effective that the washing water itself is emulsified in the mud, so the oil is dispersed in the washing water. Also both the volume and the viscosity of the mud increase (Monfreux-Gaillard et al., 2007).

The addition of detergents to destabilize such emulsions is largely ineffective, and the detergents themselves cause environmental problems (Monfreux-Gaillard et al., 2007). The combination of a non-ionic alkoxylated surfactant and an anionic sulfonate surfactant yields a stable invert emulsion, which is surprising, because neither of these agents can do this when used alone. The stable invert emulsion will rapidly and completely destabilize and disperse by simply mixing with low salinity water.

In this procedure the cuttings are separated from the wellbore fluid and then washed with a wash water until the emulsion destabilizes (Sawdon and Ballard, 1997).

For copolymers with polyoxyethylene grafts the stability of a direct oil-in-water emulsion increases with the proportion of grafts and with their length. Hydrophobically modified polyacrylates, with a hydrophilic backbone modified with long chain alkyl acrylates or alkyl methacrylates, can be used as surfactants

(Lochhead and Rulison, 1994). Such emulsions can be destabilized by adding an electrolyte.

A statistical copolymer from 2-acrylamido-2-methyl-1-propane sulfonic acid acrylate can be modified by amidification with *n*-alkylamines, such as di-*n*-dodecylamine (Monfreux-Gaillard et al., 2007). Depending on the degree of modification, the polymers are effective as stabilizers for direct or invert emulsions. The emulsion can be destabilized or reversed by reducing the salinity of the aqueous phase or neutralizing the acid. This phenomenon is used in fluids employed for petroleum wells, in particular drilling, fracturing, acidizing, or completion fluids (Monfreux-Gaillard et al., 2007).

Thinners may be added to invert emulsions. Anionic surfactants are used, particularly from the group of fatty alcohol sulfates, such as oxethylated fatty acids (Mueller et al., 2009).

Water-in-water Emulsions

When two or more different water-soluble polymers are dissolved together in an aqueous medium, the system sometimes phase separates into distinct regions, particularly, if they are water-soluble but thermodynamically incompatible. These emulsions are termed water-in-water emulsions, or aqueous two-phase systems (Sullivan et al., 2010).

In the food industry, such fluids are used to create polymer solutions that mimic the properties of fat globules, and in the biomedical industry, they are exploited as separation media for proteins, enzymes, and other macromolecules.

Such systems are also of interest in oil field applications. They can be used to create low viscosity, pre-hydrated, concentrated mixtures to allow the rapid mixing of the polymers at a well site to give a low viscosity polymer fluid.

Solutions of guar and hydroxypropyl cellulose (HPC) form aqueous, phase-separated solutions over a range of polymer concentrations. A phase-separated mixture can be formed by simultaneously dissolving dry guar and dry HPC in a blender. After continued stirring, the solution is allowed to rest to achieve phase separation, then, the solution can be gently stirred to remix the guar-rich and HPC-rich phases. The two-phase polymer solution can be activated to become an elastic gel by thermal treatment, or by changing the ionic strength (Sullivan et al., 2010). This behavior can be used for zone isolation.

Oil-in-water-in-oil Emulsions

Oil-in-water-in-oil emulsions can be used as a drive fluid for enhanced oil recovery operations or as a lubrication fluid. Such emulsions exhibit better shear stability and shear thinning characteristics than water-in-oil emulsions. An oil-in-water-in-oil emulsion is prepared from an oil-in-water emulsion that is subsequently dispersed in a second oil (Varadaraj, 2010). The second oil may contain a stabilizer, i.e., micron to sub-micron sized solid particles, naphthenic acids, and asphaltenes.

Microemulsions

A microemulsion is a thermodynamically stable fluid that differs from kinetically stable emulsions, which will separate into oil and water over time. The particle size of microemulsions ranges from about 10–300 nm. Because of this small particle size, microemulsions appear as clear or translucent solutions. The particle size is measured by dynamic light scattering or neutron scattering. Microemulsions have ultra-low interfacial tension (IFT) between the water phase and the oil phase.

Water-in-oil microemulsions have been known to deliver water-soluble oil field chemicals into subterranean rock formations. Oil-in-alcohol microemulsions containing corrosion inhibitors are also used in antifreeze compositions (Yang and Jovancicevic, 2009).

Microemulsions can be used to deliver a wide variety of oil-soluble chemicals, including corrosion inhibitors, asphaltene inhibitors, and scale inhibitors. They require less organic solvent, and since the microemulsion increases the dispersibility of the chemical into the fluids, the efficiency of the particular chemical is increased (Yang and Jovancicevic, 2009).

Microemulsions may be broken by a variety of mechanisms, including use of chemicals or by temperature changes, but the most simple way is by dilution.

An example of a microemulsion that caries a corrosion inhibitor is given in Table 21.2. This formulation can easily be diluted to the water phase. If the amount of toluene is increased in favor of water, a microemulsion is obtained that can be diluted by a hydrocarbon solvent. Still other examples are given elsewhere (Yang and Jovancicevic, 2009).

Solids-stabilized emulsion

Emulsions can be stabilized using partially oleophilic undissolved solid particles (Bragg, 2000). Three-phase emulsions that are stabilized with solids have

TABLE 21.2 Microemulsion with Corrosion Inhibitor (Yang and Jovancicevic, 2009)

Component	Amount/[%]
Toluene	2
Oleic imidazoline (corrosion inhibitor)	4
Oleic acid (corrosion inhibitor)	4
Dodecyl benzene sulfonic acid	2
Ethanolamine	2
Butyl alcohol	20
Water	66

been reviewed (Menon and Wasan, 1988), and the phenomenon of oil loss due to entrainment in emulsion sludge layers has been assessed. A semi-empirical approach has suggested for estimating the loss of oil.

The solid particles may be either indigenous to the formation or obtained from outside it. Non-formation particles include clays, quartz, feldspar, gypsum, coal dust, asphaltenes, and polymers. Preferably, however, the particles contain small amounts of an ionic compound, and exhibit a composite irregular shape (Bragg, 2000). The solid particles should have either some oleophilic character for making an oil-external emulsion or some hydrophilic character for making a water-external emulsion. This is important to ensure that the particles can be wetted by the external continuous phase that holds the internal, discontinuous phase.

The oleophilic or hydrophilic character may be an inherent characteristic of the solid particles or it can be acquired by chemical treatment. For example, oleophilic fumed silicas, e.g., Aerosil™ R972 or CAB-O-SIL™ consist of small spheres of fumed silica that have been treated with organosilanes or organosilazanes to make the surfaces oleophilic, and are effective in stabilizing many crude oil emulsions. Such particles are extremely small, with diameters of about 10–20 nm, although the primary particles interact to form larger aggregates. These silicas are effective at concentrations of 0.5–20 $\mathrm{g\,l^{-1}}$.

Figure 21.4 shows the viscosity of an emulsion that contains solid particles at a shear rate of 75 $\mathrm{s^{-1}}$, as a function of the water content. The oil in the emulsion can be pretreated with a sulfonating agent prior to emulsification, which enhances its ability to make a solids-stabilized water-in-oil emulsion

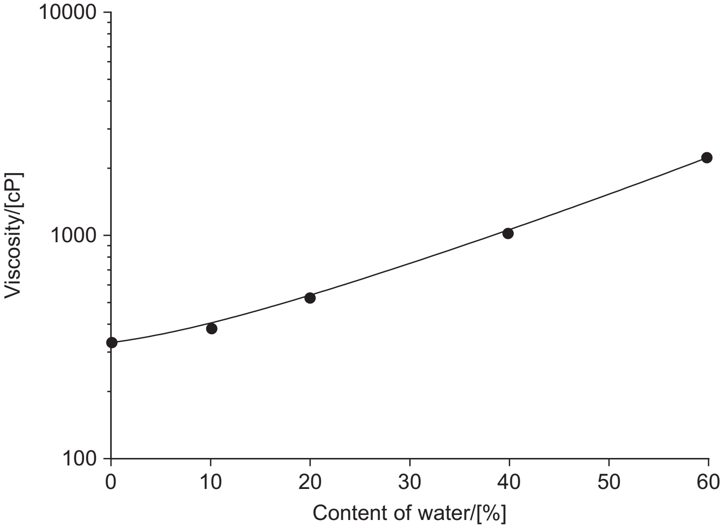


FIGURE 21.4 Viscosity viz. water content.

TABLE 21.3 Effect of Various Methods of Pretreatment of Crude Oil (Varadaraj et al., 2007)

Method	Saturated	Unsaturated	NSO[a]	Asphaltene
	Compounds/[%]			
Untreated crude oil	35.4	39.8	15.4	9.4
Dye sensitized photochemically treated	34.2	26.6	26.6	12.7
Photochemically treated	31.1	20.5	30.7	17.9
Thermally air oxidized	34.2	19.3	33.6	13.0
Biologically oxidized	32.4	39.8	18.4	9.4

a) Polycondensed aromatic benzene units with oxygen, nitrogen, and sulfur (NSO-compounds)

(Varadaraj et al., 2004). A specific procedure for the sulfonation of both the solids and the oil has been disclosed:

Preparation 21–1: The crude oil and the solid particles are cosulfonated. 12 g of crude oil and solids comprised of 0.06 g of 2-methylbenzyl tallow intercalated monomorillonite and 0.12 g of asphalt are stirred at 50°C for 72 hours. Subsequently, concentrated sulfuric acid is added at 3 parts per 100 parts of oil at 50°C during 24 hours. ■

In a variant of the above method, the sulfonated crude oil can be combined with a maleic acid-grafted copolymer of ethylene and propylene (Varadaraj et al., 2007).

Alternatively, photochemical treatment of the oil has been examined (Varadaraj et al., 2007), where a bentonite clay gel is mixed with the crude oil before photochemical treatment. In a dye-sensitized photochemical treatment process, the crude oil is first mixed with Rhodamine-B, a red dye that increases the quantum efficiency of the photo-chemical conversion of oil into oxidized products.

Table 21.3, shows the various methods of crude oil pretreatment.

Biotreated Emulsion

Biotreating the oil prior to emulsification is also possible, using oil degrading microbes. Water-in-oil emulsions made from a biotreated oil exhibit enhanced stability (Varadaraj et al., 2007).

Preparation 21–2: The oil is placed into a bioreactor biotreatment with water in a 10- to 100-fold excess. Oil-degrading microbes, e.g., inoculum are then added to the reactor. Inoculum is a culture of microbes. The concentration of microbes in the inoculum can be measured by colony forming units. The oil degrading microbes can be obtained from an oil waste water treatment facility.

Nutrients preferably containing nitrogen and phosporus can be provided to feed the microbes. The bioreactor is purged with air or oxygen at a temperature of 20–70°C.

The biotreated oil can then be separated from the aqueous phase prior to forming a water-in-oil emulsion with the biotreated oil. However, it is preferred to form an emulsion using both the biotreated oil and the aqueous phase of the bioreaction as the aqueous phase contains components that will help further enhance the stability of the resulting water-in-oil emulsion. ■

It is believed that biotreatment enhances the stability of a water-in-oil emulsion by the following mechanisms (Varadaraj et al., 2007):

- Some of the aliphatic components of the oil are oxidized, and polar ketone or acid functionalities are introduced into the aliphatic chains. Organo sulfur compounds are also susceptible to oxidization to the corresponding sulfoxides. The oxygenated compounds are more surface active than the aliphatic components themselves, and thus contribute to improving the stability of the water-in-oil emulsion.
- If naphthenic acids are present as salts of divalent cations like calcium, biooxidation is likely to convert them to decarboxylated naphthenic hydrocarbons or lower carbon number naphthenic acids and the corresponding metal oxide. These constituents serve to enhance the stability of the water-in-oil emulsion.
- In the process of biotreating oil, the aqueous phase of the bioreaction also undergoes substantial changes. After completion, the aqueous phase is a dispersion of biosurfactants, i.e., rhammanolipids produced by the microbes, and dead microbe cells. These components act synergistically to enhance the stability of water-in-oil emulsions. The aqueous phase of the bioreaction may therefore be used to make the water-in-oil emulsion, and serve to further enhance the stability of the resulting emulsion.

Shale Inhibition

Shale stabilization is necessary in order to prevent bit balling and sloughing off of shale, which can be achieved by using a high concentration of an inorganic salt in the dispersed phase.

Clay chemistry has shown that cationic base exchange with the negatively charged clay minerals commonly found in shale formations limits their ability to hydrate, soften, and swell, thereby making them more stable in the presence of water-based fluids and reducing or preventing screen blinding. Unfortunately, concentrated solutions of inorganic salts are toxic.

Organic amines, including substituted or unsubstituted triethanol amines, diaminocyclohexanes, and hexamethylene diamines have been proposed as alternative shale inhibitors (Summerhill et al., 2006).

Transportation

Water-external emulsions can be transported in pipelines to improve the net flow rates of oil (Bragg and Varadaraj, 2006). The percentage of oil in water may vary between 70–80%. The oil is combined with an aqueous solution comprising water, a pH enhancing agent, and solid particles and mixed until the solids-stabilized oil-in-water emulsion is formed. The pH of the resulting oil-in-water emulsion should be at 7.5–10.

The inner walls of the pipe should first be coated with a wettability altering agent to make them water-wet, which cases the transport of the oil-in-water emulsion.

High-oil content, solids-stabilized, oil-in-water emulsions can therefore be easily transported through pipelines using flow regimes of either self-lubricating core annular flow, or as uniform, lower-viscosity water-external emulsions (Bragg and Varadaraj, 2006). In core annular flow, the formation of a low-viscosity annulus near the pipe wall reduces pressure drop further.

The viscosity of water, i.e., the continuous phase, is not greatly affected by temperature, hence, neither is the viscosity of a solids-stabilized oil-in-water emulsions, meaning they do not have to be heated to high temperatures to maintain an acceptably low viscosity for economical transport.

In these systems the oil phase does not tend to wet the steel so they have less tendency to wet or foul the pipeline walls (Bragg and Varadaraj, 2006).

Acid-rich Oils

Crude oils produced from the North Sea, the Far East, and Western Africa exhibit high total acid numbers, and high concentrations of naphthenic acids (Ubbels, 2010). Such crude oils may form calcium naphthenate precipitates or naphthenate stabilized emulsions.

Naphthenates can act as natural surfactants leading either to stabilized emulsions or solid deposits following complexation with certain cations present in the aqueous phase. Naphthenate inhibitors include strong acids that protonate the rather weak naphthenic acids (Ubbels, 2010).

Characterization of Emulsions

Hansen Solubility Parameters

Hansen solubility parameters may be useful for preparing emulsions and to estimate their miscibility (Hansen, 1967, 2007). They are an extension of the Hildebrand solubility parameters (Burke, 1984).

For a certain molecule, three Hansen parameters are needed, which have a physical dimension as $\mathrm{Pa}^{1/2}$, which is an energy density.

The distance Ra of two solvents 1 and 2, $\Delta\delta_i = \delta_{i,1} - \delta_{i,2}$ between the Hansen parameters is:

$$Ra^2 = 4(\Delta\delta_d)^2 + (\Delta\delta_p)^2 + (\Delta\delta_h)^2 \qquad (21.1)$$

δ_d is the energy density from dispersion bonds between molecules, δ_p is the energy from dipolar intermolecular force between molecules, and δ_h is the energy from hydrogen bonds between molecules.

Further, a radius of interaction R_0 is needed. A pair of compounds is soluble, if:

$$\frac{Ra}{R_0} > 1 \tag{21.2}$$

The solubility parameter of a liquid mixture is proportional to the amount of each liquid assuming the two liquids are completely miscible.

The solubility parameters can be determined by measurement of the solubility, similar to the Hildebrand parameters. Several solvents are chosen and trials of the solubility of a substance with unknown Hansen solubility parameters are performed. They can also be determined by inverse gas chromatography (Adamska et al., 2008).

Solubility parameters are compiled in Perry's standard tables (Speight, 2004), and examples of the use of the Hansen solubility parameters in petroleum applications are presented elsewhere (Chakrabarty, 2010; Frost et al., 2008; Reese and Rey, 2009).

Micro-percolation Test

Unstable emulsions will eventually form two separate macroscopic phases of oil emulsion and water. The emulsion stability can be assessed by its flow through porous media in a rapid and convenient assay (Varadaraj et al., 2007). An emulsion sample that would pass completely through porous media can be centrifuged into two distinct phases, and the respective volumes used as a measure of the stability of an emulsion. The greater the proportion of water that forms a clear phase after this treatment, the more unstable the emulsion.

Brine-breakout is defined as the fraction of the water or brine present in the emulsion and forming a distinct, separate, aqueous phase. The value ranges between one, indicating completely unstable, and zero, maximally stable. Details of the procedure have been presented elsewhere (Varadaraj et al., 2007).

Field Bottle Test

Oil field emulsions are often characterized using the field bottle test (Poindexter and Marsh, 2009), which has been used since the 1950s (Kirkpatrick and Alice, 1960). Experimental details of this test have been described (Leopold, 1992; Manning and Thompson, 1995), but it is not standardized (Kokal, 2005).

Procedure 21–3: Manning and Thompson have given the following procedure (Manning and Thompson, 1995). Put the sample in a 5 gal can with a screw cap. Drain off all free water. Shake the can and determine sediments and water of the emulsion.

Number 8 precipitation bottles. Add 100 ml of emulsion, normal emulsion breaker, and reverse emulsion breakers to each bottle. Heat to the treating temperature, place the bottles into a shaker and shake for 3 min. Place into a thermostat and start the timer. After the required time, read the water breakout in each bottle. With a syringe remove some of the oil. Analyze the oil. ■

By coupling the data obtained from field bottle test and data that characterize the samples themselves, it is possible to gain insight into the factors that describe and are responsible for the stability of the emulsion.

Since many variables flow into the analysis, the method is considered as multivariate. A broad spectrum of oils has been characterized using 18 different parameters, and statistical analysis of the data sets has been performed. It has been found that the solid content, rather than the asphaltene content or any other crude oil parameter, is the best single predictor for the emulsion stability. Statistical analysis reveals that the stability of an emulsion is most aptly described using several crude oil parameters, in contrast to one single factor (Poindexter et al., 2006; Poindexter and Lindemuth, 2004).

Separation Index

The emulsion separation index has been developed to characterize emulsions in order to select and screen demulsifiers.

The fraction of the total water separated in a regular bottle test using different demulsifier dosages is averaged to determine a separation index, which ranges from zero (with no separation) up to 100% indicating full separation. The conditions of test must be given, in particular the temperature and the nature of demulsifier system. Details of how to conduct a separation test have been given by Kokal (2006).

Procedure 21–4: The samples are remixed with a standard bottle shaker for 1 min. The sample is then added to 100 ml standard centrifuge tubes, which are placed into a water bath to reach the desired temperature for 30 min. Then, the chemical to be tested (demulsifier) is added to the centrifuge tubes and the tubes are shaken and again placed in the water bath. After some predefined time intervals, e.g., 5, 10, 15, 20 min, the amount of water separated is controlled. After 20 min the tubes are centrifuged and the final amount of water separated is measured. ■

The emulsion separation index I is then calculated by:

$$I = \frac{\sum w}{w_f n} \times 100 \qquad (21.3)$$

Here, w is the water separation at a given demulsifier concentration, as the percentage of basic sediment and water after a certain time interval, i.e., it runs from 5, 10, 15, 20 min and final w_f. n is the number of readings of the water content, here 5, i.e., reading after 5, 10, 15, 20 min and final w_f.

Examples of how to evaluate the emulsion separation index have been presented (Kokal, 2006), and it has been used to explore the factors that affect the oil-water separation, including

- Temperature,
- Shear,
- Asphaltene content,
- Watercut,
- Demulsifier dosage, and
- Mixing different crude oil types.

The use of the emulsion separation index has clarified demulsifier selection and the diagnosis of emulsion treatment problems.

Field case studies have been described in which the emulsion separation index was used to select the best demulsifier, diagnose, and ultimately solve emulsion related problems during oil production. The results show a strong correlation of asphaltene content in the crude oil with emulsion separation index or emulsion tightness. Recommendations can be made for reducing and optimizing the dosage of the demulsifier by adding other chemicals (Kokal and Wingrove, 2000).

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) can be used to determine the composition of water-in-oil emulsions, as it can distinguish free water from emulsified water (Dalmazzone and Seris, 1998; Díaz-Ponce et al., 2010), since free water crystallizes at higher temperatures than do water droplets in the emulsion. DSC gives information about (Audibert-Hayet et al., 2007):

- The type of emulsion: simple (water-in-oil or oil-in-water) or multiple (water-in-oil-in-water, or oil-in-water-in-oil, respectively),
- The quantity of liquid and its state: bound, dispersed or free,
- The compositions of the free and dispersed forms,
- The mean diameter of the droplets and their evolution with time due to coalescence or Ostwald ripening, and
- Matter transfers between droplets due to their compositional differences.

Stability of Invert Emulsions

The stability of invert emulsions can be tested according to the following procedures (Summerhill et al., 2006):

Procedure 21–5: A small portion of the emulsion is placed in a beaker that contains an oleaginous fluid. If the emulsion is an invert emulsion, the small portion will disperse in the oleaginous fluid, which can be determined by visual inspection. ■

The electrical stability of the invert emulsion can be tested as follows:

Procedure 21–6: A voltage is applied between two electrodes immersed in the emulsion, which is increased until the emulsion breaks and a surge of current flows between the electrodes. The voltage required to break the emulsion is a common measure of the stability of an emulsion. ■

Low Fluorescence Emulsifiers

Citric-acid-based polyamide (PA) emulsifiers have been developed that exhibit a very low fluorescence.

PAs are conventionally prepared by reacting a fatty acid with diethylenetriamine in order to form the amide, and then the amide is reacted with citric acid. These products exhibit a relatively high fluorescence. The reaction is shown in Figure 21.5.

Alternatively, a PA with pendent citric acid units can be made via a cyclic intermediate, an imidazoline structure. This is followed by a ring opening reaction, to yield an isomeric amide. The reaction is shown in Figure 21.6. The products of this reaction exhibit a much lower fluorescence. Discharged fluids having low fluorescence are less likely to impart a sheen to the ocean's surface (Cravey, 2010), hence discharge operations will become less obvious.

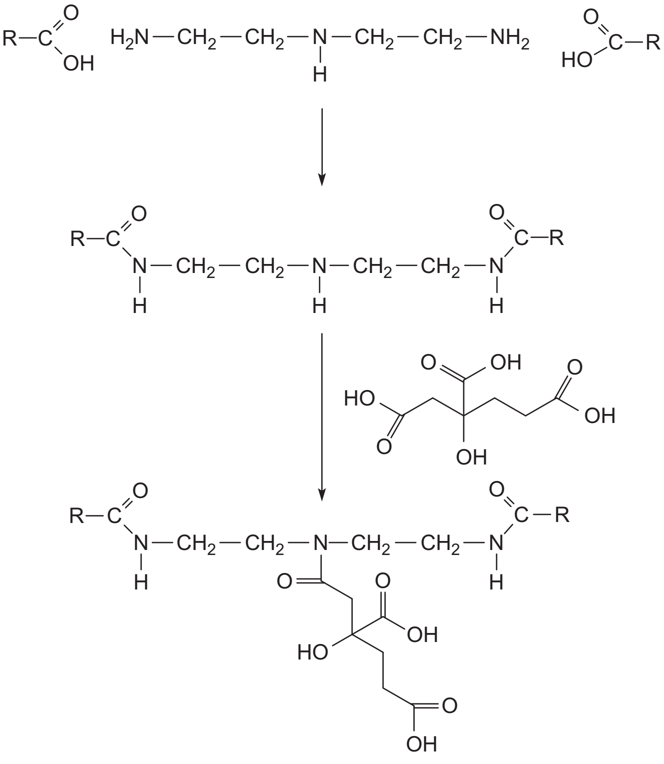


FIGURE 21.5 Conventional synthesis of polyamide surfactants (Cravey, 2010).

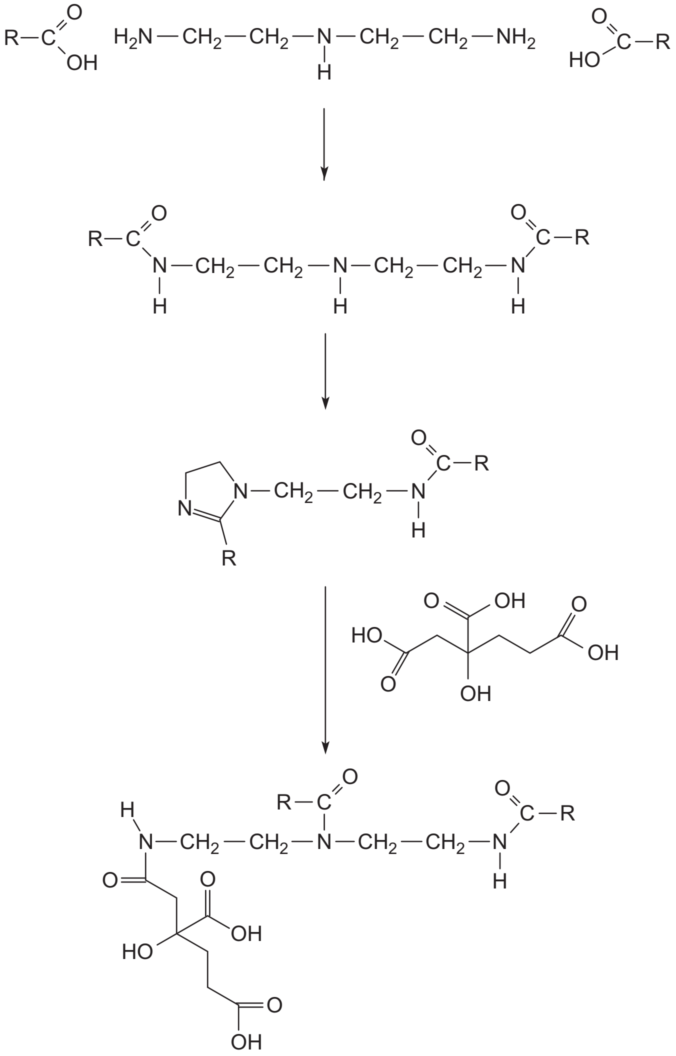


FIGURE 21.6 Synthesis of polyamide surfactants via imidazoline (Cravey, 2010).

FOAMS

A foam is a liquid that encloses gas cells, first investigated by Joseph A. F. Plateau, whose monograph appeared in 1783 (Plateau, 1783). Foams find use in

- Foam drilling,
- Foam cementing,
- Foam flooding,
- Foam-based fracturing, and
- Water shutoff.

According to thermodynamics, there is an excess pressure Δp in a spherical bubble, which is related to the radius r and the surface tension σ by Young's law:

$$\Delta p = \frac{\sigma}{r}. \tag{21.4}$$

Aphrons

An aphron is a phase that is surrounded by a tenside like film, e.g., a soap bubble. The term originates from the Greek $\alpha\phi\rho o\sigma$ for foam. The topic has been described by Sebba, who obviously coined the term (Sebba, 1984, 1987). Aphrons are also known as biliquid foams because they are foams in which the liquid skin is built up from two phases. So, in contrast to a conventional air bubble, which is stabilized by a surfactant monolayer, the outer shell of an aphron consists of a much more robust surfactant trilayer.

Colloidal gas aphrons, as proposed by Sebba, consist of a gaseous inner core surrounded by a thin aqueous surfactant film, which is composed of two surfactant layers. There is also a third surfactant layer that stabilizes the structure (Watcharasing et al., 2008). The basic structure of a colloidal gas aphron is shown in Figure 21.7.

The aphron includes a spherical core, which is usually gas encapsulated in a thin shell of surfactant molecules. The surfactants point their hydrophobic, nonpolar ends into the gas core, and the hydrophilic ends point into a second phase, often water that contains a thickening agent, an aphron stabilizer, and surfactant molecules at the outer boundary. These surfactants have their hydrophobic

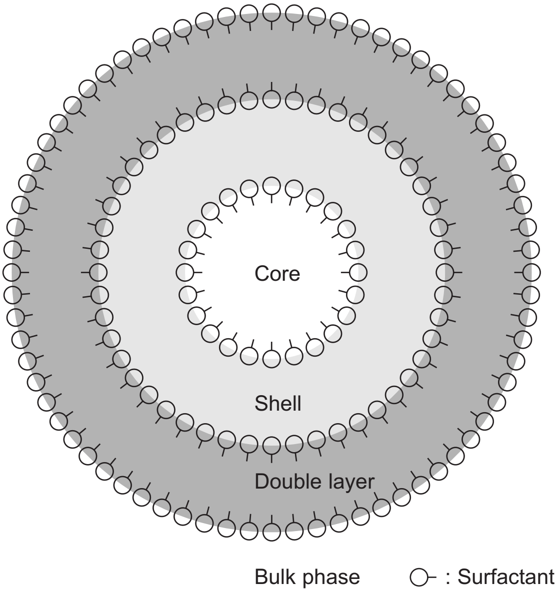


FIGURE 21.7 Basic structure of an aphron (Watcharasing et al., 2008).

ends into the third outer phase. This phase also contains an additional layer of surfactant molecules whose hydrophilic ends extend into the bulk fluid. The surrounding phase is therefore a bilayer of surfactant molecules, which serves as an effective barrier to coalescence with adjacent aphrons. It is believed that the exterior surfactant layer is not strongly associated with the rest of the aphron, and may be shed when several aphrons come into contact with each other, so that they agglomerate rather than coalesce. The surfactant molecules are not necessarily the same material, so each layer may be comprised of different types of surfactants (Growcock and Simon, 2006). Colloidal gas aphrons are of interest, because they (Watcharasing et al., 2008):

- Have a comparatively large interfacial area,
- Exhibit a relatively high stability,
- Show similar flow properties to those of pure water, and
- Can be easily separated from the bulk liquid phase.

Aphrons can survive a compression of at least 27.3 MPa (4,000 psig), whereas conventional bubbles do not survive pressures much higher than a tenth of that (Growcock et al., 2007). An apparatus for investigating aphron bubbles under high pressure has been designed (Growcock, 2005, p. 35), in which two viewing cells simultaneously record the size and the concentration of bubbles before and after filtration through a sintered metal filter.

Aphrons are important in fluids used for oil field applications (Belkin et al., 2005; Growcock et al., 2007). The first use of aphrons in a drilling fluid application was described in 1998 (Brookey, 1998).

When a drilling fluid migrates into a loss zone, aphrons move faster than the surrounding liquid phase and quickly form a layer of bubbles at the front of the fluid. This bubble front and the radial flow pattern of the fluid rapidly reduce the shear rate and raise the fluid viscosity, which lessens the invasion of the fluid. Aphrons exhibit a small amount of affinity for each other, or for the mineral surfaces of the pores or fractures. Consequently, the sealings they form are soft. Their lack of adhesion enables them to be flushed out easily when desired (Growcock et al., 2007). They reduce the density of a drilling fluid and provide bridging and sealing of the formations contacted by the fluid as the bubbles expand to fill the openings, which are exposed while drilling. Low shear rate polymers strengthen the microbubbles and act as fluid loss agents (Brookey, 2004). In this way, lost circulation is prevented. Also the IFT between the base fluid and produced oils or gases is low, so the fluids do not damage the formation. Depleted wells, which are very expensive to drill underbalanced or with other remediation techniques, have been drilled overbalanced with the aid of aphron drilling fluids (Growcock et al., 2007).

In a water-lamella foam, small globules of oil are encapsulated in a surfactant-stabilized film and separated from one another by a further thin lamella of water. Biliquid foams are essentially of two types (Sebba, 1984):

- Oil-lamella and
- Water-lamella.

An oil-lamella biliquid foam consists of aqueous cells coated with an oil film and separated from each another by an oil-lamella. The oil phase corresponds to the aqueous phase of a conventional gas foam, and the water globules correspond to the gas cells.

The second type of biliquid foam has an oil or a nonpolar liquid discontinuous phase and the encapsulating phase is water or a hydrogen-bonded liquid, which contains a soluble surfactant. The encapsulating film and foam lamella are stabilized by the surfactant. In both types, the cells are held together by capillary pressures, just like the soap bubbles in a gas foam. A water-lamella biliquid foam is distinguished from oil-in-water emulsions, in which the discontinuous oil phase is separated from the continuous aqueous phase by a single interface.

At moderate gas concentrations, the stability of bubbles in an aqueous medium depends primarily on the viscosity of the bulk fluid and the IFT. More specifically, the stability is determined by the rate of mass transfer between the viscous water shell and the bulk phase, known as Marangoni convection (Bjorndalen and Kuru, 2008). Carlo Marangoni published his results in 1865 in the course of his doctoral thesis at the University of Pavia.

If a temperature gradient is disturbed, such as a gradient is introduced in the surface tension, a convection or movement of liquid will occur that contributes to the decomposition of foams. If the mass transfer rate is high, aphrons will become unstable. Therefore, the shell fluid must be designed to have a certain viscosity to minimize the Marangoni effect (Bjorndalen and Kuru, 2008). Bulk viscosity is generally controlled by the addition of polymers and clays, and the IFT is usually lowered with a surfactant. In contrast to a typical bubble, an aphron is stabilized by a very high interfacial viscosity of the second phase (Brookey, 2004).

Fluids with a low shear rate viscosity are helpful in controlling the invasion of a filtrate by creating an impermeable layer close to the formation openings.

Since the fluid moves at a very slow rate, the viscosity becomes very high, and the depth of invasion of the fluid into the formation is kept shallow.

PVA, in combination with surfactants, such as cocamidopropyl betaine or an alkyl ether sulfate (Growcock and Simon, 2006), form aphron stabilizers that modify the viscosity of the water layer to such an extent that it creates an elastomeric membrane improving the stability and sealing capability of the aphrons.

The surfactants must be compatible with the polymers present in the fluid, so they will generally be non-ionic or anionic (Brookey, 2004). A series of surfactants have been screened using a low pressure API filtration cell (API, 2009).

Test procedure 21–7: The cylindrical body of the cell is made from plexiglas of a thickness 0.5 in. (1.3 cm). 200 g of sand is added with a particle size of 50–70 mesh (210–297 μm). In this way, a sand bed depth of 2.1 cm is obtained. No filter paper is used in the cell. 350 ml of the fluid to be tested is slowly added to the cell, the cell assembled, and a pressure of nitrogen of 0.7 MPa (100 psi) is applied. The pressure is released after the nitrogen blows through the bed for 30 s. Upon releasing the pressure the sand bed will expand in height as the bubbles in the sand bed expand. The average increase in height of the bed is measured. Surfactants that increase the sand bed by at least 50% are considered to be preferred for the generation of aphrons (Brookey, 2004). ■

The average percent increase in height of the sand bed is given in Table 21.4, tested according to Test Procedure 21–7.

The effects of polymer and surfactant concentration, surfactant type, shear rate, mixing time, and water quality on the bubble size of colloidal gas aphrons have been studied (Bjorndalen and Kuru, 2008).

Several other tests suitable to characterize aphrons have been described in detail, including (Growcock, 2005):

- Survivability of bubbles under high pressure,
- Disk leak-off test,
- Syringe sand pack leak-off test, and
- Capillary flow test.

TABLE 21.4 Average Increase of the Height of a Sand Bed Using API RP 13B-1 (Brookey, 2004)

Surfactant	Increase/[%]
Sodium dioctyl sulfosuccinate	118.8
Chubb national foam-high expansion	96.4
Alpha olefin sulfonate	63.7
Ethoxylated 2,4,7,9-tetramethyl-5-decyn-4-diol	56.0
Linear C_9–C_{11} alcohol ethoxylates, 6 mol EO/ mol	56.0
Tetrasodium *N*-(1,2-dicarboxyethyl)-*N*-octadecyl sulfosuccinate	50.6
Mixture of diethanolamides of fatty acids	50.0
Sodium disopropyl naphthalene sulfonate	38.1
Linear C_{12}–C_{15} alcohol ethoxylates, 7 mol EO/ mol	38.1
Modified alkyl ether sulfate	28.6
Ethoxylated octadecylamine-octadecylguanidine complex	19.0
Ethoxylated (20 moles) methyl glucoside sesquistearate	19.0
2,4,7,9-tetramethyl-5-decyne-4,7-diol	<10
Ethoxylated nonyl phenol	<10
Sodium alkyl sulfate	<10
Polyoxypropylene-polyoxyethylene block copolymer	<10

REFERENCES

Adamska, K., Bellinghausen, R., Voelkel, A., 2008. New procedure for the determination of hansen solubility parameters by means of inverse gas chromatography. J. Chromatogr. A 1195 (1–2), 146–149.

API, 2009. Recommended practice for field testing water-based drilling fluids, API Standard API RP 13B-1. American Petroleum Institute, Washington, DC.

Audibert-Hayet, A., Giard-Blanchard, C., Dalmazzone, C., 2007. Organic emulsion-breaking formula and its use in treating well bores drilled in oil-base mud. US Patent 7 226 896, assigned to Institut Francais du Petrole (Rueil Malmaison Cedex, FR), June 5, 2007.

Banavali, R.M., Chheda, B.D., Manari, G.M., 2010. Formulations useful as asphaltene dispersants in petroleum products. US Patent 7 674 365, assigned to Rohm and Haas Company (Philadelphia, PA), March 9, 2010.

Baret, J.F., Drecq, P., 1989a. Additives for oilfield cements and corresponding cement slurries. EP Patent 314 242, assigned to Pumptech NV, May 03, 1989.

Baret, J.F., Drecq, P., 1989b. Dispersant for oil-well cement slurries and corresponding slurries (dis-persant pour laitiers de ciment petroliers, et laitiers correspondants). FR Patent 2 622 572, May 05, 1989.

Baret, J.F., Drecq, P., 1990. Dispersant for oilfield cement slurries and corresponding slurries (dispersant pour laitiers de ciment petroliers, et laitiers correspondants). FR Patent 2 635 469, February 23, 1990.

Belkin, A., Irving, M., O'Connor, R., Fosdick, M., Hoff, T., Growcock, F.B., 2005. How aphron drilling fluids work. In: Annual Technical Conference and Exhibition, vol. 5. Society of Petroleum Engineers, Richardson, TX, 2005, pp. 2380–2386.

Bergenholtz, J., 2001. Theory of rheology of colloidal dispersions. Curr. Opin. Colloid Interface Sci. 6 (5–6), 484–488.

Bibette, J., Leal-Calderon, F., Schmitt, V., Poulin, P., 2002. Emulsion Science: Basic principles, An Overview, Springer Tracts in Modern Physics, vol. 186. Springer, Berlin.

Bjorndalen, N., Kuru, E., 2008. Physico-chemical characterization of aphron based drilling fluids. J. Can. Pet. Technol. 47 (11), 15–21.

Bloys, J.B., Wilson, W.N., Malachosky, E., Carpenter, R.B., Bradshaw, R.D., 1993. Dispersant compositions for subterranean well drilling and completion. EP Patent 525 037, February 03, 1993.

Bloys, J.B., Wilson, W.N., Malachosky, E., Bradshaw, R.D., Grey, R.A., 1994. Dispersant compositions comprising sulfonated isobutylene maleic anhydride copolymer for subterranean well drilling and completion. US Patent 5 360 787, assigned to Atlantic Richfield Co., November 01, 1994.

Bouchut, P., Rousset, J., Kensicher, Y., 1989. A non-polluting dispersing agent for drilling fluids based on freshwater or salt water. AU Patent 590 248, November 02, 1989.

Bouchut, P., Rousset, J., Kensicker, Y., 1990. Non-polluting fluidizing agents for drilling fluids having soft or salt water base (agent fluidifiant non polluant pour fluides de forage a base d'eau douce ou saline). CA Patent 1 267 777, April 17, 1990.

Bouchut, P., Kensicher, Y., Rousset, J., 1992. Non-polluting dispersing agent for drilling fluids based on freshwater or salt water. US Patent 5 099 928, March 31, 1992.

Bragg, J.R., 2000. Oil recovery method using an emulsion. US Patent 6 068 054, assigned to Exxon Production Research Co., May 30, 2000.

Bragg, J.R., Varadaraj, R., 2006. Solids-stabilized oil-in-water emulsion and a method for preparing same. US Patent 7 121 339, assigned to ExxonMobil Upstream Research Company (Houston, TX), October 17, 2006.

Brookey, T., 1998. Micro-bubbles: new aphron drill-in fluid technique reduces formation damage in horizontal wells. In: SPE Formation Damage Control Conference. SPE, Society of Petroleum Engineers, The Woodlands, TX.

Brookey, T.F., 2004. Aphron-containing well drilling and servicing fluids. US Patent 6 716 797, assigned to Masi Technologies, L.L.C. (Houston, TX), April 6, 2004.

Burke, J., 1984. Solubility parameters: theory and application, AIC Book and Paper Group Annual 3, 13–58, [electronic:] http://cool.conservation-us.org/byauth/burke/solpar/, March 15, 2011.

Burrafato, G., Carminati, S., 1994a. Aqueous drilling muds fluidified by means of zirconium and aluminium complexes. EP Patent 623 663, assigned to Eniricerche SPA and Agip SPA, November 09, 1994.

Burrafato, G., Carminati, S., 1994b. Aqueous drilling muds fluidified by means of zirconium and aluminum complexes. CA Patent 2 104 134, November 08, 1994.

Burrafato, G., Carminati, S., 1996. Aqueous drilling muds fluidified by means of zirconium and aluminum complexes. US Patent 5 532 211, July 02, 1996.

Burrafato, G., Gaurneri, A., Lockhart, T.P., Nicora, L., 1997. Zirconium additive improves field performance and cost of biopolymer muds. In: Proceedings of SPE International Symposium on Oilfield Chemicals, Society of Petroleum Engineers, The Woodlands, TX, Volume, Houston, February 18–21, 1997, Society of Petroleum Engineers, The Woodlands, TX, pp. 707–710.

Chadwick, R.E., Phillips, B.M., 1995. Preparation of ether carboxylates. EP Patent 633 279, assigned to Albright & Wilson Ltd., January 11, 1995.

Chakrabarty, T., 2010. Solvent for extracting bitumen from oil sands. US Patent Application 20100130386, May 27, 2010.

Chapman, H., Purnell, K., Law, R.J., Kirby, M.F., 2007. The use of chemical dispersants to combat oil spills at sea: a review of practice and research needs in Europe. Mar. Pollut. Bull. 54 (7), 827–838.

Conley, R.F., 1996. Practical Dispersion: A Guide to Understanding and Formulating Slurries. Wiley VCH, Weinheim.

Cravey, R.L., 2010. Citric acid based emulsifiers for oilfield applications exhibiting low fluorescence. US Patent 7 691 960, assigned to Akzo Nobel N.V. (Arnhem, NL), April 6, 2010.

Crema, S.C., Kucera, C.H., Gousetis, C., Oppenlaender, K., 1991. Cementing compositions containing polyethyleneimine phosphonate derivatives as dispersants. EP Patent 444 542, assigned to BASF Corp., September 04, 1991.

Cronje, I.J., 1989. Process for the oxidation of fine coal. EP Patent 298 710, assigned to Council Sci & Ind. Researc, January 11, 1989.

Dalmazzone, C., Seris, H., 1998. Use of the DSC technique to characterize water in crude oil emulsions stability. Rev. Inst. Franc. Petr. 53 (4), 436–471.

Detroit, W.J., 1989. Oil well drilling cement dispersant. US Patent 4 846 888, assigned to Reed Lignin Inc., July 11, 1989.

Dı́az-Ponce, J.A. and Flores, E.A. and Lopez-Ortega, A. and Hernańdez-Cortez, J.G. and Estrada, A. and Castro, L.V. and Vazquez, F., 2010. Differential scanning calorimetry characterization of water-in-oil emulsions from Mexican crude oils. J. Therm. Anal. Calorim. 102 (3), 899–906.

Dispersion (chemistry), N.N., 2010. Wikipedia: http://en.wikipedia.org/wiki/Dispersion_(chemistry) (accessed 10.04.11.).

Emmons, D.H., 1993. Sulfur deposition reduction. US Patent 5 223 160, June 29, 1993.

Endo, Y., Kousaka, Y., 1996. Dispersion mechanism of coagulated particles in liquid flow. Colloids Surf. A 109, 109–115.

Eoff, L., 1994a. Acetone/formaldehyde/cyanide resins. US Patent 5 290 357, assigned to Halliburton Co., March 01, 1994.

Eoff, L., 1994b. Dispersant for cement in water. EP Patent 604 000, June 29, 1994.

Farrar, D., Hawe, M., Dymond, B., 1992. Use of water soluble polymers in aqueous drilling or packer fluids and as detergent builders. EP Patent 182 600, assigned to Allied Colloids Ltd., August 12, 1992.

Frost, K.A., Daussin, R.D., Domelen, M.S.V., 2008. New, highly effective asphaltene removal system with favorable HSE characteristics. In: SPE International Symposium and Exhibition on Formation Damage Control. Society of Petroleum Engineers, Lafayette, Louisiana, USA.

Garvey, C.M., Savoly, A., Weatherford, T.M., 1987. Drilling fluid dispersant. US Patent 4 711 731, December 08, 1987.

Giddings, D.M., Fong, D.W., 1988. Calcium tolerant deflocculant for drilling fluids. US Patent 4 770 795, September 13, 1988.

Grey, R.A., 1993. Process for preparing alternating copolymers of olefinically unsaturated sulfonate salts and unsaturated dicarboxylic acid anhydrides. US Patent 5 210 163, assigned to Arco Chemical Technol. Inc., May 11, 1993.

Growcock, F., 2005. Enhanced wellbore stabilization and reservoir productivity with aphron drilling fluid technology. Project Report DE-FC26-03NT42000. MASI Technologies LLC, Houston, TX.

Growcock, F.B., Belkin, A., Fosdick, M., Irving, M., O'Connor, B., Brookey, T., 2007. Recent advances in aphron drilling-fluid technology. SPE Drill. Completion 22 (2), 74–80.

Growcock, F.B., Simon, G.A., 2006. Stabilized colloidal and colloidal-like systems. US Patent 7 037 881, May 2, 2006.

Hale, A.H., 1988. Well drilling fluids and process for drilling wells. US Patent 4 728 445, March 01, 1988.

Hale, A.H., Lawson, H.F., 1988. Well drilling fluids and process for drilling wells. US Patent 4 740 318, April 26, 1988.

Hale, A.H., Rivers, G.T., 1988. Well drilling fluids and process for drilling wells. US Patent 4 721 576, January 26, 1988.

Hansen, C.M., 1967. The three dimensional solubility parameter – key to paint component affinities. I: solvents, plasticizers, polymers and resins. J. Paint Technol. 39 (505), 104–117.

Hansen, C., 2007. Hansen Solubility Parameters: A User's Handbook, second ed. CRC Press, Boca Raton, FL.

Hendriks, H., 1989a. Dispersing agent for cement-slurry compounds, compounds containing this agent and procedures for the cementing of oil wells or similar (dispersant pour compositions de laitiers de ciment, compositions le contenant et procedes correspondants de cimentation de puits petroliers ou analogues). FR Patent 2 620 442, March 17, 1989.

Hendriks, H., 1989b. Dispersing agent for cement-slurry compounds, compounds containing this agent and procedures for the cementing of oil wells or similar. EP Patent 307 997, assigned to Pumptech NV, March 22, 1989.

Ian D. Morrison, S.R., 2002. Colloidal Dispersions: Suspensions, Emulsions, and Foams. Wiley-Interscience, New York.

Jones, T.A., Wentzler, T., 2008. Polymer hydration method using microemulsions. US Patent 7 407 915, assigned to Baker Hughes Incorporated (Houston, TX), August 5, 2008.

Just, E.K., Nickol, R.G., 1989. Phosphated, oxidized starch and use of same as dispersant in aqueous solutions and coating for lithography. EP Patent 319 989, June 14, 1989.

Kirby, M.F., Law, R.J., 2010. Accidental spills at sea – Risk, impact, mitigation and the need for co-ordinated post-incident monitoring. Mar. Pollut. Bull. 60 (6), 797–803.

Kirkpatrick, W.H., Alice, W., 1960. Chemical compositions. US Patent 2 925 429, assigned to Visco Products Company, February 16, 1960.

Kokal, S.L., 2005. Crude oil emulsions: a state-of-the-art review. SPE Prod. Facil. 20 (1), 5–13.

Kokal, S.L., 2006. Crude oil emulsions. In: Fanchi, J.R. (Ed.), Petroleum Engineering Handbook, vol. I, chap. 12. Society of Petroleum Engineers, Richardson, TX, pp. 533–570.

Kokal, S.L., Wingrove, M., 2000. Emulsion separation index: from laboratory to field case studies. In: Proceedings of SPE Annual Technical Conference and Exhibition, vol. 63165-MS, 1–4 October 2000. Society of Petroleum Engineers, Dallas, TX.

Lawson, H.F., Hale, A.H., 1989. Well drilling fluids and process for drilling wells. US Patent 4 812 244, March 14, 1989.

Leighton, J.C., Sanders, M.J., 1988. Water soluble polymers containing allyloxybenzenesulfonate monomers. EP Patent 271 784, June 22, 1988.

Leighton, J.C., Sanders, M.J., 1990. Water soluble polymers containing allyloxybenzenesulfonate monomers. US Patent 4 892 898, January 09, 1990.

Leopold, G., 1992. Breaking produced-fluid and process-stream emulsions. In: Schramm, L.L. (Ed.), Emulsions–Fundamentals and Applications in the Petroleum Industry. American Chemical Society, Washington, DC, pp. 341–383.

Lessard, R.R., DeMarco, G., 2000. The significance of oil spill dispersants. Spill Sci. Technol. Bull. 6 (1), 59–68.

Lochhead, R.Y., Rulison, C.J., 1994. An investigation of the mechanism by which hydrophobically modified hydrophilic polymers act as primary emulsifiers for oil-in-water emulsions 1. Polyacrylic acids and hydroxyethyl celluloses. Colloids Surf. A 88 (1), 27–32.

MacKay, R.B. (Ed.), 1994. Technological Applications of Dispersions, Surfactant Science Series, vol. 52. Dekker, New York.

Manning, F.S., Thompson, R.E., 1995. Dehydration of Crude Oil, vol. 2. PennWell Publishing, Tulsa, OK, chap. 7, p. 117.

McCallum, T.F.I., Weinstein, B., 1994. Amine-thiol chain transfer agents. US Patent 5 298 585, assigned to Rohm & Haas Co., March 29, 1994.

Menon, V.B., Wasan, D.T., 1988. Characterization of oil-water interfaces containing finely divided solids with applications to the coalescence of water-in-oil emulsions: a review. Colloids Surf. 29 (1), 7–27.

Monfreux-Gaillard, N., Perrin, P., LaFuma, F., Sawdon, C., 2007. Reversible emulsions stabilized by amphiphilic polymers and application to drilling fluid. US Patent 7 262 152, assigned to M-I L.L.C. (Houston, TX), August 28, 2007.

Mueller, H., Kirsner, J., Burrows, K., 2009. Thinners for invert emulsions. US Patent 7 638 466, assigned to Halliburton Energy Services, Inc. (Duncan, OK), December 29, 2009.

Patel, B.B., Stephens, M., 1990. Well cement slurries and dispersants therefor. US Patent 4 923 516, May 08, 1990.

Patel, B., Stephens, M., 1991. Well cement slurries and dispersants therefor. US Patent 5 041 630, August 20, 1991.

Peiffer, D.G., Bock, J., Elward-Berry, J., 1991. Zwitterionic functionalized polymers as deflocculants in water based drilling fluids. US Patent 5 026 490, assigned to Exxon Research & Eng. Co., June 25, 1991.

Peiffer, D.G., Bock, J., Elward-Berry, J., 1992a. Thermally stable hydrophobically associating rheological control additives for water-based drilling fluids. US Patent 5 096 603, assigned to Exxon Research & Eng. Co., March 17, 1992.

Peiffer, D.G., Bock, J., Elward-Berry, J., 1992b. Zwitterionic functionalized polymers. GB Patent 2 247 240, assigned to Exxon Research & Eng. Co., February 26, 1992.

Peiffer, D.G., Bock, J., Elward-Berry, J., 1992c. Zwitterionic functionalized polymers as deflocculants in water based drilling fluids. CA Patent 2 046 669, assigned to Exxon Research & Eng. Co., February 09, 1992.

Peiffer, D.G., Bock, J., Elward-Berry, J., 1993a. Thermally stable hydrophobically associating rheological control additives for water-based drilling fluids. CA Patent 2 055 011, assigned to Exxon Research & Eng. Co., May 07, 1993.

Peiffer, D.G., Bock, J., Elward-Berry, J., 1993b. Zwitterionic functionalized polymers as deflocculants in water based drilling fluids. AU Patent 638 917, assigned to Exxon Research & Eng. Co., July 08, 1993.

Plateau, J.A.F., 1783. Statique experimentale et theorique des liquides soumis aux seules forces moleculaires. Gauthiers-Villars, Paris.

Poindexter, M.K., Chuai, S., Marble, R.A., Marsh, S.C., 2006. The key to predicting emulsion stability: solid content. SPE Prod. Oper. 21 (3), 357–364.

Poindexter, M.K., Lindemuth, P.M., 2004. Applied statistics: crude oil emulsions and demulsifiers. J. Dispersion Sci. Technol. 25 (3), 311–320.

Poindexter, M.K., Marsh, S.C., 2009. Inorganic solid content governs water-in-crude oil emulsion stability predictions. Energy Fuels 23 (3), 1258–1268.

Portnoy, R.C., 1986. Anionic copolymers for improved control of drilling fluid rheology. GB Patent 2 174 402, assigned to Exxon Chemical Patents In, November 05, 1986.

Portnoy, R.C., 1987. Anionic copolymers for improved control of drilling fluid rheology. US Patent 4 680 128, July 14, 1987.

Reese, R.R., Rey, P., 2009. Method of fracturing subterranean formations utilizing emulsions comprising acrylamide copolymers. US Patent 7 482 310, assigned to Kroff Chemical Company, Inc. (Pittsburgh, PA) Superior Well Services, Inc. (Indiana, PA), January 27, 2009.

Riley, P., 1998. Compositions and methods for dispersing and biodegrading spilled petroleum oils and fuels. US Patent 5 753 127, assigned to Petrotech AG, May 19, 1998.

Rooney, P., Russell, J.A., Brown, T.D., 1988. Production of sulfonated asphalt. US Patent 4 741 868, May 03, 1988.

Sawdon, C.A., Ballard, D.A., 1997. Wellbore fluid. GB Patent 2 309 240, assigned to Sofitech NV, July 23, 1997.

Sebba, F., 1984. Preparation of biliquid foam compositions. US Patent 4 486 333, December 4, 1984.

Sebba, F., 1987. Foams and Biliquid Foams-Aphrons. John Wiley & Sons, Chichester.

Speight, J.G., 2004. Solubility Parameters. McGraw-Hill, New York, p. 324.

Stephenson, W.K., Kaplan, M., 1991. Asphaltene dispersants-inhibitors. CA Patent 2 029 465, assigned to Nalco Chemical Co., May 09, 1991.

Sullivan, P.F., Tustin, G.J., Christanti, Y., Kubala, G., Drochon, B., Hughes, T.L., 2010. Aqueous two-phase emulsion gel systems for zone isolation. US Patent 7 703 527, assigned to Schlumberger Technology Corporation (Sugar Land, TX), April 27, 2010.

Summerhill, J.L., Jarrett, M.A., McKellar, A.J., Young, D.B., Grover, P.E., Gusler, W.J., 2006. Organofunctional compounds for shale stabilization of the aqueous dispersed phase of non-aqueous based invert emulsion drilling system fluids. US Patent 7 067 460, assigned to Baker Hughes Incorporated (Houston, TX), June 27, 2006.

Szablikowski, K., Lange, W., Kiesewetter, R., Reinhardt, E., 1995. Easily dispersible blends of reversibly crosslinked and uncrosslinked hydrocolloids, with aldehydes as crosslinker (abmischungen von mit aldehyden reversibel vernetzten hydrokolloidmischungen und unvernetzten hydrokolloiden mit verbessertes dispergierbarkeit). EP Patent 686 666, assigned to Wolff Walsrode AG, December 13, 1995.

Tadros, T., 1993. Industrial applications of dispersions. Adv. Colloid Interface Sci. 46, 1–47.

Taylor, R.S., Funkhouser, G.P., Dusterhoft, R.G., 2009. Gelled invert emulsion compositions comprising polyvalent metal salts of an organophosphonic acid ester or an organophosphinic acid and methods of use and manufacture. US Patent 7 534 745, assigned to Halliburton Energy Services, Inc. (Duncan, OK), May 19, 2009.

Ubbels, S.J., 2010. Methods for inhibiting naphthenate salt precipitates and naphthenate-stabilized emulsions. US Patent 7 776 930, assigned to Champion Technologies, Inc. (Houston, TX), August 17, 2010.

Varadaraj, R., 2010. Oil-in-water-in-oil emulsion. US Patent 7 652 074, assigned to ExxonMobil Upstream Research Company (Houston, TX), January 26, 2010.

Varadaraj, R., Bragg, J.R., Dobson, M.K., Peiffer, D.G., Huang, J.S., Siano, D.B., et al., 2004. Solids-stabilized water-in-oil emulsion and method for using same. US Patent 6 734 144, assigned to ExxonMobil Upstream Research Company (Houston, TX), May 11, 2004.

Varadaraj, R., Bragg, J.R., Peiffer, D.G., Elspass, C.W., 2007. Stability enhanced water-in-oil emulsion and method for using same. US Patent 7 186 673, assigned to ExxonMobil Upstream Research Company (Houston, TX), March 6, 2007.

Watcharasing, S., Angkathunyakul, P., Chavadej, S., 2008. Diesel oil removal from water by froth flotation under low interfacial tension and colloidal gas aphron conditions. Sep. Purif. Technol. 62 (1), 118–127.

Weaire, D., Hutzler, S., 1999. The Physics of Foams. Clarendon Press, Oxford.

Xiang, T., 2010. Invert emulsion drilling fluid systems comprising an emulsified aqueous phase comprising dispersed integral latex particles. US Patent 7 749 945, assigned to Baker Hughes Incorporated (Houston, TX), July 6, 2010.

Yaghmur, A., Glatter, O., 2009. Characterization and potential applications of nanostructured aqueous dispersions. Adv. Colloid Interface Sci. 147–148, 333–342.

Yang, J., Jovancicevic, V., 2009. Microemulsion containing oil field chemicals useful for oil and gas field applications. US Patent 7 615 516, assigned to Baker Hughes Incorporated (Houston, TX), November 10, 2009.

TRADENAMES

TABLE 21.5 Tradenames in References

Tradename Description	Supplier
Aerosil® Fumed Silica (Bragg and Varadaraj, 2006; Varadaraj et al., 2004)	Degussa AG
BIO-COTE Wetting agent (Summerhill et al., 2006)	Baker Hughes INTEQ
Claytrol™ Amine mixture (Summerhill et al., 2006)	Baker Hughes INTEQ
Mil-Bar™ Barite weighting agent (Summerhill et al., 2006)	Baker Hughes
Organotrol™ 1665 2-Methylbenzyl tallow intercalated monomorillonite (Varadaraj et al., 2004)	Cimar Corp.

TABLE 21.5 Tradenames in References–Cont'd

Tradename Description	Supplier
Rev Dust Artificial drill solids (Summerhill et al., 2006)	Milwhite, Inc.
REV-DUST™ Calcium montmorillonite clay (Summerhill et al., 2006)	Milwhite, Inc.
Wolastafil-050-MH-0010™ Methylalkoxysilane coated calcium metasilicate (Varadaraj et al., 2004)	United Mineral Corp.

Chapter 22

Defoamers

Defoaming compositions are commonly used in the oil and gas industry to prevent the formation of foam, hinder the entrainment of a gas in a liquid, or to break a previously formed foam. Defoaming is necessary in several industrial branches and is often a key factor for efficient operation. A review of defoamers has been given by Owen (1996).

THEORY OF DEFOAMING

Stability of Foams

Foams are thermodynamically unstable but are prevented from collapsing by the following properties:

- Surface elasticity,
- Viscous drainage,
- Reduced gas diffusion between bubbles, and
- Thin-film stabilization effects from the interaction of opposite surfaces.

The stability of a foam can be explained by the Gibbs elasticity E. This results from reducing the surface concentration of the active molecules in equilibrium when the film is extended. This causes an increase in the equilibrium surface tension σ, which acts as a restoring force:

$$E = 2A\frac{d\sigma}{dA} \tag{22.1}$$

where A is the area of the surface. In a foam, where the surfaces are interconnected, the time-dependent Marangoni effect is important. A restoring force corresponding to the Gibbs elasticity will appear, because only a finite rate of absorption of the surface active agent, which decreases the surface tension, can take place on the expansion and contraction of a foam. Thus the Marangoni effect is a kinetic effect.

The surface tension effects under nonequilibrium conditions are described in terms of dilatational moduli. The complex dilatational modulus ε of a single

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TABLE 22.1 Dilatational Elasticities and Viscosities of Crude Oil at 1 mHz with Polydimethylsiloxanes (Callaghan et al., 1983)

Crude oil	Amount of PDMS/ [ppm]	ε_d/ [mN m^{-1}]	η_d/ [mN sm^{-1}]
North Sea	–	1.34	153
North Sea	12,500	0.69	90
North Sea	60,000	0.51	33
Middle East	–	1.63	105
Middle East	60,000	1.19	53

surface is defined in the same way as the Gibbs elasticity. The factor 2 is not used in a single surface:

$$\varepsilon = 2A\frac{d\sigma}{dA} \tag{22.2}$$

In a periodic dilatational experiment, the complex elasticity modulus is a function of the angular frequency:

$$\varepsilon(i\omega) = |\varepsilon|\cos\theta + i|\varepsilon|\sin\theta = \varepsilon_d(\omega) + \omega\eta_d(\omega) \tag{22.3}$$

where ε_d is the dilatational elasticity, and η_d is the dilatational viscosity. It is usual for a stable foam to exhibit a high surface dilatational elasticity and a high dilatational viscosity, hence effective defoamers should reduce these properties of the foam.

This is the case for polydimethylsiloxanes added to crude oils. The effect of adding it to crude oil on the dilatational elasticities and viscosities is shown in Table 22.1. Under nonequilibrium conditions, both high bulk and surface viscosity can delay the film thinning and the stretching deformation, which precedes the destruction of a foam. The development of ordered structures, such as liquid crystalline phases in the surface film may also stabilize the foams.

If the diffusion of gas between bubbles is reduced, their collapse is delayed by slowing changes in size and the resulting mechanical stresses. This means that single films can persist longer than the corresponding foams, but this effect is of minor importance in practical situations. Electric effects, such as double layers, form opposite surfaces only for extremely thin films, less than 10 nm, and they occur with ionic surfactants.

Action of Defoamers

At high bulk viscosity, lowering the surface tension is not relevant to foam stabilization, but for all other mechanisms of foam stabilization a change in the

TABLE 22.2 Surface Tensions of Some Defoamers

Material	Surface tension at 20°C/[$\mathrm{m\,N\,m^{-1}}$]
Polyoxypropylene 3 kDalton	31.2
Polydimethylsiloxane 3.9 kDalton	20.2
Mineral oil	28.8
Corn oil	33.4
Peanut oil	35.5
Tributyl phosphate	25.1

surface properties is essential. A defoaming agent will change the surface properties of a foam upon activation. Most defoamers have a surface tension in the range of 20–30 $\mathrm{m\,N\,m^{-1}}$, as shown in Table 22.2.

Two related antifoam mechanisms have been proposed for low surface tension effects of certain defoamer formulations:

1. The defoamer is dispersed in fine droplets in the liquid. From the droplets, the molecules may enter the surface of the foam, which creates tensions that result in the eventual rupture of the film.
2. Alternatively, it is suggested that the molecules form a monolayer rather than spreading. This has less coherence than the original film and so destabilizes it.

Spreading Coefficient

The spreading coefficient is defined as the difference between the surface tension of the foaming medium σ_f, the surface tension of the defoamer σ_d, and the interfacial tension (IFT) of both materials σ_{df}.

$$S = \sigma_f - \sigma_d - \sigma_{df} \tag{22.4}$$

It can be seen that the spreading coefficient S becomes increasingly positive as the surface tension of the defoamer becomes smaller. This indicates the thermodynamic tendency of defoaming.

The above statements are adequate for liquid defoamers that are insoluble in the bulk. However, experience has shown that certain dispersed hydrophobic solids can greatly enhance the effectiveness of defoaming. A strong correlation between the effectiveness of a defoamer and the contact angle for silicone-treated silica in hydrocarbons has been established. It is believed that the dewetting process of the hydrophobic silica causes the collapse of a foam by direct mechanical shock.

CLASSIFICATION OF DEFOAMERS

Defoamer formulations currently contain numerous ingredients. Various classification approaches are possible, including by application, physical form, and chemical type of the defoamer. In general, defoamers contain a variety of active ingredients, both in solid and in liquid states, and a number of ancillary agents such as emulsifiers, spreading agents, thickeners, preservatives, carrier oils, compatibilizers, solvents, and water.

Active Ingredients

Active ingredients are the components of the formulation that control the actual foaming. These may be liquids or solids.

Liquid Components

Because lowering the surface tension is the most important physical property of a defoamer, it is reasonable to classify them by the hydrophobic action of the molecule. Four classes of defoamers are known:

- Hydrocarbons,
- Polyethers,
- Silicones, and
- Fluorocarbons.

Synergistic Antifoam Action by Solid Particles

Dispersed solids are often active defoamers, and some liquid defoamers are believed to be active only in the presence of a solid. The mechanism of action is thought to be that a surface active agent carries the solid particles to the interface where they destabilize the foam.

For example, synergistic defoaming occurs when hydrophobic solid particles are used in conjunction with a liquid that is insoluble in the foamy solution (Frye and Berg, 1989). Mechanisms for film rupture by either the solid or the liquid alone have been elucidated, along with explanations for the observed poor effectiveness of many single-component defoamers.

Silicone Antifoaming Agents

Polydimethylsiloxane is active in nonaqueaous systems, but shows little foam-inhibiting effect in aqueous systems. However, when it is compounded with a hydrophobic-modified silica, a highly active defoamer emerges.

Several factors contribute to the dual nature of silicone defoamers. Soluble silicones can concentrate at the air-oil interface to stabilize bubbles, while dispersed drops of silicone can accelerate the coalescence process by rapidly spreading at the gas-liquid interface of a bubble, causing film thinning by surface transport (Mannheimer, 1992).

Silicones exhibit an apparently low solubility in different oils. In fact, they dissolve slowly, at a rate that depends on the viscosity of the oil and the concentration of the dispersed drops. The mechanisms of the critical bubble size and the reason for a significantly faster coalescence at a lower concentration of silicone can be explained in terms of the higher interfacial mobility, as shown by the bubble rise velocities.

Ancillary Agents

In addition to the defoamer itself, certain ancillary chemicals are incorporated into the formulation, for example, to effect emulsification or to enhance the dispersion of the formulation.

Surface Active Components

Emulsifiers are essential in oil-water emulsion systems to promote dispersion in aqueous foaming systems.

Carriers

The formulation of a defoamer should be suitable for prolonged storage before use. A carrier system makes the defoamer easy to handle, able to deliver the active defoamer components to the foaming system, and stabilize the defoaming formulation.

Often, carriers are low viscosity organic solvents, such as aliphatic hydrocarbons. The carrier itself may also exhibit defoaming properties. Water is often used as carrier fluid for oil-in-water emulsions.

USES IN PETROLEUM TECHNOLOGY

Defoamers are used in oil extraction, such as in drilling muds and cementation, and also directly with crude oil.

Aqueous Fluid Systems

Alcohols

Higher aliphatic alcohols with polyethylene oxide and polypropylene oxide are particularly effective at reducing the gas content of drilling solutions (Ponomarev et al., 1992).

An aliphatic alcohol with 8–32 carbon atoms can be used together with a solid carrier. The carrier should not swell in aqueous media and consists of particles with an average size of less than 150–200 μ. The carrier adsorbs the alcohol (Pless et al., 1989, 1991). Carrier materials can be sawdust, ground rice hulls, ground nutshells, or clays. Other carrier materials may include solids that are commonly added to drilling and other well fluids as fluid loss additives or bridging agents.

Fatty Acid Esters

More environmentally acceptable defoamers are based on fatty acid esters of hydroxy alcohols, such as sorbitan monooleate (Zychal, 1986) or sorbitan monolaurate in combination with diethylene glycol monobutyl ether as a cosolvent (Davidson, 1995). They are as effective as conventional materials, but those based on acetylenic alcohols are less toxic, especially to marine organisms, and are readily biodegradable. The defoamer compositions are used in water-based hydrocarbon well fluids during oil and gas well drilling, completion, and workover, especially in marine conditions.

Aerosil®

Aerosil as a solid additive in combination with diesel is active as a defoamer (Khoma, 1993). The aerosil is modified with bifunctional silicoorganic compounds and the composition is added to the drilling solution as a 3–5% suspension, in an amount of 0.02–0.5% of Aerosil.

Polyoxirane

Polyoxirane-containing formulations have a low cloud point, good ability to reduce surface and IFTs, good wettability, and limited tendency to disperse. The oxirane-methyloxirane copolymers (Matyschok and Janik, 1990) are nontoxic and show high stability in both acidic and alkaline environments. Their poor stability against oxidation can be improved through chemical modification (blocking hydroxide groups) or by using an alkaline catalyst, which acts as an inhibitor of the self-oxidation process.

A composition of polypropylene glycol, particulate hydrophobic silica, and a fatty acid methyl ester, or an olefin or linear paraffin as a liquid diluent, are proposed for well stimulation jobs (Chatterji et al., 2000).

Well Treatment and Cementation

When a foamed well treatment fluid must be disposed of on the surface, a defoaming composition may be added to destroy the foam, thus facilitating its disposal (Chatterji and King, 2009).

Examples of such defoaming compositions include compositions of glycerol tristerate and aliphatic hydrocarbons, or propylene glycol and polyethylene oxide.

An example is shown in Table 22.3.

Polyethylene oxide esters can be included in drilling or treatment fluids to provide a demulsifying and defoaming action on foams (Smith et al., 2008). Their action is time and temperature dependent; it can be controlled in situ.

Lecithin is a phospholipid found in living organisms as a major component of cell membranes, along with protein and cholesterol. Lecithin may be synthesized from choline, is used as a stabilizer and emulsifier in foods, and is environmentally acceptable.

TABLE 22.3 Defoaming Composition (Chatterji and King, 2009)

Compound	[%]
Isononanoic acid amide	15
Polypropylene glycol 3000	20
Ethoxlated and propoxylated fatty alcohol	35
Ethoxlated and propoxylated *n*-butanol	27.5
Hydrophobic precipitated silica	2
Hydrophobic fumed silica	0.5

Lecithin can be used in defoaming agents in cement compositions, but because of its high inherent viscosity, a solvent that is capable of reducing this viscosity, e.g., butanol is also included. In addition, hydrophobic particles, such as calcium stearate may be added (Szymaski et al., 2007).

Plugging Agents

The foaming of plugging agents that have a large content of lignosulfonate can be prevented by introducing polymethylsiloxane and tributyl phosphate (Zobs et al., 1989). A synergistic effect is observed since polymethylsiloxane simultaneously displaces the adsorbed molecules of the foam stabilizer (lignosulfonate) from the foam film, and tributyl phosphate reduces the surface viscosity of the film.

Gas-Oil Separation

In its natural state, at the pressure of the reservoir, crude oil contains dissolved gases. When the pressure is reduced, the gases are liberated and troublesome foam can develop. There are three ways to prevent foaming in gas-oil separation (Callaghan et al., 1986):

1. Based on prior knowledge of crude oil foaming properties, a separator large enough to cope with foam formation may be installed.
2. The amount of foam can be reduced by injecting a defoamer.
3. The gas-oil separator can be equipped with a mechanical device to destroy or prevent a foam.

So understanding the factors that inhibit foaming is of great importance, since it yields a basic knowledge of how the materials in question will foam. It can also be used to predict how individual crude oil compositions will work with different defoamers.

Fluorosilicones and Fluorocarbons

Chlorofluorocarbons were early defoamers, but the use of these compounds has been replaced by pure fluorosilicones (Callaghan and Taylor, 1991). One of the first formulations free of chlorofluorocarbons was described in the early 1990s.

A water-continuous emulsion containing 85–98% of a fluorosilicone oil and 2–15% of an aqueous surfactant solution (Taylor, 1991) is suitable for use in the separation of crude oil that contains associated gas. The additive may be used in both aqueous and nonaqueous systems and allows fluorosilicone oils to be used without the need for environmentally damaging chlorofluorocarbons.

Freshly extracted degassing crude oil can be defoamed with fluorinated norbornylsiloxanes (Berger et al., 1986). The compounds are highly effective and show a broad area of application for defoaming degassing crude oils of different origins. The compounds can be used in concentrations as low as 20 ppm.

Polydienes

Polydienes modified with organosilicons find application as antifoaming or deaeration agents for oil field treating of crude oil (Berger et al., 1988).

High-Temperature Defoamers

Polyisobutylene compounds are particularly effective in high-temperature [300–1000°F (150–540°C)] treatments of hydrocarbon fluids (Hart, 1995, 1998), such as the distillation of crude oil and coking of crude oil residues. They are less expensive than silicone-based compounds.

Natural Gas

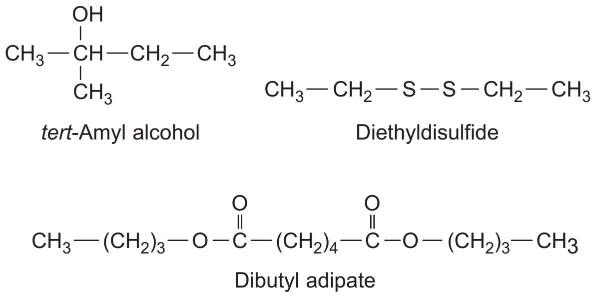
Desulfurization of natural gas can be achieved by bubbling it through an alkaline solution. Defoamers are added to avoid foaming.

A mixture of dialkylphthalate of higher isoalcohols, in excess of the respective isoalcohols, is used as an antifoaming composition in the purification of natural gas. H_2S and CO_2 are removed by using aqueous solution of amine (Denisov et al., 1992). Amyl alcohol and diethyl disulfide are used to enhance the defoaming (Agaev and Kuliev, 1992). The mixture contains 35–50% tributyl phosphate and 20–25% amyl alcohol. The rest, diethyl disulfide, is an industrial waste.

Esters such as dialkyl polypropyleneglycol adipate and dibutyl adipate are also used as defoamers to remove H_2S and CO_2 from natural gas by bubbling it through an amine solution (Gabidulina et al., 1992). Use of the these components increases the efficiency of foam destruction. The compounds in question are shown in Figure 22.1.

Distillation and Petroleum Production

Air entrainment and foaming in hydrocarbon liquids can cause operational problems in high-speed machinery in physiochemical processes such as petroleum production, distillation, cracking, coking, and asphalt processing.



$CH_3-\overset{OH}{\underset{CH_3}{C}H}-CH_2-CH_3$

$CH_3-CH_2-S-S-CH_2-CH_3$

$CH_3-(CH_2)_3-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-CH_3$

FIGURE 22.1 Amyl alcohol, diethyl disulfide, and dibutyl adipate.

Antimicrobial Antifoam Compositions

In addition to the typical constituents of a defoamer formulation, a water carrier with a quaternary ammonium salt silane compound (Gentle and White, 1990) can be included, which acts as an antimicrobial agent. The silane is fixed to the surface of the silica.

REFERENCES

Agaev, G.A., Kuliev, T.A., 1992. Antifoam composition for amine desulphurisation of natural gas – contains tributylphosphate, and additional amyl alcohol and diethyl-disulphide to increase efficiency. SU Patent 1 736 550, assigned to Nat Gas Trans Process Inst., May 30, 1992.

Berger, R., Fink, H.F., Heilen, W., Holthoff, H., Weitemeyer, C., 1988. Use of organosilicon modified polydienes as antifoaming and antibubble agents in organic systems (verwendung von organosiliciummodifizierten polydienen als entschaeumungs- und entlueftungsmittel fuer organische systeme). EP Patent 293 684, assigned to Goldschmidt AG, December 7, 1988.

Berger, R., Fink, H.F., Koerner, G., Langner, J., Weitemeyer, C., 1986. Use of fluorinated norbornylsiloxanes for defoaming freshly extracted degassing crude oil. US Patent 4 626 378, assigned to Goldschmidt AG, December 2, 1986.

Callaghan, I.C., Gould, C.M., Hamilton, R.J., Neustadter, E.L., 1983. The relationship between the dilatational rheology and crude oil foam stability. i. preliminary studies. Colloids Surf. 8 (1), 17–28.

Callaghan, I.C., Hickman, S.A., Lawrence, F.T., Melton, P.M., 1986. Antifoams in gas-oil separation. In: Proceedings Volume no. 59, Royal Society of Chemical Industry Div Ind. Appl of Surfactants Symp., Salford, England, April 15–17, 1986, pp. 48–57.

Callaghan, I.C., Taylor, A.S., 1991. Fluorosilicone anti-foam additive composition for use in crude oil separation. GB Patent 2 234 978, assigned to British Petroleum Co. Ltd., February 20, 1991.

Chatterji, J., Cromwell, R.S., King, B.J., 2000. Defoaming compositions for well treatment fluids. EP Patent 1 018 354, assigned to Halliburton Energy Serv., July 12, 2000.

Chatterji, J., King, B.J., 2009. Defoaming methods and compositions. US Patent 7 517 836, assigned to Halliburton Energy Services, Inc., Duncan, OK, April 14, 2009.

Davidson, E., 1995. Defoamers. WO Patent 9 509 900, assigned to Imperial Chemical Inds Pl, April 13, 1995.

Denisov, M.A., Matishev, V.A., Safronov, K.K., Smirnova, L.A., Sverdlik, V.L., Andre, L.S., et al., 1992. Antifoaming composition – contains higher 4–20C iso-alcohol dialkyl phthalate, and

8–12C iso-alcohol. SU Patent 1 775 125, assigned to Moscow Gubkin Oil Gas Inst., Orenburg Gas Process Wks, and Kuskovo Plast Assoc. Chem., November 15, 1992.

Frye, G.C., Berg, J.C., 1989. Mechanisms for the synergistic antifoam action by hydrophobic solid particles in insoluble liquids. J. Colloid. Interface Sci. 130 (1), 54–59.

Gabidulina, L.I., Matishev, V.A., Safronov, K.K., Sverdlik, V.L., Zarubina, T.P., Andre, L.S., et al., 1992. Antifoam composition for use in purification of natural gas – contains dialkyl polypropylene-glycol adipate, and dibutyl adipate. SU Patent 1 775 126, assigned to Moscow Gubkin Oil Gas Inst., Kuskovo Plast Assoc. Chem., and Orenburg Gas Process Wks, November 15, 1992.

Gentle, T.M., White, W.C., 1990. Antimicrobial antifoam compositions and methods. EP Patent 351 828, assigned to Dow Corning Corp., January 24, 1990.

Hart, P.R., 1995. Control of foam in hydrocarbon fluids. US Patent 5 472 637, assigned to Betz Laboratories Inc., December 5, 1995.

Hart, P.R., 1998. Methods for inhibiting foam in crude oils. US Patent 5 800 738, assigned to Betzdearborn Inc., September 1, 1998.

Khoma, M.I., 1993. Composition of foam-extinguishing agent for drilling solutions – contains waste from production of hydrophilic and hydrophobic aerosil, modified with bifunctional silico-organic compound and diesel oil. SU Patent 1 795 977, assigned to Assoc. Ukr. Surface Chem. Inst., February 15, 1993.

Mannheimer, R.J., 1992. Factors that influence the coalescence of bubbles in oils that contain silicone antifoamants. Chem. Eng. Commun. (113), 183–196.

Matyschok, H., Janik, R., 1990. Defoamers in drilling muds (srodki przeciwpianowe w pluczkach wiertniczych). Nafta (Pol) 46 (7–9), 120–123.

Owen, M.J., 1996. Defoamers. In: Kirk-Othmer, (Ed.), Encyclopedia of Chemical Technology, 4th ed., vol. 7. John Wiley and Sons, New York, Chichester, Brisbane, pp. 929–945.

Pless, M.L., Kercheville, J.D., Augsburger, J.J., 1989. Defoamer composition for use in water based drilling fluids. EP Patent 339 762, assigned to Baroid Technology Inc., November 2, 1989.

Pless, M.L., Kercheville, J.D., Augsburger, J.J., 1991. Defoamer composition for use in water based drilling fluids. AU Patent 608 681, assigned to Baroid Technology Inc., April 11, 1991.

Ponomarev, D.M., Vakhrushev, L.P., Gavrilov, B.M., Gorlov, S.G., Koshelev, V.N., Mojsa, Y.N., et al., 1992. Foam-extinguishing agent for drilling solutions – contains individual higher alcohol(s) or their mixture and block copolymer of ethylene and propylene oxide. SU Patent 1 720 681, assigned to Borehole Reinforc Res. Inst., March 23, 1992.

Smith, K.W., Miller, J., Gatlin, L.W., 2008. Topical defoamer and demulsifier. US Patent 7 348 297, assigned to Clearwater International, LLC, Houston, TX, March 25, 2008.

Szymaski, M.J., Wilson, J.M., Lewis, S.J., Waugh, B.K., 2007. Cement compositions comprising environmentally compatible defoaming agents and methods of use. US Patent 7 273 103, assigned to Halliburton C Energy Services, Inc., Duncan, OK, September 25, 2007.

Taylor, A.S., 1991. Fluorosilicone anti-foam additive. GB Patent 2 244 279, assigned to British Petroleum Co. Ltd., November 27, 1991.

Zobs, V.Y., Belikov, G.V., Sheldybaev, B.F., Shaposhnikov, Y.I., Tikhonov, V.N., 1989. Regulating the density of plugging agents. Neft Khoz (5), 29–31.

Zychal, C., 1986. Defoamer and antifoamer composition and method for defoaming aqueous fluid systems. US Patent 4 631 145, assigned to Amoco Corp., December 23, 1986.

Chapter 23

Demulsifiers

EMULSIONS IN PRODUCED CRUDE OIL

During its production most crude oil occurs as a water-in-oil emulsion whose continuous phase depends on the water to oil ratio, the natural emulsifier systems contained in the oil, and the origin of the emulsion. The emulsifiers are complex chemically, and to overcome their effect, petroleum-emulsion demulsifiers developed. As new oil fields are developed, and as production conditions change in older fields, there is a constant need for new, effective demulsifiers.

The emulsion must be separated before the crude oil can be accepted for transportation, to meet the residual salt and water content quality criteria for a delivered crude oil. The water content must be less than 1%.

The separated salt water still contains certain amounts of residual oil, in an oil-in-water emulsion. Separation of the residual oil is necessary for ecological and technical reasons, because the water is used for secondary production by waterflooding, and residual oil would increase the injection pressure. Also, the presence of water-in-oil emulsions often leads to corrosion and to the growth of microorganisms in the water-wetted parts of the pipelines and storage tanks.

Before distillation, at the refinery, the salt content is often further reduced by a second emulsification with fresh water, followed by demulsification. Crude oils with high salt contents could cause breakdown and corrosion at the refinery, and an emulsion breaker, or demulsifier, is used to break the emulsion at the lowest possible concentration and, with little or no additional consumption of heat, to bring about a complete separation of the water and reduce the salt content to a minimum.

Both oil- and water-soluble demulsifiers are in use, the latter most widely. Emulsions vary in stability with the oil type and degree of weathering. Emulsions that have a low stability will break easily with chemical emulsion breakers.

Broken emulsions will form a foam-like material, called *rag*, which retains water that is not part of the stable emulsions. The most effective demulsifier must always be determined for the particular emulsion. Demulsifiers are often

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added to the emulsion at the wellhead to take advantage of the temperature of the freshly raised emulsion to hasten the demulsification step.

WATERFLOODING

Waterflooding is used to improve oil recovery. The entrained water forms a water-in-oil emulsion with the oil. In addition, salts such as sodium chloride, calcium chloride, and magnesium chloride may be dissolved in the emulsified water.

OIL SPILL TREATMENT

Specific oil spill demulsifiers can be applied to oil spills in low concentrations to prevent mousse formation for significant periods of time and cause a large reduction in oil-water interfacial tension (IFT). The best of these was found to prevent emulsification at dosages as low as 1 part inhibitor to 20,000 parts of fresh oil at 20°C (Buist and Ross, 1987). At dosages of 1:1000, at temperatures higher than 10°C, the chemical also results in significant and rapid dispersion of the oil. The performance of the chemical falls off sharply at for very low temperatures or highly weathered oil.

DESIRED PROPERTIES

Demulsifiers for crude oil emulsions should have the following properties:

- Rapid breakdown into water and oil with minimal amounts of residual water,
- Good shelf life, and
- Rapid preparation.

MECHANISMS OF DEMULSIFICATION

Stabilization of Water-oil Emulsions

The stability of water-oil emulsions relies on interfacial layers, which mainly consist of colloids present in the crude oil-asphaltenes and resins. Water-soluble demulsifiers displace the original emulsion stabilizers from the interface, and a change in wetting by the formation of inactive complexes may occur. Oil-soluble demulsifiers displace the colloids originally present, and neutralize the stabilization effect of additional emulsion breakers and the breakup resulting from interface eruptions (Kotsaridou-Nagel and Kragert, 1996).

Interfacial Tension Relaxation

The effectiveness of a crude oil demulsifier correlates with a reduction in the shear viscosity and the dynamic tension gradient of the oil-water interface. The IFT relaxation occurs faster with an effective demulsifier (Tambe et al., 1995). Short relaxation times imply that IFT gradients at slow film thinning are suppressed. Electron spin resonance experiments with labelled demulsifiers indicate that they form reverse-micelle-like clusters in the bulk oil (Mukherjee and Kushnick, 1987). The slow unclustering of the demulsifier at the interface appears to be the rate-determining step in the tension relaxation process.

PERFORMANCE TESTING

The trial-and-error method of choosing an optimal demulsifier to treat a given oil field water-in-oil emulsion effectively is time-consuming, but there are methods to correlate and predict performance.

Spreading Pressure

The performance of demulsifiers can be predicted by the relationship between its film pressure and solvent properties (Singh, 1994). The surfactant activity of the demulsifier depends on its bulk phase behavior when dispersed in the crude oil emulsions, which can be monitored by determining the demulsifier pressure-area isotherms for adsorption at the crude oil-water interface.

Characterization by Dielectric Constant

In a study, the dielectric constants of emulsions and demulsifiers were measured using a portable capacitance meter, and bottle tests were conducted according to the API specification (Ajienka et al., 1993). The results showed that the dielectric constants can be used effectively to screen and rank demulsifiers, but a confirmatory bottle test should be conducted to assist in the rapid selection of the most effective.

Shaker Test Methods

A study by Environment Canada and the U.S. Minerals Management Service attempted to develop a standard test for emulsion breaking agents (Fingas et al., 1993). Nine types of shaker test methods were tried. Although the results are comparable, a stable water-in-oil emulsion must be used to yield reproducible results. Tests with unstable emulsions showed non-reproducible and inconsistent results.

Viscosity Measurements

Water content and viscosity measurements in certain systems show a correlation to emulsion stability (Fingas et al., 1994). Viscosity provides a more reliable measure of emulsion stability, but measurements of the water content are more convenient. Mixing time, agent amount, settling time, and mixing energy all impact the effectiveness of an emulsifier.

Screening

^{13}C nuclear magnetic-resonance spectrometric (NMR) chemical shifts give information about structure chemicals. The chemical shifts can be correlated with other data, such as bottle tests, and evaluated by statistical methods. In a series of experimental work (Macconnachie et al., 1993, 1994) using principal component analysis, NMR and bottle test data were used to cluster more than 100 demulsifiers into only a few distinctly different chemical groups. Similar chemical types showed similar demulsification performances, which means that evaluations can be made on the basis of demulsifier chemistry.

Only a few of the distinctly different emulsifiers need to be tested before the optimization procedure can start. Because the chemical characterization by NMR imaging takes only a fraction of the time of a bottle test, it is possible to focus more rapidly on optimizing the dosage of the demulsifier.

CLASSIFICATION OF DEMULSIFIERS

The chemicals used as demulsifiers can be classified according to their chemical structure, their application, or according to the oil type used.

Two major groups of chemicals are used:

- Non-ionic demulsifiers and
- Ionic demulsifiers.

Common Precursor Chemicals

Polyalkylene Oxides

Polyalkylene oxides are substances of the following general structure:

$$HO{-}(CH_2{-}CHR{-}O)_x{-}H$$

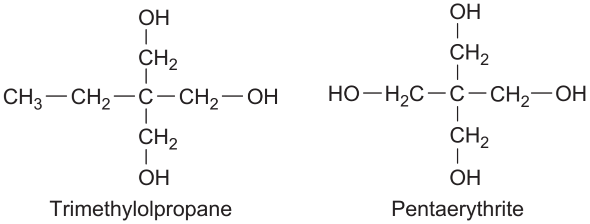
The most important additives are polyethylene oxide, polypropylene oxide, and polybutylene oxide. They are also referred to as polyalkylene glycol (PAG), but this name is only correct strictly for derivatives of 1,2-diols.

Polypropylene oxide has a molar mass of 250–4,000 Dalton. The lower molecular homologs are miscible with water, whereas the higher molecular weight polypropylene oxides are only sparingly soluble. They are formed by the polyaddition of, for example, propylene oxide (PO) to water or propanediol. The simplest examples are di-, tri-, and tetrapropyleneglycol.

There are also block copolymers of ethylene oxide (EO) and PO:

$$HO{-}(R_1{-}O)_x{-}(R_2{-}O)_y{-}H$$

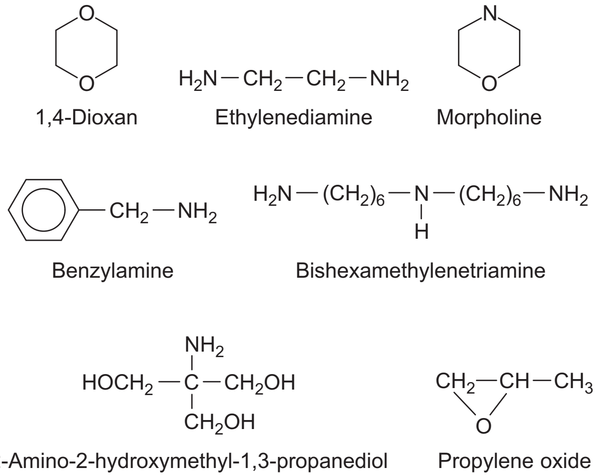
Polytetramethyleneglycol (polytetrahydrofuran) is formed by the ring opening polyetherification of tetrahydrofuran. Branched polyalkylene oxides are formed using polyfunctional alcohols such as trimethylolpropane and pentaerythrite, c.f., Figure 23.1. The products are liquids or waxes depending on the molar mass. Polyalkylene oxides are often precursors for demulsifiers.



Trimethylolpropane

Pentaerythrite

FIGURE 23.1 Polyfunctional alcohols.



1,4-Dioxan

Ethylenediamine

Morpholine

Benzylamine

Bishexamethylenetriamine

2-Amino-2-hydroxymethyl-1,3-propanediol

Propylene oxide

FIGURE 23.2 Ethers and amines.

Polyamines

Polyamines are usually open chain compounds with primary, secondary, or tertiary amino groups. Alternatively, polyimines can be used. Imines are compounds with the =N− group or cycles such as ethyleneimine. Examples of oligoamines and polyamines are ethylene diamine, propanediamine, and 1,4-butanediamine and the respective products of condensation such as diethyleneamine, dipropylenetriamine, and triethylenetetramine. The compounds are colorless to yellowish liquids or solids that react with alkalis. Suitable amines and ethers are shown in Figure 23.2.

Polyamines can also be synthesized by the cationic ring opening polymerization of ethyleneimines (aziridines), trimethyleneimines (azetidines), and 2-oxazolines.

Polyalkylene imines are polyamines whose structure is divided into linear and branched types as shown below.

Linear: $H_2N{-}(CH_2{-}CH_2{-}NH)_xH$ and
Branched: $H_2N{-}(CH_2{-}CH_2{-}N(CH_2{-}CH_2{-}NH_2))_xH_2$.

Linear polyalkylene imines only have amino groups in the main chain, whereas branched polyalkylene imines have amino groups in both the main and side chains. In general, nitrogen atoms comprise every third or fourth atom. Linear polyethyleneimine is insoluble in benzene, diethyl ether, acetone, and water at room temperature, but is soluble in hot water.

Ethoxylation

The reaction is also referred to as *ethoxylation*, *oxethylation*, or more generally, *oxalkylation*. It is the insertion of one or more $CH_2CH_2{-}O{-}$ groups into a molecule of EO. The reaction works with compounds with acidic hydrogen atoms.

Fatty alcohols, alkyl phenols, fatty amines, fatty acid esters, mercaptans, and imidazoline are suitable compounds for ethoxylation. The reaction runs at 120–220°C under pressure (approximately 1–5 bar). The products are generally linear ethers and polyethers that have a hydroxyl functionality at one end of the chain. Depending on the amount of EO used, a distribution of homologous ethoxylates are formed. Alkaline catalysts, such as sodium methylate, are used to obtain a broad Schulz-Flory distribution, whereas bivalent salts (calcium acetate, strontium phenolate) give a narrow Poisson distribution. Acid catalysts, e.g., antimony pentachloride, also give a narrow distribution, but give 1,4-dioxan as an undesired by-product.

Acetylenic Surfactants

These compounds can be used to resolve or break water and oil emulsions, particularly those encountered in desalter or oil field dehydration vessels (Engel et al., 2010).

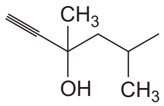
Some acetylenic compounds that form precursors for surfactants are shown in Figure 23.3. These tertiary acetylenic diols are reacted with EO or PO to form oligomers. As a catalyst, trimethylamine is recommended. This type of surfactant is known for its good balance of equilibrium and dynamic surface-tension-reducing capabilities with few of the negative features of traditional non-ionic and anionic surfactants (Lassila et al., 2005).

DEMULSIFIERS IN DETAIL

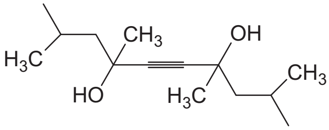
Common demulsifiers are listed in Table 23.1.

Polyoxyalkylenes

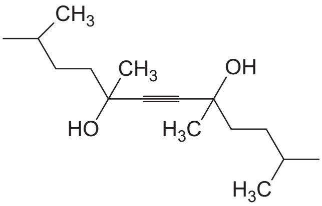
A process for separating crude oil emulsions of the water-in-oil type based on certain EO–PO block polymers and certain polyglycidol ethers of phenol-formaldehyde–condensation products has been described (Kupfer et al., 1989a, 1991, 1993a).



3,5-Dimethyl-1-hexyn-3-ol



2,4,7,9-Tetramethyl-5-decyne-4,7-diol



2,5,8,11-Tetramethyl-6-dodecyne-5,8-diol

FIGURE 23.3 Acetylenic diol precursors (Engel et al., 2010).

Polypropylene glycol or a polybutylene oxide with a molecular weight in the range of 7–20 kDalton is modified with EO or a diglycidyl ether (Taylor and Mgla, 1995). Glycide derivates of polyethylene glycols (PEGs) can be prepared by acid-catalyzed or base-catalyzed reaction with 0.5–10% diepoxides (McCoy et al., 1987). The diepoxides are aromatic or aliphatic precondensates that are used commonly as constituents for epoxide resins, such as the diglycidyl ether from bisphenol-A, and their oligomers. The modification leads to increased molecular weight.

Because of the high molecular weight of the modified PAG, the oil dehydration already occurs when used alone. The compound acts synergistically with other conventional demulsifiers.

Several patents propose polyalkylene oxide block copolymers as demulsifiers. The block copolymers can be modified with a vinyl monomer (Buriks and Dolan, 1986). Diglycidyl ethers (Buriks and Dolan, 1988) can be used as modifiers or they can be modified with polyamines.

The preparation procedure can be quite complex. For example, a water-in-oil demulsifier is prepared by the following steps (Taylor, 1996):

1. Reacting a high molecular weight PAG with EO to form a PAG/EO adduct,
2. Esterifying the PAG/EO adduct with a diacid anhydride to form a diester,
3. Reacting the diester with a vinyl monomer, and
4. Additionally esterifying the product of step (3) with a polyhydric material.

TABLE 23.1 Demulsifiers

Demulsifier	Type	References
Tannin-based blends	WiO	Kremer (1993)
Diallyl dimethyl ammonium chloride polymer	OiW	Hart et al. (1999), and Ramesh and Sivakumar (1994, 1997)
Amphoteric acrylic acid (AA) copolymer	OiW	Braden (1996)
Copolymer of polyglycol acrylate	OiW	Fock et al. (1986b)
Poly1-acryloyl-4-methyl piperazine	OiW	
Vinyl phenol polymers[b]	OiW	
Ethoxylated or epoxidized PAG	WiO	
Polydimethyl diallyl ammonium chloride	OiW	Hart (1995)
Alkoxylated fatty oil		
Oxalkylated polyalkylene polyamines	WiO	Elfers et al. (1993)
Crosslinked oxalkylated polyalkylene polyamines	OiW	
Phenol-formaldehyde resins		Abdullaev et al. (1992), and Stephenson and Deshazo (1993)
Dithiocarbamates	OiW	Durham et al. (1989); Rivers (1992), and Thompson and Asperger (1987, 1989a,b, 1990a,b, 1991a,b,c, 1992a,b)
Polythioalkyloxides	WiO	Scholl et al. (1989a)
Polyether polyurethane	WiO	Scholl et al. (1989b), and Taylor (2000)
Sulfonated polystyrenes	OiW	Lundberg et al. (1988)
Asphaltenes		
Acid-modified polyol	LS	Lauer et al. (2001)

LS Liquid-solid separation
OiW Oil-in-water use
WiO Water-in-oil use

A blend of a propoxylated-ethoxylated block copolymer of a bis-hydroxyalkyl ether and a propoxylated-ethoxylated block copolymer of 2-hydroxymethyl-1,3-propanediol has been described as a demulsifier (Toenjes et al., 1992a,b). The blend is partially crosslinked with a vinyl monomer dissolved in an organic aprotic solvent with a pH of 5.0 or lower. The first block copolymer is prepared by polycondensing a dipropylene glycol, or diethylene glycol with PO. Next, the resulting propoxylated diol is reacted with EO to produce the block copolymer. The second copolymer is prepared by polycondensing 2-amino-2-hydroxymethyl-1,3-propanediol, with PO to provide a polymer having preferably 10–25 oxypropylene units.

Next, the propoxylated diol is reacted with EO to produce a block copolymer of 5–10 EO units. The two block copolymers are dissolved together in an organic aprotic solvent, such as toluene, xylene, trialkyl benzene, cyclohexane, heptane, or hexane.

Branched polyesters contain oxalkylated primary fatty amines or oxalkylated polyamines together with at least trivalent oxalkylated alkanol that is responsible for branching. The condensation is achieved with a dicarboxylic acid or a dicarboxylic acid anhydride (Böse et al., 1988). In this way, branched polyoxyalkylene mixed polyesters are formed. Suitable solvents are water or organic solvents.

The branched polyoxyalkylene mixed polyesters have a high demulsifier effect. Over usual range of oil-processing temperatures, complete water removal, and a reduction of the salt content is rapidly achieved.

In heavy oil reservoirs with highly porous sands, cyclic steamflooding may cause the formation of stable emulsions, which can block the production paths in the wellbore. In steam cycle treatments, a blend of oxyalkylated alkanolamines and sulfonates showed a dramatic improvement over non-chemically enhanced steam cycles (Castro, 2001).

Block polymers or copolymers of EO and PO can be chain-extended or crosslinked, respectively, with diisocyanates, dicarboxylic acids, formaldehyde, and diglycidyl ethers (Augustin and Kehlenbach, 1992).

A blend of a polyoxyalkylene-polysiloxane copolymer and an alkoxylated phenol-formaldehyde resin is useful as a demulsifier (Psaila, 1987, 1990). The polyoxyalkylene units in the copolymer have a molecular weight below 500 Dalton, and the polysiloxane units have 3–50 silicon atoms. The resin has a phenol/aldehyde ratio of 2:1 to 1:5 and an average molecular weight of 500–20,000 Dalton.

The composition shows synergistic demulsification activity when compared with the individual components. The siloxane units can be either in blocks (Koerner and Schaefer, 1988, 1991) of the polyoxyalkylene-polysiloxane copolymer or randomly distributed (Graham et al., 1987a,b).

Vinyl Polymers

A water-soluble demulsifier is an emulsion tetrapolymer of methyl methacrylate, butyl acrylate, AA, and methacrylic acid (MA) (Bhattacharyya, 1992). Styrene may also be added to give a pentapolymer. The polymer is of random orientation and has a molecular weight of approximately 10 k Dalton. It is a low viscous chalk-white fluid that is soluble in water at a pH of 6–7.

Emulsion breakers are made from AA or MA copolymerized with hydrophilic monomers (Barthold et al., 1995). The acid groups of AA and methacrylic acid are oxalkylated by a mixture of polyglycols and polyglycol ethers to provide free hydroxyl groups on the molecule.

The copolymers are made by conventional methods, for example, by free radical copolymerization in solution, emulsion, or suspension, and the oxalkylation is performed in the presence of an acid catalyst, which is neutralized by an amine when the reaction is complete.

Hydrophobic polymers with some hydrophilic groups can be obtained by an emulsion polymerization technique. Suitable monomers are nitrogen-containing acrylics and methacrylics: allyl monomers such as dimethyl amino ethyl methacrylate, dimethyl aminopropyl methacrylamide, diethylaminoethyl methacrylate, dimethyl amino ethyl acrylate, diethylaminoethyl acrylate, and nitrogen containing allyl monomers (e.g., diallylamine and *N*,*N*-diallylcyclohexylamine) (Braden and Allenson, 1991a,b). Methacrylic momomers are shown in Figure 23.4.

If the polymer is to remain in emulsion, it is important that the pH of the water phase remains at or above 8 otherwise it will start to dissolve in water, and the polymer emulsion will break.

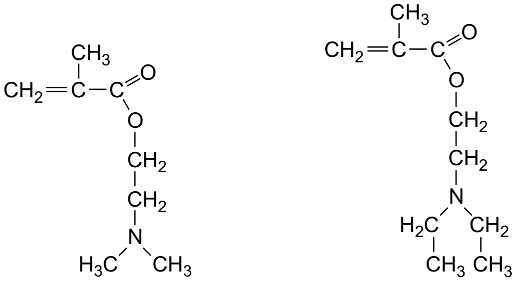
The pH of the aqueous phase of the broken emulsion, after doing the job, can be adjusted to alkaline ranges, which will cause the salts of the polymers converted into inactive species. The aqueous phase of the broken emulsion can then be reinjected into a hydrocarbon-containing formation to recover additional hydrocarbons or bitumen (McCoy et al., 1987) as an improved oil recovery process.

Substrates coated with alkyl phenol-polyethylene oxide-acrylate polymer (Fitzgerald et al., 1992) are useful for demulsifying naturally occurring crude oils. The monomers include oxethylated alkyl phenols, such as oxethylated nonyl phenol with 6–12 ethoxy units, which are esterified with acrylate.

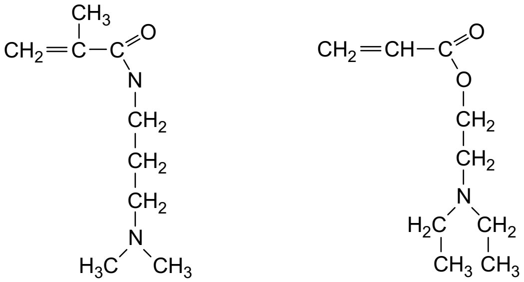
Quaternary ammonium salts of 1-acryloyl-4-methyl piperazine, shown in Figure 23.5, can be prepared by methylation with methyl chloride and dimethyl sulfate. These monomers can be polymerized by radical polymerization, either alone or with a comonomer (Fong and Halverson, 1989) such as acrylamide (AAm). Certain basic polyamides can be further prepared by reacting piperazine derivatives with amines (Hendricks et al., 1996).

A terpolymer can be obtained from a water-soluble non-ionic monomer, such as AAm; a cationic monomer, such as 3-acrylamidopropyltrimethyl ammonium chloride; and a hydrophobic monomer, such as an alkyl-AAm or alkyl acrylate (Jacques et al., 1988) or methacrylamide or methacrylate, respectively. The terpolymer is water-dispersible.

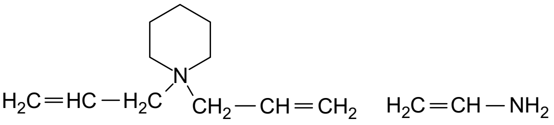
A cationic copolymer of acryloxyethyltrimethyl ammonium chloride and AAm (Hart et al., 1995, 1996) shows efficacy in breaking oil-in-water and water-in-oil emulsions under a wide variety of conditions. The preferred



Dimethylaminoethyl methacrylate Diethylaminoethyl methacrylate



Dimethylaminopropyl methacrylamide Diethylaminoethyl acrylate



N,*N*-diallylcyclohexylamine Diallylamine

FIGURE 23.4 Methacrylic monomers for demulsifiers.

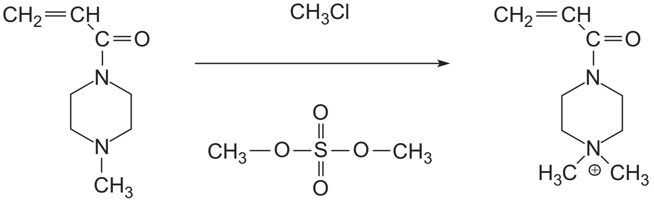


FIGURE 23.5 Quaternary ammonium salts of 1-acryloyl-4-methyl piperazine.

copolymer contains 40–80 mol-% acryloxyethyltrimethyl ammonium chloride, and is effective in a matrix that includes high percentages of oil at high temperatures.

Special polymerization techniques (Byrne et al., 1994) have been performed in aqueous solution with a polyvalent anionic salt in the presence of a water-soluble cationic polymer. The latter acts as a dispersant. A water-soluble seed polymer and an insoluble cationic polymer are also present.

A polymer of monoallylamine is water-soluble (Roark, 1986, 1990). It is used for breaking oil-in-water emulsions.

A combination of aluminum chlorohydrate and a polyamine, such as polydimethyl diallyl ammonium chloride, in aqueous solution is effective oil-in-water emulsion at elevated temperatures (Hart, 1995).

Copolymers of a cationic monomer and a vinyl alkoxysilane may be prepared by conventional vinyl polymerization technique including solution polymerization in water and emulsion polymerization with either free radical initiators or redox initiators.

The cationic monomer can be a diallyl dimethyl ammonium halide, a dimethyl amino ethyl acrylate quaternary salt, or a dimethyl amino ethyl methacrylate quaternary salt (Sivakumar and Ramesh, 1996). The copolymers may be in solid, dispersion, latex, or solution form. In particular, copolymers of diallyl dimethyl ammonium chloride and vinyl trimethoxysilane will have a molecular weight in the range from 100–1,000 k Dalton.

The following are monomers for copolymers of allyl-polyoxyalkylenes with acrylics (Fock et al., 1986a,b):

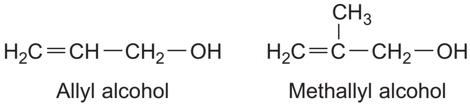
- Polyoxyalkylene ethers of allyl alcohol or methallyl alcohol,
- Acrylic or methacrylic alkyl esters with up to 20 carbon atoms in the alkyl group,
- Acrylic or methacrylic acid, and
- Acrylamide or methacrylamide.

The copolymers may be mixed with other demulsifiers, in particular with alkoxylated novolaks and copolymers that are obtainable by copolymerization of one or more polyoxyalkylene ethers of allyl or methallyl alcohol, c.f., Figure 23.6, with vinylesters of alkyl monocarboxylic acids.

Polymers of vinyl phenol are obtained by hydrolyzing polyacetoxystyrene, c.f., Figure 23.7 (Buriks et al., 1991, 1992). The respective phenol salts can be used. The demulsifier is applicable to oil-in-water emulsions and does not require the use of zinc or other heavy metals, hence it does not cause the environmental problems inherent to such metals.

Polyamines

Extensive examples of the preparation of polyamine-based demulsifiers have been given in the literature (Treybig et al., 2009).



$H_2C{=}CH{-}CH_2{-}OH \qquad H_2C{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2{-}OH$

FIGURE 23.6 Allyl alcohol and methallyl alcohol.

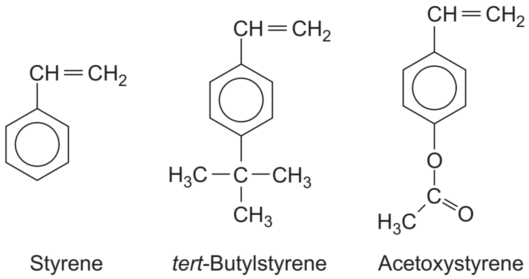


FIGURE 23.7 Styrenes.

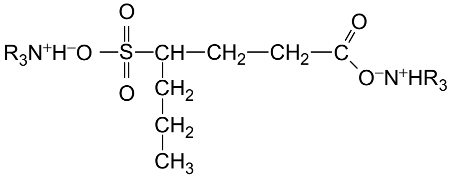


FIGURE 23.8 Quaternized carboxylic sulfonic acid salts.

Polyalkylene polyamine salts are prepared by contacting polyamines with organic or inorganic acids. The polyamines have a molecular weight of at least 1 kDalton and ranging up to the limits of water solubility (McCoy, 1987). In the demulsification of the aqueous phase of broken bitumen emulsions, the pH is adjusted to deactivate the demulsifier, so that the water may then be used in subsequent in situ hot water or steamfloods of the tar sand formation.

To mitigate the effects of corrosion resulting from the presence of salts, the salt concentration should be reduced to around 3–5 ppm. Brine droplets in crude oil are typically, stabilized by a mixture of surface active components such as waxes, asphaltenes, resins, and naphthenic acids that bind electrostatically to the surface of the droplets. Such components provide an interfacial film, resulting in diminished droplet coalescence. Adding water can decrease the concentration of the surface active components on the surface of each droplet, since the number of droplets goes up while the concentration of the demulsifier remains constant.

The amount of water required for desalting may be minimized by adding a chemical emulsion breaker that is capable of displacing surface active components from the brine droplets. Quaternized carboxylic sulfonic acid salts, shown in Figure 23.8, are useful for desalting (Varadaraj et al., 2001). Preferably, the chemical emulsion breaker is used in combination with a delivery solvent, such as diethylene glycol monobutyl ether.

Alkoxylated polyethyleneimines are obtained by reacting polyethyleneimine with a molecular weight of 2.5–35 kDalton with an excess of PO and EO with respect to the ethyleneimine unit in the polyethyleneimine (Elfers et al., 1993, 1995). The compounds can be used for the demulsification of petroleum emulsions in a temperature range of 10–130°C.

Alkyl amine ethoxylates may be used as quaternary salts (Hart, 1993). The amount necessary to break the emulsion is generally 1–100 ppm.

In the same way, a crosslinked oxalkylated polyalkylene polyamine can be obtained by preparing a completely oxalkylated polyalkylene polyamine with a degree of polymerization of 10 to 300, crosslinked with a polyalcohol. The demulsifying agent is made from a mixture of the crosslinked oxalkylated polyalkylene polyamine with 25–75% of an oxethylated or oxypropylated isoalkyl phenol-formaldehyde resin (Baur, 1989).

Crosslinking can also be achieved, if the polyamine is modified with a vinyl monomer (Buriks and Dolan, 1989a,b, 1993). Such mixtures are substantially free of copolymers derived from a PAG and a diglycidyl ether.

Glycidyl ether additives are obtained by esterification of alkoxylated primary fatty amines and additives of polyether-block polymers and glycidyl ethers with dicarboxylic acids (Kupfer et al., 1989b). They are used as demulsifiers to break oil emulsions and, as quaternized products, they are suitable as corrosion inhibitors.

Polyamides

Cationic condensation products of the reaction between a dicarboxylic acid or an ester or acid halide and a quaternized aminoalkyl amine are recommended for breaking crude oil emulsions from fireflooding (Chen and Son, 1992).

In general, polyalkylene polyamides-amines are obtained by their condensation with dicarboxylic acids. The materials are alkoxylated with an excess of EO or PO or 1,2-butylene oxide (Barthold et al., 1991).

Compositions of an *N*,*N*-dialkylamide of a fatty acid in a hydrocarbon solvent and a mutual oil-water solvent are useful for the prevention of sludge formation or emulsion formation during the drilling or workover of producing oil wells (Romocki, 1995, 1996a,b).

Ordinary dicarboxylic or dimeric fatty acids are condensed with fatty amines to give emulsion breakers (Hille et al., 1994a,b; Kupfer et al., 1993b, 1995). Oxalkylated fatty amines and fatty amine derivatives can also act as corrosion inhibitors and pour point depressants.

Quaternary oxalkylated polycondensates can be prepared by esterification of an oxalkylated primary fatty amine with a dicarbonic acid, with an organometallic titanium compound catalyst (Hofinger and Schellenberg, 1989). The reaction product is then oxalkylated in the presence of a carbon acid (Hofinger et al., 1987). These polycondensates can be used as demulsifiers for crude oil emulsions, or as corrosion inhibitors in installations for the production of natural gas and crude oil.

Phenolics

A study on a phenol-formaldehyde resin, a commonly used demulsifier, elucidated how various parameters such as IFT, interfacial shear viscosity, dynamic

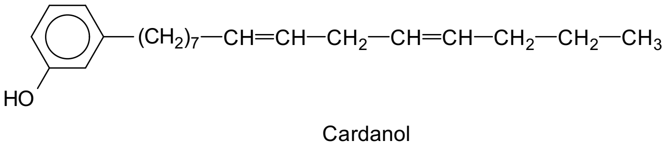


FIGURE 23.9 Cardanol.

IFT gradient, dilatational elasticity, and demulsifier clustering affected the demulsification effectiveness (Mukherjee and Kushnick, 1987).

Products from oxalkylated alkyl phenol-formaldehyde resins, alcohols, bisphenols, or amines have been described as demulsifiers (Elfers et al., 1996).

Condensation products of cardanol (Figure 23.9), an alkyl phenol, and an aldehyde can be further ethoxylated, or may be sulfonated by the addition of sodium bisulfite in the presence of a free radical initiator. Cardanol is a naturally occurring phenol manufactured from cashew nut shell liquid.

Unsaturated acids may be added to the phenolic hydroxides of these resins, and the resulting adduct may be copolymerized with AA (Diaz-Arauzo, 1995). The compositions show good emulsion-breaking performance, especially when used in blends with other compositions.

Alkoxylated Fatty Oils

An alkoxylated fatty oil is used in a non-ionic composition (Wall et al., 1996). It has low solubility in the main emulsion phase. The process is used for breaking emulsions used in wellbore drilling fluids and in oil recovery.

Biodemulsifiers

Microbial cell surfaces form microbial demulsifying agents (biodemulsifiers). Three bacteria, namely *Nocardia amaraebacteria*, *Corynebacterium petrophilum*, and *Rhodococcus aurantiacus*, were tested for their ability to break simple and complex water-in-oil and oil-in-water emulsions (Kosaric, 1989). It was found that cells harvested at the early stage of growth were more active in the demulsification of water-in-oil emulsions, whereas the cells harvested at a stationary phase of growth were more active for oil-in-water emulsions.

The demulsifying capability was associated with the cell surface itself and could not be destroyed by heating or drastic chemical treatments, except for alkaline methanolysis, which destroyed the activity. Microbial aerobic and anaerobic sludges have also been shown to demulsify water-in-oil emulsions, which opens interesting opportunities for biologic waste water treatment processes.

Cactus Extract

A biodemulsifier has been developed that is based on a cactus extract, an activator for the cactus extract, and a carrier liquid. The cactus extract is made from the leaves and stems of the prickly pear, or *Opuntia*, family (Kunkel, 1991). The leaves and stems of the cactus are brought to a rolling boil in water at the ratio of about 1 pound of prickly pear cactus parts to 1.75 gallons of water. The fibrous solids are then separated from the extract by screening, filtering, centrifuging, pressing, or other suitable techniques. The resulting extract is then treated with citric acid to inhibit fermentation. The resulting cactus extract is most effective as a water-oil separator and is accompanied by a detergent activator.

Alkylpolyglycosides

Oxalkylated alkylpolyglycosides have a low toxicity and are biodegradable (Berkhof et al., 1992). The amount of demulsifier to be used to break crude oil emulsions is related to the mass of the emulsion. The maximal mass is 1–1,000 ppm; the temperature is preferably 40–80°C.

REFERENCES

Abdullaev, Y.G., Aliev, R.G., Akhmedov, S.M., Zejnally, S.M., Mekhtieva, N.A., Salaeva, K.A., et al., 1992. Breaking down of oil emulsion – by treating with potassium salt of phenol-formaldehyde resin, modified with benzylamine. SU Patent 1 705 332, January 15, 1992.

Ajienka, J.A., Ogbe, N.O., Ezeaniekwe, B.C., 1993. Measurement of dielectric constant of oilfield emulsions and its application to emulsion resolution. J. Pet. Sci. Eng. 9 (4), 331–339.

Augustin, T., Kehlenbach, R., 1992. Breaking of water-in-oil emulsions. CA Patent 2 057 425, assigned to Bayer AG, June 15, 1992.

Barthold, K., Baur, R., Crema, S., Oppenlaender, K., Lasowski, J., 1995. Method of demulsifying crude oil and water mixtures with copolymers of acrylates or methacrylates and hydrophilic comonomers. US Patent 5 472 617, December 5, 1995.

Barthold, K., Baur, R., Fikentscher, R., Lasowski, J., Oppenlaender, K., 1991. Alkoxylated polyamines containing amide groups and their use in breaking oil-in-water and water-in-oil emulsions (alkoxylierte amidgruppenhaltige polyamine und deren verwendung zum brechen von oel-in-wasser und wasser-in-oel-emulsionen). EP Patent 264 755, April 10, 1991.

Baur, R., Oppenlaender, K., Barthold, K., 1989. Crosslinked oxyalkylated polyalkylenepolyamines and their use as crude oil demulsifiers (vernetzte oxalkylierte polyalkylenpolyamine und ihre verwendung als erdoelemulsionsspalter). EP Patent 147 743, June 28, 1989.

Berkhof, R., Kwekkeboom, H., Balzer, D., Ripke, N., 1992. Demulsifiers for breaking petroleum emulsions (demulgatoren zur spaltung von erdoelemulsionen). EP Patent 468 095, January 29, 1992.

Bhattacharyya, B.R., 1992. Water soluble polymer as water-in-oil demulsifier. US Patent 5 100 582, assigned to Nalco Chemical Co., March 31, 1992.

Böse, W., Hofinger, M., Hille, M., Böhm, R., Staiss, F., 1988. Branched polyoxyalkylene polyesters, process for their preparation and application (verzweigte polyoxalkylenmisch-polyester, verfahren zu ihrer herstellung und ihre verwendung). EP Patent 267 517, May 18, 1988.

Braden, M.L., 1996. Preparation of amphoteric acrylic acid copolymers suitable as oil-in-water emulsion breakers. US Patent 5 552 498, assigned to Nalco Chemical Co., September 3, 1996.

Braden, M.L., Allenson, S.J., 1991a. Method for separating liquid from water using amine containing polymers. US Patent 5 021 167, assigned to Nalco Chemical Co., June 4, 1991.

Braden, M.L., Allenson, S.J., 1991b. Reverse emulsion breaking method using amine containing polymers. US Patent 5 032 285, assigned to Nalco Chemical Co., July 16, 1991.

Buist, I.A., Ross, S.L., 1987. Emulsion inhibitors: a new concept in oil spill treatment. In: Proceedings Volume, 10th Bien, API et al Oil Spill Conference, Baltimore, MD, April 6–9, 1987, pp. 217–222.

Buriks, R.S., Dolan, J.G., 1986. Demulsifier composition and method of use thereof. US Patent 4 626 379, December 2, 1986.

Buriks, R.S., Dolan, J.G., 1988. Demulsifier composition and method of use thereof. EP Patent 268 713, June 1, 1988.

Buriks, R.S., Dolan, J.G., 1989a. Demulsifier compositions and methods of preparation and use thereof. EP Patent 331 323, September 6, 1989.

Buriks, R.S., Dolan, J.G., 1989b. Demulsifier compositions and methods of preparation and use thereof. US Patent 4 877 842, October 31, 1989.

Buriks, R.S., Dolan, J.G., 1993. Demulsifier compositions and methods of preparation and use thereof. CA Patent 1 318 053, May 18, 1993.

Buriks, R.S., Fauke, A.R., Poelker, D.J., 1991. Vinyl phenol polymers for demulsification of oil-in-water emulsions. CA Patent 2 031 122, assigned to Petrolite Corp., June 20, 1991.

Buriks, R.S., Fauke, A.R., Poelker, D.J., 1992. Vinyl phenol polymers for demulsification of oil-in-water emulsions. US Patent 5 098 605, assigned to Petrolite Corp., March 24, 1992.

Byrne, N.E., Marble, R.A., Ramesh, M., 1994. New dispersion polymers for oil field water clarification. EP Patent 595 156, assigned to Nalco Chemical Co., May 4, 1994.

Castro, L.U., 2001. Demulsification treatment and removal of in-situ emulsion in heavy-oil reservoirs. In: Proceedings Volume, SPE West Reg Mtg., Bakersfield, CA, March 26–30, 2001.

Chen, R.G., Son, A.J., 1992. Cationic amide/ester compositions as demulsifiers. US Patent 5 117 058, May 26, 1992.

Diaz-Arauzo, H., 1995. Phenolic resins and method for breaking crude oil emulsions. US Patent 5 460 750, October 24, 1995.

Durham, D.K., Conkle, U.C., Downs, H.H., 1989. Additive for clarifying aqueous systems. GB Patent 2 219 291, assigned to Baker Hughes Inc., December 6, 1989.

Elfers, G., Sager, W., Vogel, H.H., Oppenlaender, K., 1993. Petroleum emulsion breakers. CA Patent 2 082 287, May 8, 1993.

Elfers, G., Sager, W., Vogel, H.H., Oppenlaender, K., 1995. Petroleum emulsion breakers. US Patent 5 445 765, August 29, 1995.

Elfers, G., Sager, W., Vogel, H.H., Oppenlaender, K., 1996. Demulsifier based on an alkoxylate and process for the preparation of the alkoxylate (erdoelemulsionsspalter auf der basis eines alkoxilats und verfahren zur herstellung dieses alkoxilats). EP Patent 549 918, March 27, 1996.

Engel, D.B., Goliaszewski, A.E., McDaniel, C.R., 2010. Separatory and emulsion breaking processes. US Patent 7 771 588, assigned to General Electric Company (Schenectady, NY), August 10, 2010.

Fingas, M., Fieldhouse, B., Bier, I., Conrod, D., Tennyson, E., 1993. Development of a test for water-in-oil emulsion breakers. In: Proceedings Volume, Vol. 2, 16th Environ. Can. Arctic & Mar Oil Spill Program Tech. Seminar, Calgary, Canada, June 7–9, 1993, pp. 909–954.

Fingas, M.F., Tennyson, E., Fieldhouse, B., Bier, I., Conrod, D., 1994. Laboratory effectiveness testing of water-in-oil emulsion breakers. In: Proceedings Volume, 2nd Astm Use of Chem. in Oil Spill Response Symposium, Victoria, Canada, October 10–11, 1994, pp. 41–54.

Fitzgerald, P.H., Wolf, N.O., Clark, C.R., Cords, D.P., 1992. Emulsion breaking using alkylphenol-polyethylene oxide-acrylate polymer coated coalescer material. US Patent 5 156 767, assigned to Conoco Inc., October 20, 1992.

Fock, J., Esselborn, E., Hohner, W., 1986a. Copolymers of polyoxyalkylene ethers and acrylic or methacrylic esters and their use as demulsifiers for petroleum containing water. GB Patent 2 174 096, October 29, 1986.

Fock, J., Esselborn, E., Hohner, W., 1986b. Use of copolymers of polyoxyalkylene ethers of allyl or methallyl alcohols and acrylic or methacrylic esters as emulsion breakers for crude oil containing water (verwendung von copolymerisaten von polyoxyalkyleneth-ern des allyl- und/oder methallylalkohols und acryl- oder methacrylestern als dismul-gatoren fuer wasser enthaltendes erdoel). DE Patent 3 513 550, November 6, 1986.

Fong, D.W., Halverson, A.M., 1989. Removal of dispersed oil from water. US Patent 4 802 992, February 7, 1989.

Graham, D.E., Lidy, W.A., McGrath, P.C., Thompson, D.G., 1987a. Demulsifying process. CA Patent 1 221 602, May 12, 1987.

Graham, D.E., Lidy, W.A., McGrath, P.C., Thompson, D.G., 1987b. Demulsifying process using polysiloxane polyalkene oxide block copolymer. AU Patent 565 533, September 17, 1987.

Hart, P.R., 1993. Method of breaking water-in-oil emulsions by using quaternary alkyl amine ethoxylates. US Patent 5 250 174, October 5, 1993.

Hart, P.R., 1995. Method of breaking reverse emulsions in a crude oil desalting system. CA Patent 2 126 889, assigned to Betz Laboratories Inc., March 3, 1995.

Hart, P.R., Brown, J.M., Connors, E.J., 1995. Method of resolving oil and water emulsions. CA Patent 2 126 782, December 28, 1995.

Hart, P.R., Brown, J.M., Connors, E.J., 1996. Method of resolving oil and brine emulsions. CA Patent 2 156 444, assigned to Betz Laboratories Inc., March 31, 1996.

Hart, P.R., Chen, F., Liao, W.P., Burgess, W.J., 1999. Copolymer formulations for breaking oil-and-water emulsions. US Patent 5 921 912, assigned to Betzdearborn Inc., July 13, 1999.

Hendricks, U.W., Lehmann, B., Litzinger, U., 1996. Process for the separation of oil-in-water emulsions, and basic polyamides (verfahren zur spaltung von oel-in-wasser-emulsionen und basische polyamide). EP Patent 691 150, January 10, 1996.

Hille, M., Kupfer, R., Boehm, R., 1994a. Polyfunctional demulsifiers for crude oils. CA Patent 2 104 506, February 23, 1994.

Hille, M., Kupfer, R., Boehm, R., 1994b. Polyfunctional demulsifiers for crude oils (polyfunktionelle demulgatoren fuer rohoele). EP Patent 584 708, March 2, 1994.

Hofinger, M., Böse, W., Hille, M., Böhm, R., 1987. Quaternary oxyalkylated polycondensates, process for their manufacture and their utilization (quaternaere oxalkylierte polykon-densate, verfahren zu deren herstellung und deren verwendung). EP Patent 212 265, March 4, 1987.

Hofinger, M., Schellenberg, H., 1989. Process for the preparation of polycondensation products from alkoxylated fatty amines, diols and aliphatic dicarboxylic acids (verfahren zur herstellung von polykondensationsverbindungen aus oxalkylierten fettaminen, diolen und aliphatischen dicarbonsaeuren). EP Patent 299 348, January 18, 1989.

Jacques, D.F., Bock, J., Valint, P.L., 1988. Oil-in-water emulsion breaking with hydrophobically functionalized cationic polymers. US Patent 4 741 835, May 3, 1988.

Koerner, G., Schaefer, D., 1988. Utilization of polyoxyalkylene-polysiloxane block mix polimers as demulsifiers for crude oil containing water (verwendung von polyoxyalkylen-polysiloxan-blockmischpolymerisaten als demulgatoren fuer wasser enthaltendes er-doel). DE Patent 3 622 571, June 9, 1988.

Koerner, G., Schaefer, D., 1991. Polyoxyalkylene-polysiloxane block copolymers as demulsifiers for water-containing oil. US Patent 5 004 559, assigned to Goldschmidt AG, April 2, 1991.

Kosaric, N., 1989. Bio-de-emulsifiers. In: Proceedings Volume, 2nd Inst. Gas Technol. Gas, Oil, Coal, & Environ. Biotechnol. Int. Symposium, New Orleans, LA, December 11–13, 1989, pp. 549–587.

Kotsaridou-Nagel, M., Kragert, B., 1996. Demulsifying water-in-oil-emulsions through chemical addition (Spaltungsmechanismus von Wasser-in-Erdöl-Emulsionen bei Chemikalienzusatz). Erdöl Erdgas Kohle 112 (2), 72–75.

Kremer, L.N., 1993. Demulsifying composition. US Patent 5 176 847, assigned to Baker Hughes Inc., January 5, 1993.

Kunkel, F.R., 1991. Water-oil separation method. US Patent 5 000 857, March 19, 1991.

Kupfer, R., Böse, W., Hille, M., Böhm, R., Staiss, F., 1989a. Process for the separation of crude oil emulsions of the water-in-oil type (verfahren zum trennen von erdoelemulsionen vom typ wasser-in-oel). EP Patent 333 141, September 20, 1989.

Kupfer, R., Böse, W., Hille, M., Böhm, R., Staiss, F., 1989b. Esterified glycidyl ether additives and their application (veresterte glycidylether- additionsprodukte und deren verwendung). EP Patent 333 135, September 20, 1989.

Kupfer, R., Böse, W., Hille, M., Böhm, R., Staiss, F., 1991. Process for the separation of crude oil emulsions of the water-in-oil type. US Patent 5 039 450, assigned to Hoechst AG, August 13, 1991.

Kupfer, R., Böse, W., Hille, M., Böhm, R., Staiss, F., 1993a. Process for the separation of crude oil emulsions of the water-in-oil type. CA Patent 1 319 876, July 6, 1993.

Kupfer, R., Hille, M., Boehm, R., Staiss, F., 1993b. Process for separating petroleum emulsions of the water-in-oil type (verfahren zum trennen von erdoelemulsionen vom wasser-in-oel-typ). EP Patent 572 881, December 8, 1993.

Kupfer, R., Hille, M., Boehm, R., Staiss, F., 1995. Process for separation of petroleum emulsions of the water-in-oil type. US Patent 5 385 674, January 31, 1995.

Lassila, K.R., Uhrin, P.A., Schwartz, J., 2005. Acetylenic diol ethylene oxide/propylene oxide adducts and processes for their manufacture. US Patent 6 864 395, assigned to Air Products and Chemicals, Inc. (Allentown, PA), March 8, 2005.

Lauer, R.S., Kremer, L.N., Stark, J.L., McCallum, A., 2001. Method for separating solids from hydrocarbon slurries. EP Patent 1 108 775, assigned to Baker Hughes Inc., June 20, 2001.

Lundberg, R.D., Peiffer, D.G., Newlove, J.C., Werlein, E.R., 1988. Drilling fluids. EP Patent, March 9, 1988.

Macconnachie, C.A., Mikula, R.J., Kurucz, L., Scoular, R.J., 1993. Correlation of demulsifier performance and demulsifier chemistry. In: Proceedings Volume, no. 39, 5th Cim. Petrol. Soc. et al Saskatchewan Petrol. Conference, Regina, Canada, October 18–20, 1993, Preprints.

Macconnachie, C., Mikula, R.J., Scoular, R.J., Kurucz, L.J., 1994. Optimizing demulsifier performance: a fundamental approach. In: Preprints, no. CIM 94-09, 45th Annu. Cim. Petrol. Soc. et al Tech. Mtg., Calgary, Canada, June 12–15, 1994.

McCoy, D.R., 1987. Demulsification of bitumen emulsions using polyalkylene polyamine salts. CA Patent 1 220 151, April 7, 1987.

McCoy, D.R., Cuscurida, M., Speranza, G.P., 1987. Demulsification of bitumen emulsions using water soluble epoxy-containing polyethers. CA Patent 1 225 004, August 4, 1987.

McCoy, D.R., McEntire, E.E., Gipson, R.M., 1987. Demulsification of bitumen emulsions. CA Patent 1 225 003, August 4, 1987.

Mukherjee, S., Kushnick, A.P., 1987. Effect of demulsifiers on interfacial properties governing crude oil demulsification. In: Proceedings Volume, Annu. Aiche Mtg., New York, November 15–20, 1987.

Psaila, A.F., Demulsifiers. 1987. EP Patent 222 587, May 20, 1987.

Psaila, A.F., Demulsifiers. 1990. CA Patent 1 267 584, April 10, 1990.

Ramesh, M., Sivakumar, A., 1994. Hydrophobic demulsifiers for oil-in-water systems. CA Patent 2 124 301, assigned to Nalco Chemical Co., December 10, 1994.

Ramesh, M., Sivakumar, A., 1997. Hydrophobically-modified demulsifiers for oil-in-water systems. US Patent 5 635 112, June 3, 1997.

Rivers, G.T., 1992. Water clarifier. US Patent 5 152 927, assigned to Chemlink Inc., October 6, 1992.

Roark, D.N., 1986. Demulsification of oil-in-water emulsions. US Patent 4 614 593, September 30, 1986.

Roark, D.N., 1990. Demulsification of oil-in-water emulsions. CA Patent 1 264 263, January 9, 1990.

Romocki, J., 1995. Application of *N*,*N*-dialkylamides to control the formation of emulsions or sludge during drilling or workover of producing oil wells. WO Patent 9 522 585, assigned to Buckman Labs Internat. Inc., August 24, 1995.

Romocki, J., 1996a. Application of *N*,*N*-dialkylamides to control the formation of emulsions for sludge during drilling or workover of producing oil wells. EP Patent 745 111, December 4, 1996.

Romocki, J., 1996b. Application of *N*,*N*-dialkylamides to control the formation of emulsions or sludge during drilling or workover of producing oil wells. US Patent 5 567 675, assigned to Buckman Labs Canada Ltd. and Buckman Labs Internat. Inc., October 22, 1996.

Scholl, T., Oberkirch, W., Perrey, H., 1989a. Application of condensation products of thioalkyloxides or polythioalkyloxides with polyalkyloxides as breakers of water-in-oil emulsions (verwendung von kondensationsprodukten von thioalkylenoxiden oder polythio-alkylenoxiden mit polyalkylenoxiden als spalter fuer wasser-in-oel- emulsionen). EP Patent 192 999, April 5, 1989.

Scholl, T., Perrey, H., Augustin, T., Wegner, C., 1989b. Polyurea-modified polyetherurethanes and their use as emulsion breakers for water-in-oil emulsions. US Patent 4 870 151, September 26, 1989.

Singh, B.P., 1994. Performance of demulsifiers: prediction based on film pressure-area isotherms and solvent properties. Energy Sources 16 (3), 377–385.

Sivakumar, A., Ramesh, M., 1996. Demulsification of oily waste waters using silicon containing polymers. US Patent 5 560 832, assigned to Nalco Chemical Co., October 1, 1996.

Stephenson, W.K., Deshazo, J.D., 1993. Method of breaking crude oil emulsions using ethylene carbonate adducts of alkylphenol-formaldehyde resins. US Patent 5 205 964, assigned to Nalco Chemical Co., April 27, 1993.

Tambe, D., Paulis, J., Sharma, M.M., 1995. Factors controlling the stability of colloid-stabilized emulsions. Pt. 4: evaluating the effectiveness of demulsifiers. J. Colloid Interface Sci. 171 (2), 463–469.

Taylor, G.N., 1996. Demulsifier for water-in-oil emulsions and method of use. EP Patent 696 631, assigned to Exxon Chemical Patents In, February 14, 1996.

Taylor, G.N., 2000. Demulsification of water-in-oil emulsions using high molecular weight polyurethanes. GB Patent 2 346 378, assigned to Nalco Exxon Energy Chem. L, August 9, 2000.

Taylor, G.N., Mgla, R., 1995. Method of demulsifying water-in-oil emulsions. EP Patent 641 853, March 8, 1995.

Thompson, N.E.S., Asperger, R.G., 1987. Use of tridithiocarbamic acid compositions as demulsifiers. US Patent 4 689 177, August 25, 1987.

Thompson, N.E.S., Asperger, R.G., 1989a. Dithiocarbamates for treating hydrocarbon recovery operations and industrial waters. US Patent 4 864 075, September 5, 1989.

Thompson, N.E.S., Asperger, R.G., 1989b. Methods for treating hydrocarbon recovery operations and industrial waters. US Patent 4 826 625, May 2, 1989.

Thompson, N.E.S., Asperger, R.G., 1990a. Methods for treating hydrocarbon recovery operations and industrial waters. EP Patent 349 681, January 10, 1990.

Thompson, N.E.S., Asperger, R.G., 1990b. Methods for treating hydrocarbon recovery operations and industrial waters. US Patent 4 956 099, September 11, 1990.

Thompson, N.E.S., Asperger, R.G., 1991a. Methods for treating hydrocarbon recovery operations and industrial waters. US Patent 5 026 483, June 25, 1991.

Thompson, N.E.S., Asperger, R.G., 1991b. Methods for treating hydrocarbon recovery operations and industrial waters. US Patent 5 019 274, May 28, 1991.

Thompson, N.E.S., Asperger, R.G., 1991c. Methods for treating hydrocarbon recovery operations and industrial waters. US Patent 5 013 451, May 7, 1991.

Thompson, N.E.S., Asperger, R.G., 1992a. Method for treating hydrocarbon recovery operations and industrial waters. US Patent 5 089 227, February 18, 1992.

Thompson, N.E.S., Asperger, R.G., 1992b. Methods for treating hydrocarbon recovery operations and industrial waters. US Patent 5 089 619, February 18, 1992.

Toenjes, A.A., Williams, M.R., Goad, E.A., 1992a. Demulsifier compositions and demulsifying use thereof. US Patent 5 102 580, assigned to Petrolite Corp., April 7, 1992.

Toenjes, A.A., Williams, M.R., Goad, E.A., 1992b. Demulsifier compositions and demulsifying use thereof. CA Patent 2 059 387, November 29, 1992.

Treybig, D.S., Chang, K.-T., Williams, D.A., 2009. Demulsifiers, their preparation and use in oil bearing formations. US Patent 7 504 438, assigned to Nalco Company (Naperville, IL), March 17, 2009.

Varadaraj, R., Savage, D.W., Brons, C.H., 2001. Chemical demulsifier for desalting heavy crude. US Patent 6 168 702, assigned to Exxon Research & Eng. Co., January 2, 2001.

Wall, K., Zard, P.W., Barclay-Miller, D.J., Martin, D.W., 1996. Oil recovery process. WO Patent 9 611 044, April 18, 1996.

Appendix 1

List of Tradenames

Accolade® Drilling fluid
Activator™ I 90% oligosaccharide, 10% magnesium oxide
Aculyn™ 28 hydrophobically-modified polyacrylate
Adapta® Filtration control agent
Aerosil® Fumed Silica
Airflex® (Series) Vinyl acetate/ethylene copolymer emulsions
Aldacide® G Biocide, glutaraldehyde
ALL-TEMP® Acrylate tetrapolymer
Aquacol-S® Polyether glycol
Aquagel® Sodium montmorillonite clay
AquaPAC® Polyanionic cellulose
Avanel™ S150 Sulfonated ethylene oxide derivate

BARABUF® Buffer
BARACARB® Ground marble
Barasil™ −S Shale Stabilizer
BARASIL® S Sodium silicate shale stabilizer
BARAZAN® Polysaccharide
Barodense® Ground hematite
BAROID® 41 Ground barium sulfate
Baromega™ Aqueous-based silicate containing resilient graphitic carbon
Benol® White mineral oil
BIO-COTE Wetting agent
BIO-LOSE™ Complexed polysaccharide, filtration control agent
BIO-PAQ™ Water soluble polymer
BIOZAN® Heteropolysaccaride
Black Pearls® Carbon black
Blue Streak™ Compostion containing alcohol ether sulfate. Cocobetaine, and hydroxypropylguar (surfactants)
BORE-DRILL™ Anionic polymer
BRIQUEST® 543 Sodium diethylene triamine pentakismethylene phosphonate
Britolo® 35 USP High viscosity mineral oil
Broma™ FLA Starch

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Captivates® liquid Fish gelatin and gum acacia encapsulation coating
Carbo-Gel® Amine modified, gel-forming organophilic clay
Carbolite™ Sized ceramic proppant
Carbo-Mul™ Emulsifier
Carbotec® -S Polyfatty acids, emulsifier
Carbotron™ Cellulose derivative
Carnation® White mineral oil
CELLEX Carboxymethyl cellulose
Cellosolve® (Series) Solvents for gums, resins, cellulose esters
Celpol® (Series) Polyanionic cellulose
Ceramicrete Magnesium-based ceramic particulate bridging agent
CFR™ 3 Cement friction reducer dispersant
CFR™ (Series) Formaldehyde acetone condensate, dispersant
Chek-Loss® PLUS Ultra-fine lignin
CHEMTROL® X Blend of ground lignitic earth and synthetic maleic anhydride copolymers
ClaySeal® Shale stabilizer
Clay Sync™ Shale stabilizer
Claytrol™ Amine mixture
ClearFRAC™ Stimulating Fluid
COLALIPID™ (Series) Quaternized amines
COLALIPID™ RC Ricinoleamidopropyl PG-dimonium chloride phosphate
COLDTROL™ Fatty alcohol thinner
Corexit® 9527 Dispersant, used in a solution of water and ethylene glycol monobutyl ether
Corning® Water dilutable silicone emulsion

Dacron® Polyethylene terephthalate
Dequest® 2060 Diethylene triamine pentamethylene phosphonic acid
DFE-129™ Acrylamide/AMPS copolymer
DFE-243 Partially hydrolyzed polyacrylamide/trimethylaminoethyl acrylate
Diamond FRAQ™ VES breaker
Diamond FRAQ™ VES System
DiamondFRAQ™ VES System
Disotate® EDTA compound
Disponil® Ether sulfonates (Emulsifiyer)
DOW CORNING® 1430 Antifoam Water-dilutable, 30 percent active silicone emulsion that is designed to control foam in aqueous systems.
DrillAhead® Software
Driltreat™ Wetting agent
Driscal® D Water soluble polymer

EDC95® *n*-Alkane cuts
Elvace (Series) Vinylacetate/ethylene copolymer latex
Empol™ (Series) Oligomeric oleic acid

Endtrate® EDTA compound
Escaid® (Series) Mineral oils
Ethomeen® T-12 *N, N*-bis(2-hydroxyethyl)tallowamine
Ethyl CELLOSOLVE® 2-Ethoxyethanol
Etidronate™ Etidronic acid salt, 1-hydroxyethane 1, 1-diphosphonic acid salt
EZMUD® Partially hydrolyzed polyacrylamide
EZ-Mud® Shale stabilizer
EZ MUL® NT Emulsifier

FACTANT™ Concentrated emulsifier
FILTER-CHEK® Modified Cellulose
Finagreen® BMDF 2-ethyl hexanol fatty acid esters
FLC™ 2000 hole stabilizing fluid loss control agent
FlexPlug® OBM Reactive, nonparticulate lost-circulation materia
FlexPlug® W Reactive, nonparticulate lost-circulation materia
Flo-Chek® Lost circulation additive
FloBloc® 210 Polyvinyl alcohol (cement additive)
FLUORAD™ FC 754 *N, N, N*-trimethyl[3-(per fluorooctanesulfonylamino)-propyl]ammonium iodide
Fracsol™ Trysol Corp.

Gantrez® Methyl vinyl ether/maleic anhydride copolymer
GAS-CHEK® to provide an effective means of helping prevent gas flow into the annulus after cement has been placed
GasStop™ HT Tannin grafted with acrylamide and 2-acrylamido-2-methylpropane sulfonic acid
Geltone® (Series) Organophilic clay
GEM™ 2000 Shale stabilizer
Gencal® 7463 ammonia-basedmodified styrene butadiene latex has been designed foruse in residential carpet applications
Germall® II Biocid compostion
Gloria® High viscosity mineral oil
Glycacil® L Iodopropynl butyl carbamate (biocide)
Go Devil™ II Xanthan gum-based blend, 70% xanthan gum, 20% starch, 9% oligosaccharide, 1% magnesium oxide
Grabber® Flocculant
Gyptron® KT-178 Diethylene triamine tetramethylene phosphonic acid (DETA), Scale inhibitor

Halad® (Series) Fluid loss control additive
Hatcol™ 2372 Polyol ester of dipentaerythritol
Hatcol™ 2926 Polyol ester of dipentaerythritol
Heloxy® 107 Diglycidyl ether of cyclohexane dimethanol
HE™ 300 Polymer from 2-acrylamido-2-methylpropane sulfonic acid, N-vinylpyrrolidone, and acrylamide

Hostadrill™ 2825 Polymer from 2-acrylamido-2-methylpropane sulfonic acid, acrylamide and N-vinyl-N-alkylamide
Hostamer™ 4706 Polymer from 2-acrylamido-2-methylpropane sulfonic acid, acrylamide and N-vinyl-N-alkylamide
Hostamer® V2825 AMPS terpolymer
Hostamer™ V4707 Polymer from 2-acrylamido-2-methylpropane sulfonic acid, acrylamide and N-vinyl-N-alkylamide
HR® (Series) Organic acids (cement set retarder)
HYBRANE® HA1300 Chemical composition of polyester amide
Hydrobrite® 200 White mineral oil
Hydro-Guard® Inhibitive water-based fluid
HYPERDRILL™ CP-904L Acrylamide copolymer

IMPERMEX Pregelatinized cornstarch
Injectrol® (Series) Selants
Interdrill Emul HT® Emulgator
Interdrill® LORM Emulsification system
Invermul® Blends of oxidized tall oil and polyaminated fatty acids
Isopar® (Series) Isoparaffinic solvent
Isopar® L Isoparaffinic solvent
Isoteq™ Drilling fluid

Jeffamine® (Series) Amine capped polyalkoxylene glycol
Jeffamine® D-230 Polyoxypropylene diamine
Jeffamine® EDR-148 Triethyleneglycol diamine
Jeffamine® HK-511 Polyoxyalkylene amine
Jordapon® ACl Sodium cocoyl isothionate surfactant
Jordapon® Cl Ammonium cocoyl isothionate surfactant

Kathon® CG 5-Chloro-2-methyl4-isothiazolin-3-one (biocide)
Kaydol® oil Mineral oil
Kemseal® Fluid loss additive
KEM-SEAL® PLUS NaAMPS/N, N-dimethylacrylamide copolymer
Kleemul® Emulsifier
Kopr-Kote® Aluminum complex lubricant with copper flakes
Kraton® Styrenic block copolymer

LE BASE™ Base drilling fluid
LE SUPERMUL™ Emulsifier
Ligco® Lignite
Ligcon® Causticized lignite
LIQUI-VIS Hydroxyethyl cellulose
Lorm® Emulsifier
Lucant® HC-2000 Hydrocarbon-based non-polar synthetic oil
Lucant® HC-600 Hydrocarbon-based non-polar synthetic oil

MAX-PLEX® Resin and aluminate
MAX-SEAL™ Polyolefin hydrocarbon base fluid
MAX-TROL® Sulfonated resin
Microbond™ Cement expanding additive
MICRO MATRIX® Cement
MicroPolymer™ Multimodal polymer compostion
Microsponge™ Porous solid substrate
Mil-Bar™ Barite weighting agent
Mil-Bar® Barite weighting agent
Mil-Carb® Ground marble
Mil-Gel™ Ground montmorillonite
Mil-Gel-NT® Bentonite quartz mixture
Mil-Pac LV Low viscosity polyamine cellulose
Mil-Temp® Maleic anhydride copolymer
Mirataine® BET-O Disodium oleamidopropyl betaine
Mirataine® T2C Disodium tallowiminodipropionate
Mirataine® TM Dihydroxyethyl tallow glycinate
Mranol® Imidazoline and imidazoline derivatives (cationic surfactants)

N-Dril™ HT Plus Filtration control agent
Newdrill Plus Partially hydrolyzed polyacrylamide
NEW-DRILL® PLUS Partially hydrolyzed polyacrylamide
19N™ Cationic nonemulsifier used in acids and other aqueous fluids to help prevent acid and oil emulsions
NONIDET® P40 Octylphenolpoly(ethylenglycolether), non-ionic detergent

OMNI-MUL™ Non-ionic emulsifier
Organotrol™ 1665 2-Methylbenzyl tallow intercalated monomorillonite

PAC™ -L Filtration control agent
PAC Polyanionic cellulose
Performance® 225N Base Oil
Performatrol® Shale Stabilizer
Permseal® Polymerizable solution as cement additive
PETROFREE® LV Ester based invert emulsion
PETROFREE® SF Olefin based invert emulsion
Plex® Acrylate resin
Plioflex® Styrene butadiene rubber
Pliolite® DF01 Styrene-butadiene copolymer
Plioway® EC1 *p*-Methylstyrene copolymer
Plioway® Ultra 200 *p*-tert-Butylstyrene/p-methylstyrene/2-ethylhexylacrylate/isobutyl ethacrylate copolymer
POLYAC® Polyacrylate
Polybor® Polymeric borate
Polydrill® Anionic polymer

Poly-S.RTM Polymer encapsulation coating
Primene® Primary aliphatic amines with highly branched alkyl chains
PropNET™ Proppant-retention agent
Protecto-Magic™ Ground asphalt
PVP K™ -90 Polyvinylpyrrolidone
PYRO-TROL® Acrylamide/AMPS copolymer

Resinoline® BD2 Tall oil fatty acid
Resomer® RG506 Polylactic acid-co-glycolic acid
Retsch® ZM-1 Grinding mill
Rev Dust Artificial drill solids
REV-DUST™ Calcium Montmorillonite Clay
RHEMOD™ L Modified fatty acid
Rhodafac® RS-410 Poly(oxy-1, 2-ethandiyl) tridecyl hydroxy phosphate

SA™ -541 Causticized hydroxypropyl guar surface treated with sodium borate
Sandlock® Consolidating fluid
Scaletreat® XL14FD Polymaleate
Scotchlite™ Reflective glas
SCR™ -100 Copolymer of 2-acrylamide-2-methylpropane sulfonic acid and acrylic acid
SCR™ -500 Copolymer of 2-acrylamido-2-methylpropane sulfonic acid and itaconic acid
Seppic SIMULSOL AS-48™ Alkylglucoside
SF BASE™ Base drilling fluid
Shale Guard™ NCL100 Shale anti-swelling agent
Silicalite® High surface area amorphous silica
Silwet® Ethyleneoxy surfactants
Sodasorb® Sodium calcium hydrate
Soltex® Sulfonated asphalt
Span® 20 Sorbitan monolaurate
Span® 80 Sorbitan monooleate
Span® 40 Sorbitan monopalmitate
Span® 61 Sorbitan monostearate
Span® 85 Sorbitan trioleate
Span® 65 Sorbitan tristearate
Spectrasyn ULTRA™ Grease formulation
Staflo® PAC
Steelseal® Resilient graphitic carbon
SULFA-TROL® Sulfonated asphalt
Superfloc™ Acrylamide copolymer
Supersyn™ (Series) Lubricating oil
SurFRAQ™ VES Tallow amido propylamine oxide
Suspentone™ Attapulgite clay

Synalox® PB-200 Chain alcohols
Synthemul® (Series) Carboxylated acrylic copolymer

Teflon® Tetrafluoro polymer
Tegopren™ 7006 Siloxane emulsifier
Tergitol® 15-S (Series) Ethoxylated C11-15-secondary alcohols, surfactant
Triton® X (Series) Poly(alkylene oxide), nonionic surfactants
Truvis® Ester basestock lubricant
Tween® 20 Sorbitan monolaurate
Tween® 21 Sorbitan monolaurate
Tween® 81 Sorbitan monooleate
Tween® 85 Sorbitan monooleate
Tween® 40 Sorbitan monopalmitate
Tween® 61 Sorbitan monostearate
Tween® 65 Sorbitan tristearate
Tychem® 68710 Carboxylated styrene/butadiene copolymer
Tylac® CPS 812 Carboxylated styrene/butadiene copolymer

Ultidrill® Hydrocarbon cuts
Unirex S2® Zirconium 2-ethylhexanoate grease

Versawet® NS Wetting agent
VES-STA 1 Gel stabilizer

Wellguard™ 7137 Interhalogen gel breaker
WG-3L VES-AROMOX® APA-T Viscoelastic surfactant
Wolastafil-050-MH-0010™ Methylalkoxysilane coated calcium metasilicate
WS-44 Emulsifier

XAN-PLEX™ D Polysaccharide viscosifying polymer
XANVIS™ Polysaccharide viscosifying polymer
XP07® *n*-Alkane cuts
X-VIS™ Suspension agent

Zeogel® Attapulgite clay

Appendix 2

List of Acronyms

AA Acrylic acid
AAm Acrylamide
AMPS 2-Acrylamido-2-methyl-1-propane sulfonic acid
APG Alkylpolyglucoside
API American Petroleum Institute
ATP Adenosine triphosphate
AWCP Alkaline waste waters of caprolactam production

BIT 1,2-Benzisothiazolin

CMC Carboxymethyl cellulose
CME Carboxymethylated ethoxylated surfactants
CROSERF Chemical Response to Oil Spills Ecological Effects Research Forum
CS Crumbled sheet
CSM Colorado School of Mines
CTAB Cetyltrimethylammonium bromide

DADMAC Diallyldimethylammonium chloride
DBNPA 2,2-Dibromo-3-nitrilopropionamide
DNA Deoxyribonucleic acid
DRA Drag-reducing agent
DSC Differential scanning calorimetry

EDTA Ethylene diamine tetraacetic acid
EG Ethylene glycol
EHA Ethylhexyl acrylate
EO Ethylene oxide
EOR Enhanced oil recovery
EP Extreme pressure agent

HEC Hydroxyethyl cellulose
HPAN Hydrolyzed polyacrylonitrile
HPC Hydroxypropyl cellulose

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HPG Hydropropyl guar
HPLC High performance liquid chromatography
HTHP High temperature/high pressure
HTO Tritiated water

IFP Institute Francais du Petrole
IFT Interfacial tension

LC Liquid crystal

MA Maleic anhydride
MA Methacrylic acid
MEOR Microbial-enhanced oil recovery
MIS Microbiologically influenced souring
MNS Mackay-Nadeau-Steelman

NFC New flux correcting
NMR Nuclear magnetic-resonance
NVP N-vinylpyridine

OBM Oil-based drilling mud
OI Odor index
OOC Offshore Operators Committee

PAA Polyacrylic acid
PAC Polyanionic cellulose
PAG Polyalkylene glycol
PAM Polyacrylamide
PAO Poly-α-olefine
PA Polyamide
PEG Polyethylene glycol
PEO Polyethylene oxide
PHB Poly(3-hydroxybutyrate)
PHPA Partially hydrolyzed polyacrylamide
PMMA Polymethyl methacrylate
POBM Pseudo oil-based drilling mud
PO Propylene oxide
PPCA Phosphino-polycarboxylic acid
PPG Polypropylene glycol
PP Polypropylene
PS Expanded polystyrene
PTFE Polytetrafluoroethylene
PU Polyurethane
PVA Polyvinyl acetate
PVA Polyvinyl alcohol
PVS Polyvinyl sulfonate

RE Rounded edges

SEM Scanning electron microscope
SFI Slurry fracture injection
SWL Sulfite-waste liquor

THP Trishydroxymethylphosphine
TPH Total petroleum hydrocarbon

UHMWPE Ultra high molecular weight polyethylene
UTCHEM University of Texas Chemical Compositional Simulator

VES Viscoelastic surfactant

WBM Water based drilling mud

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