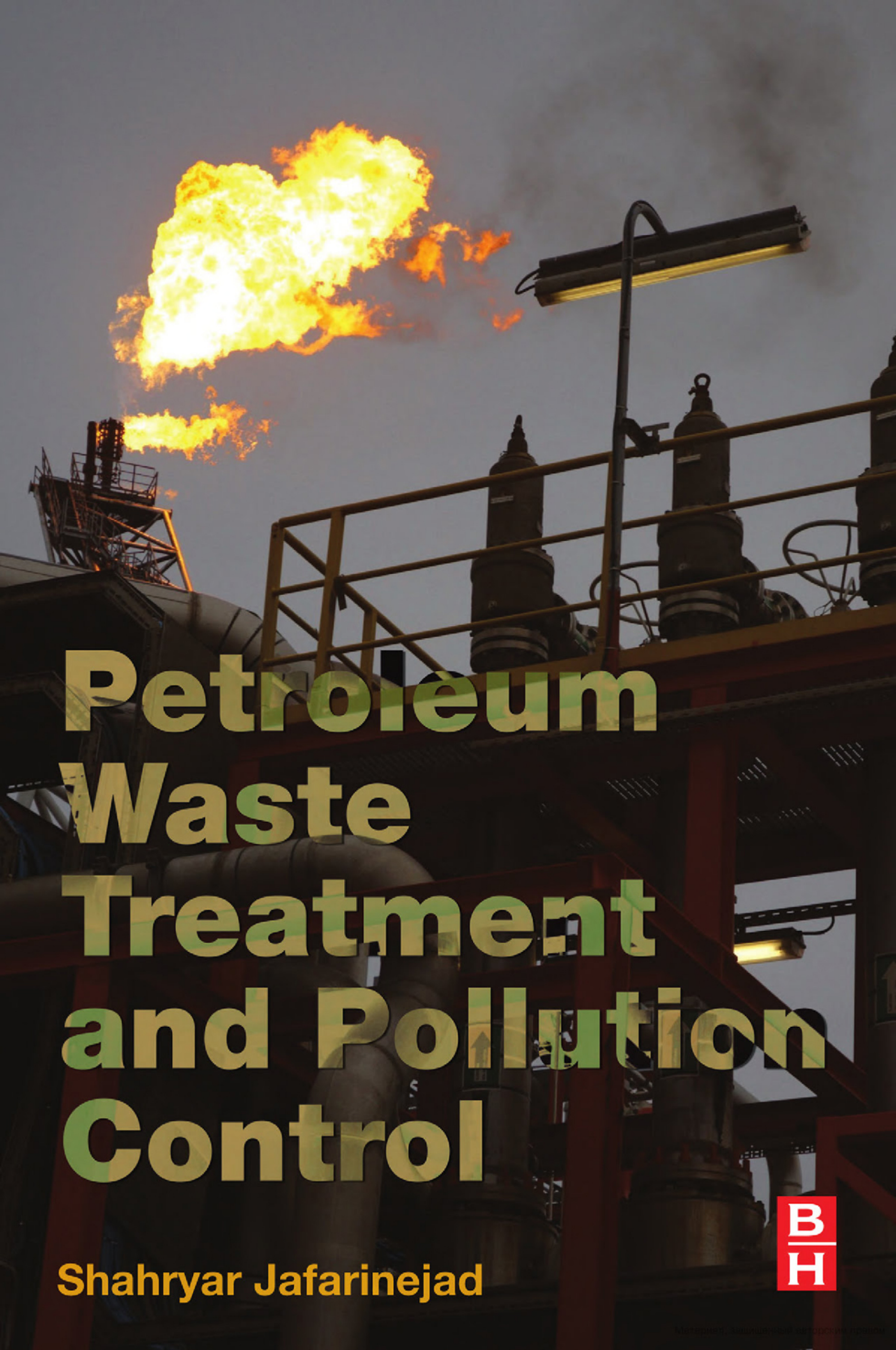

Petroleum Waste Treatment and Pollution Control

Shahryar Jafarinejad

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Dr. Shahryar Jafarinejad received his bachelor of science (B.Sc.) in chemical engineering, master of science (M.Sc.) in chemical engineering—process design, and doctor of philosophy (Ph.D.) in chemical engineering from the School of Chemical Engineering, College of Engineering, University of Tehran. He has taught chemical-engineering courses at the School of Chemical Engineering, College of Engineering, University of Tehran; College of Environment, University of Environment; and in the Department of Chemical Industries at Valiasr Technical College, Technical and Vocational University. He has also supervised undergraduate and graduate students and served as an industry consultant. He is currently an assistant professor of the College of Environment, University of Environment. He has published a book and several peer-reviewed journal and conference papers and has served as an editorial board member and reviewer of engineering journals.

Preface

Petroleum is vital to many industries and in the manufacture of a wide variety of materials; it accounts for a large percentage of the world's energy consumption and thus is a critical concern for many nations. However, the world's growth and its dependency on petroleum have raised concerns about the many environmental challenges within the industry.

The petroleum industry can be divided into four sectors: (1) exploration, development, and production; (2) hydrocarbon processing (refineries and petrochemical plants); (3) storage, transportation, and distribution; and (4) retail or marketing. A considerable amount of air emissions, wastewaters, and solid wastes are generated from the activities and processes in the petroleum industry, and release of these wastes can create adverse impacts to the environment and human health. In addition, oil spills can have disastrous social, economical, and environmental consequences. Thus it is necessary to consider the management of wastes in the petroleum industry. The effective treatment of these wastes has become a worldwide problem due to their hazardous nature and the growth of the petroleum industry around the world.

Postsecondary education and training of industry personnel are essential for environmental protection success in the petroleum industry. This book is a comprehensive reference for industry personnel, undergraduate and graduate students of chemical engineering, environmental engineering, etc., and covers environmental issues and treatment solutions in the petroleum industry.

Chapter 1 gives a general introduction to the petroleum industry. Chapter 2 explains air emissions and estimation, wastewater, and solid wastes from the exploration, development, and production of petroleum; air emissions and estimation, wastewater, solid wastes, and odor emissions from hydrocarbon processing (refineries and petrochemical plants); air emissions and estimation, wastewater, and solid wastes from storage, transportation, distribution, and marketing; and oil spills, including the major oil spills in history, estimation of oil-spill volume on water, on ice and snow, and in or on soils. Chapter 3 focuses on the environmental impacts of the petroleum industry, protection options, and regulations. Chapter 4 discusses oil-spill response technologies. Control and treatment of air emissions in the petroleum industry are explained in Chapter 5. Chapter 6 discusses wastewater management in the petroleum industry; wastewater characterization; selection of oil—water separation and treatment technologies; wastewater treatment (process wastewater pretreatment, primary treatment, secondary treatment, and tertiary treatment or polishing); and wastewater-treatment plants (WWTPs) in the petroleum industry. Finally, Chapter 7 covers solid-waste management in the petroleum industry. This chapter explains solid-waste management practices; selection of treatment and disposal methods; oil recovery and/or removal methods; water-removal methods or dewatering; disposal methods; concerns over spent catalysts in the petroleum industry and their management; and handling of heavy metals.

Although this book is scientifically and technically accurate, some errors may be present; thus constructive suggestions and comments from readers (instructors, students, etc.) using this book are appreciated. They will be incorporated into future reprints or editions of this book.

Shahryar Jafarinejad
August 2016

Acknowledgments

I would like to thank my family, friends, students, and colleagues for supporting and encouraging me while I was preparing for and writing this book. Their encouragement provided me with extra energy when I required it.

I have prepared and written this book by reading and using thousands of pages of papers, fact sheets, reports, manuals, books, etc. I would like to express my sincere gratitude to publishers, companies, and organizations such as Elsevier B.V.; Springer Science and Business Media; John Wiley & Sons, Inc.; The American Chemical Society (ACS); Taylor & Francis Group; University of Toronto Press; InTech; EOLSS Publishers; Gulf publishing company; Hindawi Publishing Corporation; ABB Oil and Gas; American Petroleum Institute (API); US Environmental Protection Agency (US EPA); CONCAWE; European Commission, Joint Research Center; Multilateral Investment Guarantee Agency (MIGA); World Bank Group; Research Triangle Institute (RTI) International; United States Department of Commerce, Bureau of Standards; United states Census Bureau; Organization of the Petroleum Exporting Countries (OPEC); United States Geological Survey (USGS); E&P Forum/UNEP; The International Tanker Owners Pollution Federation (ITOPF) Limited; National Oceanic and Atmospheric Administration (NOAA); Congress of the United States, Office of Technology Assessment (OTA); National Response Team (NRT) Science and Technology Committee; IPIECA; Alaska Clean Seas (ACS); Canadian Center for Energy Information; Department of Environment (DOE) of Malaysia; IL & FS Ecosmart Limited Hyderabad; Ministry of Environment & Forests, Govt. of India; Iranian Ministry of Petroleum; World Health Organization (WHO); Washington State Department of Ecology; United States Forest Service; Tri-State Synfuels Company; OSPAR Commission; Air & Waste Management Association (A&WMA); International Atomic Energy Agency, Vienna; National Drinking Water Clearinghouse; National Research Council; Federation of Canadian Municipalities and National Research Council; Siemens Water Technologies Corp.; Deepwater Horizon; PetroStrategies, Inc.; Statista; Blue Nation Review (BNR); Infoplease; National Atmospheric Emission Inventory (NAEI); SkyTruth; Elastec; Qingdao Guangming Environmental Technology Co., Limited; Royal Dutch Shell plc; Salient News; Ultraspin Technology Pty. Ltd.; Vikoma International Ltd.; Babcock & Wilcox Enterprises, Inc.; Barben Analytical, AMETEK; Energie- en milieu-informatiesysteem (EMIS), VITO; MikroPul; WorleyParsons; The Linde Group; MARINER plus s.r.o. (Flottweg, Solenis); Trevi nv; Schwarz Global Consulting; Yokogawa Corporation of America; etc. In addition, I gratefully thank the authors of the papers, reports, books, etc., cited

in this book. I also offer a general word of thanks to the many people who helped me learn about waste (solid, liquid, and gaseous) treatment and pollution control in the petroleum industry.

Finally, I would like give thanks for the reviewers' comments, which improved the quality of this book, and the Senior Acquisitions Editor, Elsevier Science and Technology Books, Kenneth P. McCombs, Publisher, Joe Hayton, Editorial Project Manager, Peter Jardim, Production Project Manager, Mohanambal Natarajan, Designer, Miles Hitchen and Publishing Director, Cathleen Sether, who supported me in the preparation and publication of this book.

Introduction to the Petroleum Industry

1

1.1 Petroleum

The word “petroleum” means “rock oil,” and is derived from the Latin words petra (rock) and oleum (oil), which come from the Greek words πέτρα and ἔλαιον, respectively (Hyne, 2001; Organization of the Petroleum Exporting Countries (OPEC), 2013; Jafarinejad, 2016a), meaning crude oil and natural gas (Jafarinejad, 2016a). In the other words, petroleum is a mixture of naturally occurring hydrocarbons that may exist in any state, depending on the conditions of subjected pressure and temperature. Petroleum is produced from reservoirs in either liquid (crude oil) or gaseous form (natural gas), depending on the state of the hydrocarbon mixture. Clearly the word petroleum can cover both naturally occurring unprocessed hydrocarbons and petroleum products that are made up of refined hydrocarbons (Speight, 1999; OPEC, 2013; Verşan Kök, 2015; EIA Energy Kids-Oil (Petroleum), 2011; Hyne, 2001).

1.1.1 History

It is not clear exactly when humankind first used petroleum. However, according to Fagan (1991) ancient peoples worshipped sacred fires that were fueled by natural gas seeping into the surface through pores and cracks. It is also known that asphalt, a very viscous form of petroleum, was used to waterproof boats and heat homes as early as 6000 BC. Asphalt was also used as an embalming agent for mummies and in the construction of the Egyptian pyramids around 3000 BC (Fagan, 1991). In addition, more than 4000 years ago, according to Herodotus and Diodorus Siculus, asphalt was used in the construction of the walls and towers of Babylon; there were oil pits near Ardericca (near Babylon), and a pitch spring on Zacynthus (Chisholm, 1911). Great quantities of it were found on the banks of the river Issus, one of the tributaries of the Euphrates. Ancient Persian tablets indicate the medicinal and lighting uses of petroleum in the upper levels of their society (Totten, 2006). Written sources from 500 BC describe how the Chinese used natural gas to boil water (Devold, 2013). By AD 347, oil was produced from bamboo-drilled wells in China (Totten, 2006). Early British explorers to Myanmar documented a flourishing oil extraction industry based in Yenangyaung that, in 1795, had hundreds of hand-dug wells under production (Longmuir, 2001).

Petroleum’s importance to humankind took a giant leap in the late 1800s when it replaced coal as the primary fuel for the machines of the industrial revolution (Fagan, 1991). In 1847, the process to distill kerosene from petroleum was invented by James Young. He noticed natural petroleum seepage in the Riddings colliery at Alfreton, Derbyshire from which he distilled light-thin oil suitable for use as lamp oil, while

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at the same time obtaining a thicker oil suitable for lubricating machinery. In 1848, Young set up a small business refining crude oil (Russell, 2003). In 1859, Colonel Edwin Drake drilled the first successful oil well, with the sole purpose of finding oil. The Drake well was located in the middle of quiet farm country in northwestern Pennsylvania and sparked the international search for an industrial use for petroleum (Devold, 2013). From then many researchers, engineers, companies, and countries helped to develop the petroleum industry. In today's industrialized society, petroleum means power, and it is now important across societies, including in economy, politics, and technology.

1.1.2 Crude Oil

Crude oil consists of approximately 10—14wt% hydrogen and 83—87wt% of carbon. Oxygen (0.05—1.5wt%), sulfur (0.05—6wt%), nitrogen (0.1—2wt%), and metals such as vanadium, nickel, iron, and copper (nickel and vanadium<1000 ppm) are some of the impurities found in crude oil. Crude oil is not a uniform material and its exact molecular and fractional composition varies widely with formation of oil, location, age of the oil field, and the depth of the individual well. Crude oils obtained from different oil reservoirs have widely different characteristics (Speight, 1999; Verşan Kök, 2015; Jafarinejad, 2016a). Speight (1999) reported that the hydrocarbon portion may be as low as 50% by weight, eg, in heavy crude oil and bitumens, or as high as 97% by weight in lighter paraffinic crude oil. Many oil reservoirs contain live bacteria (Ollivier and Magot, 2005; Speight, 1999). Some crude oils are black, heavy, and thick like tar, and others are brown or nearly clear with low viscosity and low specific gravity (Verşan Kök, 2015). Usually four different types of hydrocarbon molecules (alkanes or paraffins (15—60%), naphthenes, or cycloparaffins (30—60%), aromatics or benzene molecules (3—30%), and asphaltics (reminder)) appear in crude oil. The relative percentage of each varies from oil to oil, which determines the properties of the oil (Hyne, 2001).

1.1.3 Natural Gas

An oil well produces predominantly crude oil, with some natural gas dissolved in it. But, a gas well produces predominantly natural gas. Natural gas consists of approximately 65—80% carbon, 1—25% hydrogen, 0—0.2% sulfur, and 1—15% nitrogen. Hydrocarbon molecules of natural gas are generally the paraffin type and range from one to four carbon atoms in length, but up to six carbon atoms may also be found in small quantities. A typical natural gas hydrocarbon composition is 70—98% methane, 1—10% ethane, trace to 5% propane, trace to 2% butane, and trace to 5% pentane and higher molecular weight hydrocarbons, including benzene and toluene (Hyne, 2001; Speight, 1999; Jafarinejad, 2016a). In addition, water vapor, hydrogen sulfide (H_2S), carbon dioxide, helium, nitrogen, and other compounds in the minority may be found in raw natural gas (Devold, 2013; Jafarinejad, 2016a). Gaseous impurities in natural gas that do not burn are called inert (noncombustible). Carbon dioxide, water vapor, helium, and nitrogen are the major inert components in natural gas (Speight, 1999; Hyne, 2001; Jafarinejad, 2016a).

The gas in which methane is the major constituent is called lean gas. Liquefied petroleum gas (LPG) is made from propane gas. Sweet natural gas has no detectable hydrogen sulfide, whereas sour natural gas contains hydrogen sulfide. The natural gas from which the higher molecular weight hydrocarbons have been extracted is called residue gas and the gas derived from petroleum but that is separated at the separation facility at the wellhead is called casing head gas. Wet natural gas contains less than 0.1 gal higher molecular weight hydrocarbons per 1000 ft^3, but dry natural gas contains more than 0.1 gal of such hydrocarbons per 1000 ft^3. Dissolved gas is the gas that occurs as a solution in the petroleum, whereas associated gas is the gas that exists in contact with the petroleum (gas cap) (Speight, 1999; Hyne, 2001). Natural gas from gas and condensate wells in which there is little or no crude oil is called nonassociated gas. Natural gas liquids (NGLs) are very valuable byproducts of natural gas processing that include ethane, propane, butane, iso-butane, and natural gasoline (Devold, 2013).

1.1.4 Petroleum Formation

Petroleum is formed from the accumulation of hydrocarbons. Hydrocarbons accumulate naturally, thousands of feet below the surface of the Earth, from the decomposition of organic materials like plants and marine animals that died many millions of years ago. It is a naturally occurring fluid found in rock formations (OPEC, 2013). In the other words, vast quantities of the remains of decomposed organic materials settled to sea or lake bottoms and mixed with sediments buried in layers of clay, slit, and sand. As further layers settled to the bed, in the lower regions, heat and pressure began to rise. This process caused the organic matter to change, first into a waxy material, which is found in various oil shales around the world, and then with more heat into liquid and gaseous hydrocarbons. Oil or natural gas formation is related to the amount of pressure and the degree of heat, along with the type of biomass. It is believed that more heat produces lighter oil, even higher heat or biomass made predominantly of plant material produced natural gas (Petroleum.co.uk, 2015; Adventures in Energy, 2015; Braun and Burnham, 1993; Kvenvolden, 2006).

1.1.5 Classification and Characterization

In the petroleum industry, crude oil can generally be classified by the geographic location it is produced in (eg, West Texas Intermediate, Brent, or Oman), its gravity, and its sulfur content. Different types of petroleum contain different chemical compositions and properties such as density, viscosity, color, boiling point, pour point, etc., and can vary widely among different crude oils (Speight, 1998, 1999). The chemical compositions of crude oil and natural gas were discussed above. As noted, sulfur is an undesirable impurity in crude oil and natural gas, and when it is burned, forms sulfur dioxide, a gas that pollutes the air and forms acid rains. On the basis of sulfur content, petroleums are classified as sour or sweet. Crude oils with less than 1wt% sulfur content and more than 1wt% sulfur content are called sweet and sour crude oils, respectively (Hyne, 2001).

Crude oils are usually classified or described by specific gravity or density. The commonly used density scales are °API (American Petroleum Institute) and Baume, but °API is usually preferred. The °API and Baume are calculated as (Hyne, 2001):

$$^{\circ}\mathrm{API} = \frac{141.5}{\text{Specific gravity at } 60^{\circ}\mathrm{F}} - 131.5 \tag{1.1}$$

$$\text{Baume} = \frac{140}{\text{Specific gravity at } 60^{\circ}\mathrm{F}} - 130 \tag{1.2}$$

The API gravity is used to classify oils as light, medium, heavy, or extra heavy. As the weight of oil is the largest determinant of its market value, API gravity is exceptionally important. The °API values for each weight are as follows:

- Light crude oil: $^{\circ}\mathrm{API} > 31.1$
- Medium crude oil: °API between 22.3 and 31.1
- Heavy crude oil: $^{\circ}\mathrm{API} < 22.3$
- Extra heavy crude oil: $^{\circ}\mathrm{API} < 10$ (Petroleum.co.uk, 2015)

Not all parties use the same grading. For example, the US Geological Survey (USGS) uses slightly different definitions. According to the USGS, crude oil with a gas-free viscosity between 10,000 and 100 cp is generally called heavy crude oil. In the absence of viscosity data, oil with °API less than 10 is generally considered natural bitumen, whereas oil with API gravity ranging from 10 to 20 °API is considered heavy crude oil. Extra heavy crude oil is used for oil with a viscosity less than 10,000 cp but with °API less than 10 (USGS, 2006). In other words, crude oil with API gravity less than 10 °API is referred to as extra heavy oil or bitumen. Bitumen derived from the oil sand deposits in the Alberta, Canada area has an API gravity of around 8 °API. It can be diluted with lighter hydrocarbons to produce diluted bitumen with an API gravity lower than 22.3 °API, or further "upgraded" to an API gravity of 31 °API to 33 °API as synthetic crude (Canadian Centre for Energy Information, 2012).

The color of crude oil may range from colorless to greenish-yellow, reddish, and brown to black. Light crude oils are transparent, rich in gasoline, and the most valuable, while heavy crude oils are dark colored, viscose, and less valuable (Hyne, 2001).

The English and metric units of crude oil measurements are barrels (bbl) (42 US gallons or 34.97 Imperial gallons) and metric tons, respectively (Hyne, 2001). In the oil industry, quantities of crude oil are often measured in metric tons. We can calculate the approximate number of barrels per metric ton for a given crude oil based on its API gravity:

$$\text{Barrel of crude oil permetric ton} = \frac{1}{\left[\frac{141.5}{\text{API gravity}+131.5} \times 0.159\right]} \tag{1.3}$$

For example, a metric ton of West Texas Intermediate (39.6 °API) would contain about 7.6 barrels (Petroleum.co.uk, 2015).

The English unit and metric unit of volume measurements for natural gas are a standard cubic foot (scf) at 60°F and 14.65 psi and cubic meters (m^3) at 15°C and 101.325 kPa, respectively. A cubic meter is equal to 35.315 cf. Condensate content is measured in barrels per million cubic feet of gas (BCPMM). The English and metric units of heat-content measurements for fuel are British thermal unit (Btu) and kilojoules, respectively. A kilojoule is equal to about 1 Btu (Hyne, 2001).

There are paraffin molecules in all crude oils. Waxes are the paraffin molecules with 18 carbon atoms or longer in length. The pour point is a method to indicate the amount of wax in crude oil and is the lowest temperature at which the oil will still pour before it solidifies. Pour points of crude oils may vary between −60 and 52°C and higher pour points show higher oil wax content. The temperature at which the oil first appears cloudy as wax forms when the temperature is lowered is called cloudy point. It is 1−3°C above the pour point. Low or no wax oils are black, but very waxy oils are yellow (Hyne, 2001).

The correlation index (CI) is used for more direct chemical information. It is based on a plot of specific gravity versus the reciprocal of the boiling point in Kelvin and developed by the US Bureau of Mines. The CI can be calculated as:

$$\mathrm{CI} = 473.7d - 456.8 + \frac{48{,}640}{K} \tag{1.4}$$

where d is specific gravity and K is the average boiling point for a petroleum fraction determined by the standard Bureau of Mines distillation method. Values for CI indicate species in the fraction as:

- CI between 0 and 15: predominance of paraffinic hydrocarbons;
- CI between 15 and 50: predominance of either naphthenes or of mixture of paraffins, naphthenes, and aromatics; and
- CI above 50: predominance of aromatic species.

The viscosity−gravity constant (VGC) and the universal oil products (UOP) characterization factor are generally employed to give an indication of the paraffinic character of the crude oil. The VGC is calculated as:

$$\mathrm{VGC} = 10d - \frac{1.0752\log(\upsilon - 38)}{10 - \log(\upsilon - 38)} \tag{1.5}$$

where d is the specific gravity 60/60°F and υ is the Saybolt viscosity at 39°C (100°F). Because it is difficult to measure the low-temperature viscosity for heavy oil, an alternative equation has been developed in which the 99°C (210°F) Saybolt viscosity is used. The equation is:

$$\mathrm{VGC} = d - 0.24 - \frac{0.022\log(\upsilon - 35.5)}{0.755} \tag{1.6}$$

These equations are not good for low-viscosity oils. The lower amount of the index number indicates the more paraffinic content. The UOP characterization factor can be calculated as:

$$K = \sqrt[3]{\frac{T_B}{d}} \tag{1.7}$$

where d is the specific gravity 60/60°F and T_B is the average boiling point in °R (°F + 460). It depicts the thermal cracking characteristics of heavy oils; this factor for naphthenic oils is approximately 10.5—12.5 and for highly paraffinic oils is approximately 12.5—13 (Speight, 2005).

At a constant volume, the total heat of combustion of a petroleum product can be approximated as:

$$Q_v = 12{,}400 - 2100d^2 \tag{1.8}$$

where Q_v is measured in cal/gram and d is the specific gravity at 60°F. If values in cal/gram multiply by 1.8, it will yield values in Btu/pound.

The thermal conductivity of petroleum-based liquids can be modeled as:

$$K = \frac{0.183}{d}[1 - 0.0003(T - 32)] \tag{1.9}$$

in which K is thermal conductivity in Btu/h.ft^2. °F, d is the specific gravity 60/60°F, and T is temperature in °F.

The specific heat of petroleum oils can be calculated from the following formula:

$$c = \frac{1}{\sqrt{d}}(0.388 + 0.00045T) \tag{1.10}$$

where c is the specific heat in Btu/lb.°F, d is the specific gravity 60/60°F, and T is the temperature in °F. The latent heat of vaporization of petroleum oils can also be modeled as follows:

$$L = \frac{1}{d}(110.9 + 0.09T) \tag{1.11}$$

where L is the latent heat of vaporization in Btu/lb.°F, d is the specific gravity 60/60°F, and T is the temperature in °F.

The heat content of petroleum liquids and vapors can be calculated using the following equations:

$$H_l = \sqrt{d}\left(3.235T + 0.0001875T^2 - 105.5\right) \tag{1.12}$$

$$H_v = \sqrt{d}\left(3.235T + 0.0001875T^2 - 105.5\right) + 925 - 075T \tag{1.13}$$

where H_l and H_v are the heat content of the petroleum liquids and vapors, respectively, d is the specific gravity 60/60°F, and T is the temperature in $°F$ (US Department of Commerce, Bureau of Standards, 1929).

1.2 World Distribution of Petroleum Resources and Reserves

Petroleum is vital to many industries for the maintenance of industrial civilization and thus is a critical concern for many nations. Petroleum accounts for a large percentage of the world's energy consumption (Jafarinejad, 2014, 2016a, 2015a,b). World distributions of petroleum resources and reserves are shown in Figs. 1.1 and 1.2, respectively. Distribution of global oil reserves in 1992−2013 by region is given in Fig. 1.3. These figures show that most of the world's petroleum can be found in the Middle East, which has about 60% of the world's oil reserves. In addition, oil production is largely concentrated in the Middle East and Russia. The countries with the largest petroleum reserves are Saudi Arabia, Canada, Iran, Iraq, Kuwait, UAE, Venezuela, Russia, Libya, Nigeria, Kazakhstan, United States, China, Qatar, Algeria, Brazil, and Mexico.

The types of total world oil reserves are given in Fig. 1.4. As can be seen, most of the world's oils are nonconventional and heavy oil, extra heavy, and bitumen make up about 70% of the world's total oil resources (9−13 trillion bbl; Alboudwarej et al., 2006). The Middle East has the largest conventional crude oil reserves and

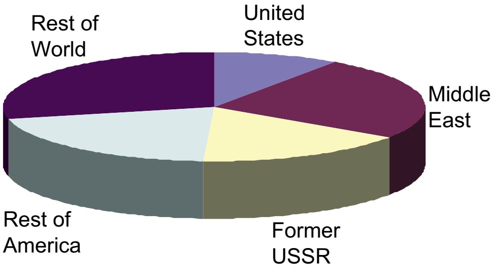

Figure 1.1 World distribution of petroleum resources.
According to Fulkerson, W., Judkins, R.R., Sanghvi, M.K., September 1990. Energy from Fossil Fuels. Scientific American, p. 129.

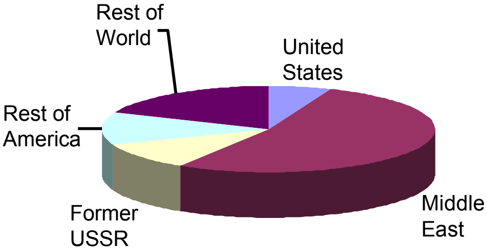

Figure 1.2 World distribution of petroleum reserves.
According to Fulkerson, W., Judkins, R.R., Sanghvi, M.K., September 1990. Energy from Fossil Fuels. Scientific American, p. 129.

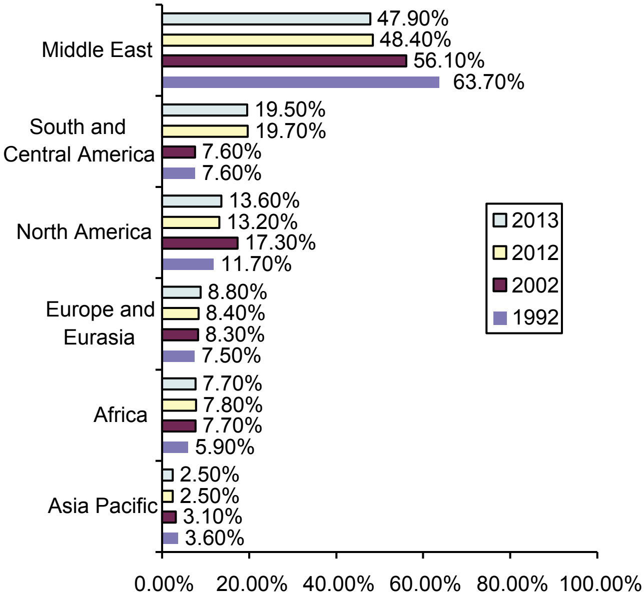

Figure 1.3 Distribution of global proved oil reserves in 1992–2013, by region.
According to Statista, 2015. Distribution of Global Proved Oil Reserves in 1992 to 2013, by Region. [Online] Available from: www.statista.com/statistics.

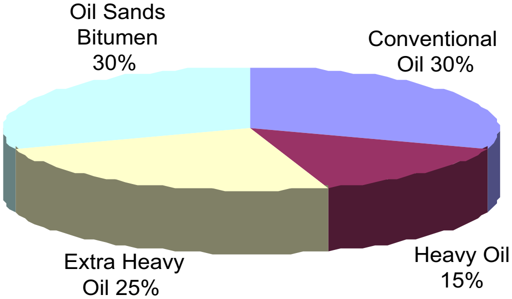

Figure 1.4 Types of total world oil reserves.
According to Alboudwarej, H., Felix, J.J., Taylor, S., Badry, R., Bremner, C., Brough, B., Skeates, C., Baker, A., Palmer, D., Pattison, K., et al., Summer 2006. Highlighting Heavy Oil, Oilfield Review. [Online] Available from: https://www.slb.com/w/media/Files/resources/oilfield_review/ors06/sum06/heavy_oil.pdf.

Canada has the largest heavy crude oil and bitumen reserves in the world (Elk Hills Petroleum, 2010).

Petroleum is usually produced by investor-owned companies (IOC) or national oil companies (NOC). The majority of the world's oil and gas reserves are controlled by NOC. The world's largest oil and gas companies by proven reserves are shown in Fig. 1.5. The National Iranian Oil Company (NIOC), Petróleos de Venezuela S.A., Saudi Arabian Oil Company, Qatar General Petroleum Corporation, Iraq National Oil Company, Abu Dhabi National Oil Company, Kuwait Petroleum Corporation, Nigerian National Petroleum Corporation, National Oil Company (Libya), Sonatrach,

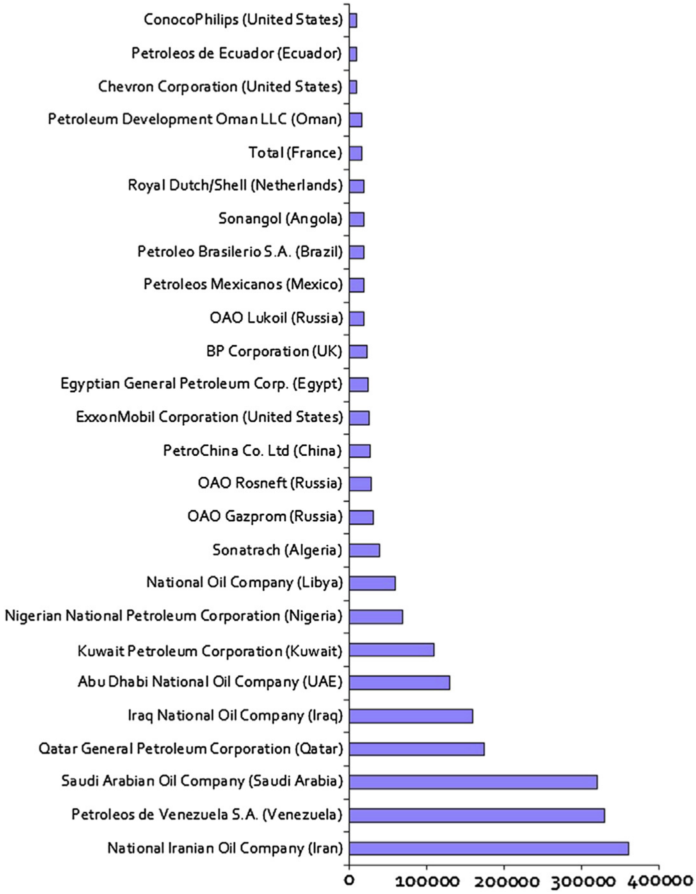

Figure 1.5 The world's largest oil and gas companies by proven reserves (in millions of oil-equivalent barrels).
According to PetroStrategies, Inc., 2015. World's Largest Oil and Gas Companies. [Online] Available from: http://www.petrostrategies.org.

Sonangol, and Petróleos de Ecuador are Organization of Petroleum Exporting Countries (OPEC) members (PetroStrategies, Inc., 2015).

1.3 Petroleum Utilization

Petroleum is recovered mostly through oil drilling (natural petroleum springs are rare) after studies of structural geology (at the reservoir scale), sedimentary basin analysis, and reservoir characterization (mainly in terms of the porosity and permeability of geologic reservoir structures) are completed (Guerriero et al., 2011, 2013). Petroleum is refined and separated, most easily by distillation, into a large number of consumer products, from gasoline (petrol) and kerosene to asphalt and chemical reagents used to make plastics, pharmaceuticals, solvents, fertilizers, pesticides, dyes, and textiles. In fact, petroleum is used as fuel (primary source of energy) and in the manufacture of a wide variety of materials, and it is estimated that the world will need it until scientists can find and develop alternative materials and technologies.

1.4 Petroleum Industry

The petroleum industry includes the global processes of exploration, extraction, refining, transporting (pipeline, oil tanker/barge, truck, and rail), and marketing petroleum products. The industry is usually divided into three major components: upstream, midstream, and downstream. Upstream usually includes exploration, development, and production of crude oil and natural gas. The midstream segment, as its name implies, encompasses facilities and processes that sit between upstream and downstream segments. Midstream activities can include processing, storage, and transportation of crude oils and natural gas. Transportation is a big part of midstream activities and can include using pipelines, trucking fleets, tanker ships, and rail cars. Downstream activities usually include refining/hydrocarbon processing, marketing, and distribution. In another classification, the petroleum industry is divided into five segments: upstream, downstream, pipeline, marine, and service and supply. Companies involved in both upstream and downstream are called integrated companies. Companies with only upstream operations are called independents. Majors are several largest integrated petroleum companies (EPA office of Compliance Sector Notebook Project (2000); E.A. Technique (M) Berhad, 2014; EKT Interactive, 2015; Devold, 2013; Macini and Mesini, 2011; Jafarinejad, 2016a,b).

The petroleum industry includes activities to explore for, produce, transport worldwide, process, and market approximately 3.5 billion tons of crude oil and 2.5 giga m^3 of natural gas and their derivatives per year. Fig. 1.6 depicts the general activities of the petroleum industry (Cholakov, 2009).

Based on earlier classifications and discussion, the petroleum industry can be divided into four sectors: (1) exploration, development, and production; (2) hydrocarbon processing (refineries and petrochemical plants); (3) storage, transportation, and distribution; and (4) retail or marketing (Jafarinejad, 2016a,b).

1.4.1 Exploration, Development, and Production

Exploration and production together is referred to as E&P. Exploration is about finding underground reservoirs of oil and gas (oil and gas fields), and includes structural geology studies, prospecting, seismic surveys, drilling activities that take place before the development of a field is finally decided, evaluate exploration well data, analysis to establish porosity and permeability, production test data to determine flow rates and maximum production potential, mathematical modeling of reservoirs, etc. Determination of the number and location of reservoirs, types of wells, assessment of oil recovery mechanism, design of wells to meet production requirements, process facilities, infrastructure facilities, terminal/export facilities, and operating and maintenance strategies is done in the development stage. Production is the process of producing the discovered petroleum using drilled wells through which the reservoir’s fluids (oil, gas, and water) are brought to the surface and separated. In fact, bringing the well fluids to the surface and preparing them for use in refinery or processing plants are called production (Devold, 2013; Aliyeva, 2011).

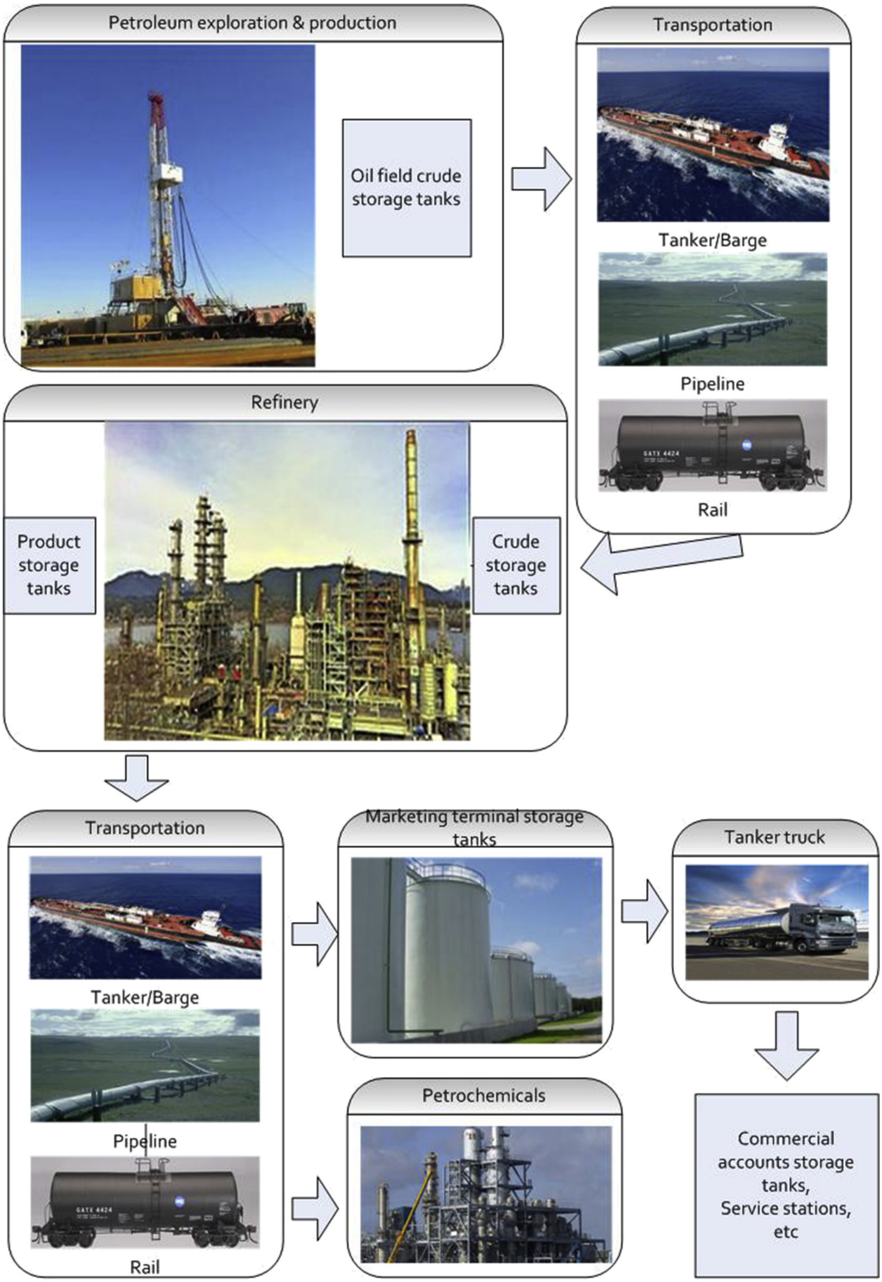

Figure 1.6 General activities of the petroleum industry.

1.4.2 Hydrocarbon Processing (Refineries and Petrochemical Plants)

Hydrocarbon fluids and gases are processed and separated into marketable products or feedstocks for the petrochemical industries in crude-oil refineries and gas-processing plants. The market products of refineries and petrochemical plants are jet fuel, petrol, diesel, asphalt, lubricants, plastics, etc. (Devold, 2013; Aliyeva, 2011; United States Environmental Protection Agency (U.S. EPA), 2015; Jafarinejad, 2016b).

More than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstocks for the petrochemical industry, are generally produced from crude oil in the petroleum refining industry. Advanced and bigger refineries associated with petrochemical plants may produce other synthetic derivatives from pure products to additives for lubricants and fuels, polymers, etc. (Cholakov, 2009; Jafarinejad, 2016b). In the other words, bottled gas, gasoline, jet fuel, fuel oil (for home heating), fuel oil (for factories), diesel oil, etc., are products of refineries, but solvents for paints, insecticides, medicines, synthetic fibers, enamel, detergents, weed killers and fertilizers, plastics, synthetic rubber, photographic film, candles, waxed paper, polish, ointments and creams, roofing, protective paints, asphalt, etc., are products of petrochemical plants (Fagan, 1991; Jafarinejad, 2016b). Different processes may be used in petroleum refineries. The composition of the crude oil and the chosen slate of products may determine the process flow scheme of a petroleum refinery. Fig. 1.7 shows a general schematic of a petroleum refinery. The arrangement of these processes will vary among petroleum refineries, and few, if any, use all of these processes. Some petroleum refining processes have direct emission sources. Refinery processes include separation processes (atmospheric distillation, vacuum distillation, and light-end recovery or gas processing); petroleum-conversion processes (catalytic and thermal cracking, reforming, alkylation, polymerization, isomerization, coking, and visbreaking); petroleum-treating processes (hydrotreating, hydrodesulfurization, chemical sweetening, acid gas removal, and deasphalting); feedstock and product handling (blending, storage, loading, and unloading); and auxiliary facilities (compressor engines, blowdown system, cooling towers, boilers, hydrogen production, sulfur recovery plant, and wastewater treatment) (Speight, 2005; Research Triangle Institute (RTI) International, 2015; Jafarinejad, 2016b).

Olefins (e.g., ethylene, propylene, butylenes, and butadiene) and aromatics (e.g., benzene, toluene, and xylenes) are the basic petrochemicals manufactured by cracking, reforming, and other processes. The capacity of naphtha crackers is generally of the order of 250,000−750,000 metric tons per year of ethylene production. Some petrochemical plants also have alcohol and oxo compound manufacturing units onsite. The base petrochemicals or products derived from them along with other raw materials are converted into a wide variety of products including resins and plastics (such as low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polypropylene, polystyrene, and polyvinyl chloride (PVC)); synthetic fibers (such as polyester and acrylic); engineering polymers (such as acrylonitrile butadiene styrene (ABS)); rubbers (including styrene butadiene rubber (SBR)

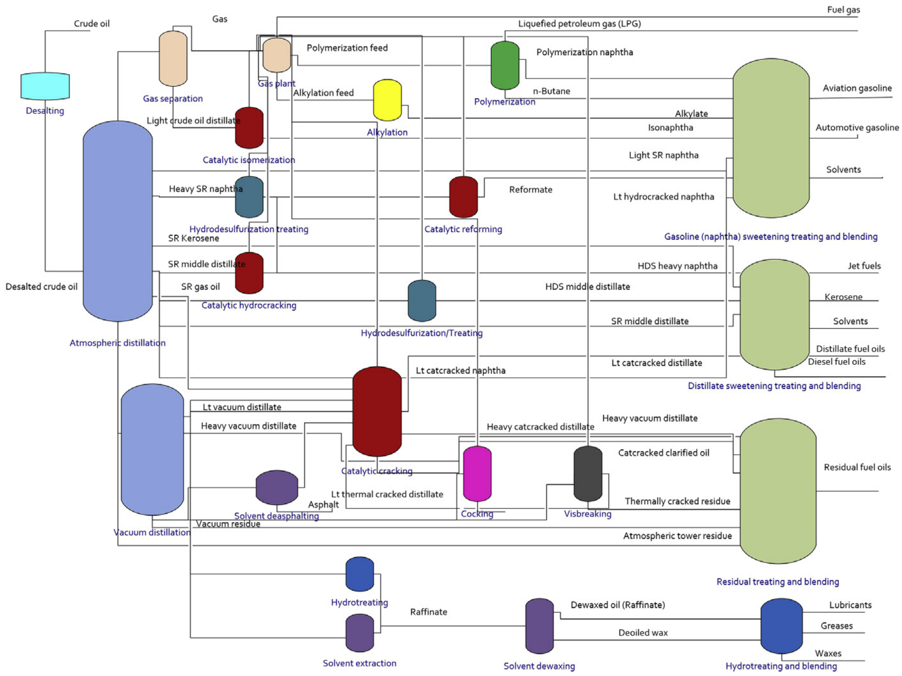

Figure 1.7 Schematic flow diagram of a typical petroleum refinery.
Modified of Devold, H., 2013. Oil and Gas Production Handbook, an Introduction to Oil and Gas Production, Transport, Refining and Petrochemical Industry, third ed. ABB Oil and Gas; Speight, J.G., 2005. Environmental Analysis and Technology for the Refining Industry. John Wiley & Sons, Inc., Hoboken, New Jersey; European Commission and Joint Research Center, 2013. Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas, Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control), Joint Research Center. Institute for Prospective Technological Studies Sustainable Production and Consumption Unit European IPPC Bureau.

and polybutadiene (PBR)); solvents; and industrial chemicals (including those used for the manufacture of detergents such as linear alkyl benzene (LAB), coatings, dyestuff, agrochemicals, pharmaceuticals, and explosives). In addition, some alternative methods are available to manufacture the desired petrochemical products (Multilateral Investment Guarantee Agency (MIGA), 2004). Petrochemical products can also be used in a wide variety of applications (Fagan, 1991; Jafarinejad et al., 2007a,b; Mohaddespour et al., 2007, 2008; Jafarinejad, 2009, 2012; Cholakov, 2009, Devold, 2013).

1.4.3 Storage, Transportation, and Distribution

Service providers provide storage facilities at terminals throughout the oil and gas distribution systems. These facilities are most often located near producing, refining, and processing facilities and are connected to pipeline systems to facilitate shipment when product demand must be met. While petroleum products are held in storage tanks, natural gas tends to be stored in underground facilities (Trench, 2001). In the other words, storage is used by all sectors of the petroleum industry. Liquid petroleum products may be stored in above-ground or underground steel or concrete tanks or in underground salt domes, mined caverns, or abandoned mines (Cholakov, 2009). Fixed-roof (vertical and horizontal), external floating roof, domed external floating roof, internal floating roof, horizontal (above ground and underground), variable vapor space, and pressure (low and high) are the basic tank designs used for organic liquid-storage vessels (Cholakov, 2009; European Commission and Joint Research Center, 2013; RTI International, 2015). Above-ground or underground steel tanks are the best vessels to store petroleum derivatives. Barrels may be used for storage of small amounts of petroleum products for shorter periods. Pressurized tanks, aquifers, depleted oil and gas wells, salt domes, cavities, etc., are the possible methods for storage of natural gas. Much smaller pressurized vessels can be used for domestic applications (Cholakov, 2009).

Crude oil and gas are transported to processing facilities and from there to end-users by pipeline, tanker/barge, truck, and rail. Pipelines are the most economical transportation method and are most suited to movement across longer distances, eg, across continents. Tankers and barges are also employed for long-distance transportation, often for international transport. Rail and truck can also be used for longer distances but are most cost-effective for shorter routes. Natural gas is usually transported by pipelines with a diameter up to 1.5 m (Trench, 2001). Note that rail and road transport is usually used for petroleum derivatives, though lower-pressure product pipelines are common in most modern and industrialized countries (Cholakov, 2009).

1.4.4 *Retail or Marketing*

The products of refineries and petrochemical plants such as gasoline, diesel, asphalt, lubricants, plastics, etc., natural gas liquids, and natural gas are marketed to various consumers in different ways (U.S. EPA, 2015).

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Pollutions and Wastes From the Petroleum Industry

2

2.1 Terminology and Definitions

Keywords such as environment, environmental technology, environmental impact assessment (EIA), pollutant, contaminant, wastes, and emission factor are defined in this section.

Environment: The word "environment" means "surround" and is derived from the French word "environia." It refers to both biotic (living) and abiotic (physical or nonliving) things. In other words, environment is all of the biotic and abiotic factors that act on an organism, population, or ecological community and influence its survival and development. Biotic factors include the organisms themselves, their food, and their interactions. Abiotic factors include such items as sunlight, soil, air, water, climate, and pollution (The American Heritage® Science Dictionary, 2002).

Environmental technology: Environmental technology is the scientific study or application of engineering principles to understand and handle problems that influence our surroundings, with the goal of improvement of the environment (Speight, 2005; Orszulik, 2008).

Environmental impact assessment (EIA): An EIA refers to a formal, written, technical evaluation of potential effects on the environment (atmosphere, water, land, plants, and animals) of a particular event or activity (E&P Forum, 1993).

Pollutant: Substance or condition that contaminates air, water, or soil. Pollutants can be artificial substances, such as pesticides, or naturally occurring substances, such as oil or carbon dioxide, that occur in harmful concentrations in a given environment. Heat transmitted to natural waterways through warm-water discharge from power plants, uncontained radioactivity from nuclear wastes, and noise are also considered pollutants. Pollutants can be classified into two categories: primary and secondary. Primary pollutants refer to pollutants emitted directly from the source. Secondary pollutants are generated by interaction of primary pollutants with another chemical or by dissociation of a primary pollutant, or by other effects within a particular ecosystem (The American Heritage® Science Dictionary, 2002; Speight, 2005).

Contaminant: A contaminant is not usually categorized as a pollutant, but this term is in some cases virtually equivalent to pollution, where the main interest is the harm done on a large scale to the environment (Speight, 2005).

Wastes: Wastes refer to any materials (solid, liquid, or gaseous) that if improperly managed or disposed of may pose substantial hazards to human health and the environment (Speight, 2005). In other words, wastes are materials that are not prime products for which the initial user has no further use for in terms of his/her own purposes of production, transformation, or consumption, and of which he/she wants to dispose. Wastes may be produced during the extraction of raw materials, the processing of

Petroleum Waste Treatment and Pollution Control. http://dx.doi.org/10.1016/B978-0-12-809243-9.00002-X

raw materials into intermediate and final products, the consumption of final products, and other human activities. Residuals recycled or reused at the place of generation are excluded (United Nations Statistics Divisions (UNSD), 1997).

Emission factor (EF): According to the US EPA (1995a), an emissions factor refers to a representative value that attempts to relate the quantity of a pollutant released to the atmosphere with an activity associated with the release of that pollutant. These factors are generally expressed as the weight of the pollutant divided by a unit weight, volume, distance, or duration of the activity emitting the pollutant (e.g., kilograms of particulate emitted per megagram of coal burned). Estimation of emissions from various sources of air pollution is facilitated by such factors. In most cases, these factors are simply averages of all available data of acceptable quality, and are generally assumed to be representative of long-term averages for all facilities in the source category (i.e., a population average).

The general equation for the estimation of emissions is:

$$E = A \times \mathrm{EF} \times \left(1 - \frac{\mathrm{ER}}{100}\right) \tag{2.1}$$

where E is the emission, A denotes the activity rate, EF is the emission factor, and ER denotes the overall emission reduction efficiency (%). ER is further defined as the product of the control-device destruction or removal efficiency and the capture efficiency of the control system. When estimating emissions for a long time period (e.g., 1 year) both the device and the capture efficiency terms should account for upset periods as well as routine operations (US EPA, 1995a; Capelli et al., 2014).

Emission-factor ratings in AP—42 (*Compilation of Air Pollutant Emission Factors*) provide indications of the robustness, or appropriateness, of EFs for predicting average emissions for the activity of a source. Emission factors may be appropriate for use in a number of situations such as making source-specific emission estimates for area-wide inventories. These inventories have many purposes including ambient dispersion modeling and analysis, control strategy development, and in screening sources for compliance investigations. Emission-factor use may also be appropriate in some permitting applications, such as in applicability determinations and in establishing operating permit fees. Use of EFs as source-specific permit limits is not recommended by the EPA. Because EFs essentially represent an average of a range of emission rates, approximately half of the subject sources will have emissions rates greater than the EF and the other half will have emission rates less than the EF. As a result, using an AP—42 EF would result in half of the sources being noncompliant (US EPA, 1995a; Capelli et al., 2014).

2.2 Wastes From Exploration, Development, and Production

As described in Chapter 1, production of crude oil and gas is an important operation of the petroleum industry. The major activities of this sector may include seismic survey, exploratory drilling, construction, development, production, maintenance, decommissioning, and reclamation (plugging and abandoning all wells, removal of building and equipment, etc.) (E&P Forum, 1993; Cholakov, 2009). Air emissions, wastewater, and solid wastes can be generated in this sector.

2.2.1 Air Emissions and Estimation

During the processes of exploration, development, and production of petroleum, a wide variety of air pollutants such as volatile organic compounds (VOCs), nitrogen oxides (NO_x), sulfur oxides (SO_x), hydrogen sulfide (H_2S), hydrocarbons (such as CH_4), carbon dioxide (CO_2), partially burned hydrocarbons (such as carbon monoxide and particulates), polyaromatic hydrocarbons (PAHs), etc., are generated and emitted. At most drilling and production sites, halon gases [determined as an ozone-depleting chlorofluorocarbon (CFC)] are also used for fire suppression that use of them releases these gases to the atmosphere (Reis, 1996; E&P Forum, 1993).

Air pollutants can be generated from combustion, operations, fugitive emissions, and site remediation in the exploration, development, and production of petroleum activities (Reis, 1996). The air emissions from the E&P of petroleum, environmentally significant components, main sources, and the type of operations that generate these pollutants are given in Table 2.1.

Generally, in the petroleum industry, as in other industries, air emissions can be divided into point and nonpoint sources. Point sources refer to emissions that exit stacks and flares and thus can be monitored and treated. Nonpoint sources refer to fugitive emissions that are difficult to locate and capture (Speight, 2005). Fugitive emissions occur throughout a production system, e.g., through leaking components such as valves, pumps, tanks, compressors, connections, fittings, hatches, dump level arms, packing seals, flanges, etc. Although individual leaks are typically small, the sum of all fugitive leaks at a production system can be one of its largest emission sources (Reis, 1996).

The average EF approach, screening ranges approach, EPA correlation approach, and unit-specific correlation approach are four methods for estimating mass emissions from equipment leaks in chemical processing units such as synthetic organic chemical manufacturing industry (SOCMI), refineries, marketing terminals and oils, and gas production operations. Except for the average EF approach, all of the approaches need screening data. Screening data are obtained by using a portable monitoring device to sample air from potential leak interfaces on individual pieces of equipment. A screening value is a measure of the concentration of leaking compounds to the atmosphere that provides an indication of the leak rate from an equipment piece, and is measured in units of parts per million by volume (ppmv) (US EPA, 1995b). The average EF, screening ranges approach, and EPA-correlation approaches for estimating mass emissions from equipment leaks are explained in this section. For further information about the unit-specific correlation approach refer to the US EPA (1995b) and Research Triangle Institute (RTI) International (2015).

The average EF approach refers to the use of average emission factors developed by the EPA in combination with unit-specific data that are relatively simple to obtain.

Table 2.1 **Air Emissions From Exploration, Development, and Production of Petroleum (E&P Forum, 1993; Bashat, 2003)**

Main Sources	Environmentally Significant Components	Type of Operation
Vent gases Flare gases Blowdown from bulk chemicals	NO_x, SO_x, H_2S, CO_x, VOC, hydrocarbons such as CH_4, carbon, particulates, PAHs, benzene, toluene, ethylbenzene, and ortho-, meta-, and para-xylene (BTEX)	Drilling Production
Engine exhausts	NO_x, SO_x, CO_x, VOC, PAHs, formaldehyde, carbon particulates	Seismic Construction and commissioning Drilling Production Maintenance Abandonment
Fugitive gases	VOC, BTEX	Construction and commissioning Drilling Production Maintenance Abandonment
Fire-protection equipment/ facilities	Halons, CFCs, HCFCs, firefighting foams	Construction and commissioning Drilling Production Maintenance Abandonment
Air conditioning/ refrigerant systems	CFC, HCFC	Construction and commissioning Production Maintenance Abandonment

These data include the number of each type of equipment (valve, pump seals, etc.), the service each equipment is in (gas, light liquid, or heavy liquid), the total organic compound (TOC) concentration of the stream, and the time period each equipment spent in that service. The average EFs for petroleum production equipment are presented in Table 2.2. In this table, emission rates are for TOC including non-VOCs such as

Table 2.2 **Average Emission Factors (TOC Emission Rates Including Non-VOCs Such As Methane and Ethane) for Petroleum Production Equipment (US EPA, 1995b)**

Equipment Type	Service	Emission Factor (kg/h/source)
Valves	Gas	4.5×10^{-3}
	Heavy oil	8.4×10^{-6}
	Light oil	2.5×10^{-3}
	Water/oil	9.8×10^{-5}
Pump seals	Gas	2.4×10^{-3}
	Heavy oil	Not available
	Light oil	1.3×10^{-2}
	Water/oil	2.4×10^{-5}
Connectors	Gas	2×10^{-4}
	Heavy oil	7.5×10^{-6}
	Light oil	2.1×10^{-4}
	Water/oil	1.1×10^{-4}
Flanges	Gas	3.9×10^{-4}
	Heavy oil	3.9×10^{-7}
	Light oil	1.1×10^{-4}
	water/oil	2.9×10^{-6}
Open-ended lines	Gas	2×10^{-3}
	Heavy oil	1.4×10^{-4}
	Light oil	1.4×10^{-3}
	Water/oil	2.5×10^{-4}
Others (compressors, diaphragms, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief valves, and vents)	Gas	8.8×10^{-3}
	Heavy oil	3.2×10^{-5}
	Light oil	7.5×10^{-3}
	Water/oil	1.4×10^{-2}

methane and ethane. Although the average EFs are in units of kilogram per hour per individual source, according to the EPA, it is important to note that these factors are most valid for predicting emissions from a population of equipment. The average factors are not intended to be applied to predicting emissions from an individual piece of equipment over a short time period (i.e., 1 h). Estimation of TOC mass emission from all of the equipment in a stream of given equipment type can be calculated by the following equation:

$$E_{\mathrm{TOC}} = F_{\mathrm{A}} \times \mathrm{WF}_{\mathrm{TOC}} \times N \tag{2.2}$$

where E_{TOC} is the emission rate of TOC from all equipment in the stream of a given equipment type (kg/h), F_{A} denotes the applicable average EF for the equipment type (kg/h/source), $\mathrm{WF}_{\mathrm{TOC}}$ is the average weight fraction of TOC in the stream, and N denotes the number of pieces of equipment of the applicable equipment type in the stream.

If, for a stream, estimating emissions of a specific VOC in the mixture is necessary, the following formula can be used:

$$E_{\mathrm{X}} = E_{\mathrm{TOC}} \times \left(\frac{\mathrm{WF}_{\mathrm{X}}}{\mathrm{WF}_{\mathrm{TOC}}}\right) \tag{2.3}$$

where E_{X} is the mass emissions of organic chemical “x” from the equipment (kg/h) and WF_{X} denotes the concentration of organic chemical “x” in the equipment in wt% (US EPA, 1995b; RTI International, 2015).

When using the screening ranges approach (formerly known as the leak/no-leak approach), it is assumed that components having screening values greater than 10,000 ppmv have a different average emission rate than components with screening values less than 10,000 ppmv. If the measured concentration at a fitting by an analyzer can be greater than 10,000 ppmv it is called leaking fitting (10,000 ppmv as the leak definition). The screening range EFs for petroleum production operations are given in Table 2.3. These factors are a better indication of the actual leak rate from individual equipment than the average EFs. To calculate TOC emissions using the screening ranges approach, the following equation is used:

$$E_{\mathrm{TOC}} = (F_{\mathrm{G}} \times N_{\mathrm{G}}) + (F_{\mathrm{L}} \times N_{\mathrm{L}}) \tag{2.4}$$

where F_{G} is the applicable EF for sources with screening values greater than or equal to 10,000 ppmv (kg/h/source), N_{G} denotes the equipment count (specific equipment type) for sources with screening values greater than or equal to 10,000 ppmv, F_{L} is the applicable EF for sources with screening values less than 10,000 ppmv (kg/h/source), and N_{L} denotes the equipment count (specific equipment type) for sources with screening values less than 10,000 ppmv (US EPA, 1995b).

The EPA correlation approach is another method for estimating emissions from equipment leaks by providing an equation to predict the mass emission rate as a function of screening value for a particular equipment type. This approach is preferred

Table 2.3 Screening Range Emission Factors (For TOC Emission Rates) for Petroleum Production Operations (US EPA, 1995b)

Equipment Type	Service	≥10,000 ppmv Emission Factor (kg/h/source)	≥10,000 ppmv Emission Factor (kg/h/source)
Valve	Gas	0.098	2.5×10^{-5}
	Heavy oil	Not available	8.4×10^{-6}
	Light oil	0.087	1.9×10^{-5}
	Water/oil	0.064	9.7×10^{-6}
Pump seals	Gas	0.074	3.5×10^{-4}
	Heavy oil	Not available	Not available
	Light oil	0.100	5.1×10^{-4}
	Water/oil	Not available	2.4×10^{-5}
Connectors	Gas	0.026	1×10^{-5}
	Heavy oil	Not available	7.5×10^{-6}
	Light oil	0.026	9.7×10^{-6}
	Water/oil	0.028	1×10^{-5}
Flanges	Gas	0.082	5.7×10^{-6}
	Heavy oil	Not available	3.9×10^{-7}
	Light oil	0.073	2.4×10^{-6}
	Water/oil	Not available	2.9×10^{-6}
Open-ended line	Gas	0.055	1.5×10^{-5}
	Heavy oil	0.030	7.2×10^{-6}
	Light oil	0.044	1.4×10^{-5}
	Water/oil	0.030	3.5×10^{-6}
Others (compressors, diaphragms, drains, dump arms, hatches, instruments, meters, pressure relief valves, polished rods, relief valves, and vents)	Gas	0.089	1.2×10^{-4}
	Heavy oil	Not available	3.2×10^{-5}
	Light oil	0.083	1.1×10^{-4}
	Water/oil	0.069	5.9×10^{-5}

when actual screening values are available. Correlations can be used to estimate emissions for the entire range of nonzero screening values, from the highest potential screening value to the screening value that represents the minimum detection limit of the monitoring device. Default zero emission rates are used for screening values of zero ppmv and pegged emission rates are used for "pegged" screening values (the screening value is beyond the upper limit measured by the portable screening device). In other words, according to the EPA, the default-zero leak rates are applicable only when the minimum detection limit of the portable monitoring instrument is 1 ppmv or less above background, and the pegged emission rates are to be used to estimate emissions when instrument readings are pegged and a dilution probe is not used. The equipment-leak rates for petroleum industry (refinery, marketing terminals, and oil and gas production) equipment components are given in Table 2.4. In this table, emission rates are for TOC including non-VOCs such as methane and ethane and C is the screening value in ppmv measured by the monitoring device. The 10,000 ppmv pegged emission rate applies only when a dilution probe cannot be used or in the case of previously collected data that contained screening values reported to be pegged at 10,000 ppmv. The 10,000 ppmv pegged emission rate was based on components screened at greater than or equal to 10,000 ppmv; however, in some cases, most of the data could have come from components screened at greater than 100,000 ppmv, thereby resulting in similar pegged emission rates for both the 10,000 and 100,000 pegged levels (e.g., connector and flanges). In addition, the "other" equipment type was developed from instruments, loading arms, pressure relief devices, stuffing boxes, vents, compressors, dump lever arms, diaphragms, drains, hatches, meters, and polished rods. This "other" equipment type should be applied to any equipment other than connectors, flanges, open-ended lines, pumps, and valves (US EPA, 1995b; RTI International, 2015; American Petroleum Institute, 1980; Schaich, 1991).

Table 2.4 **Equipment Leak Rate for Petroleum Industry (Refinery, Marketing Terminals, and Oil and Gas Production) Equipment Components (US EPA, 1995b; RTI International, 2015)**

Equipment Type/Service	Default Zero Emission Rate (kg/h/source)	Pegged Emission Rate (kg/h/source)		Correlation Equation (kg/h/source)
		10,000 ppmv	100,000 ppmv	
Valves/all	7.8×10^{-6}	0.064	0.140	$2.29 \times 10^{-6}C^{0.746}$
Pump seals/all	2.4×10^{-5}	0.074	0.160	$5.03 \times 10^{-5}C^{0.610}$
Others/all	4.0×10^{-6}	0.073	0.110	$1.36 \times 10^{-5}C^{0.589}$
Connectors/all	7.5×10^{-6}	0.028	0.030	$1.53 \times 10^{-6}C^{0.735}$
Flanges/all	3.1×10^{-7}	0.085	0.084	$4.61 \times 10^{-6}C^{0.703}$
Open-ended line/all	2.0×10^{-6}	0.030	0.079	$2.20 \times 10^{-6}C^{0.704}$

According to Sheehan (1991) and Reis (1996), there is also another approximate method related to emission rates based on the number of production wells and the gas/oil ratio; for example, emission rates (Ibm/well/day) for number of wells <10 with gas/oil ratio <500 and ≥ 500 are 2.56 and 6.85, respectively. Emission rates (Ibm/well/day) for number of wells 10−50 with gas/oil ratio <500 and ≥ 500 are 1.44 and 2.89, respectively. In addition, emission rates (Ibm/well/day) for number of wells >50 with gas/oil ratio <500 and ≥ 500 are 0.09 and 4.34, respectively.

The amount of air emissions from the E&P sector can depend on the total petroleum production and/or the level of activity in this sector. According to Ahnell and O'Leary (2008), in terms of emissions per unit production, BP emitted on average 353 tons of air emissions (excluding CO_2) for every million barrels of oil equivalent (Mboe) in 2004. BP's exploration and production sulfur dioxide emission was also 10 kilotons in 2004. In addition, of BP's total mass of emissions to air (excluding CO_2) in 2004, 56% was emitted from the E&P sector, 20% was from refining and marketing, and 24% was from the remaining operations.

Gas flaring from E&P operations is the most significant source of air emissions, especially where there is no infrastructure or market available for the gas. Integrated development and providing markets for gas in the petroleum industry can reduce the gas flaring. According to the "World Resources Institute Reports" (1994−1995), the total gas flaring in 1991 generated a contribution of 2.56×10^8 tons of CO_2 emissions (1% of global CO_2 emissions) and 2.5×10^7 tons of methane emissions (10% of global emissions) (E&P Forum/UNEP, 1997; E&P Forum, 1994a). According to Ahnell and O'Leary (2008), BP flared 1.342×10^6 tons of hydrocarbon gas during exploration and production activities in 2004. The E&P Forum (1994a) reported that total methane emissions from the North Sea E&P industry are 1.36×10^5 tons (0.05% of global methane emissions). Other emission gases such as NO_x, SO_x, CO, and VOC from North Sea production activities are <1%, <1%, <1%, and <2% of the European Union (EU) total emissions, respectively. There are a number of emerging technologies and improved practices that have the potential to reduce air emissions and help to improve performance further. Practical examples of methods for improving performance are also related to reducing flaring and venting, improving energy efficiency, developing low NO_x turbines, controlling fugitive emissions, and examining replacements for firefighting systems (E&P Forum/UNEP, 1997; E&P Forum, 1994a).

2.2.2 *Wastewater*

The major sources of aqueous waste from E&P activities are produced water, drilling fluids, cuttings, well treatment chemicals, cooling water, process, wash and drainage water, spills and leakage, and sewerage, sanitary, and domestic wastewater. The volumes of produced wastewater rely on the step of the E&P process. During seismic operations, the volumes of waste are minimal and relate to camp or vessel activities. Drilling fluids and cuttings are the main waste effluents from exploratory drilling, but produce water is the primary discharge from production operations (after the development wells are completed) (E&P Forum/UNEP, 1997). The aqueous effluents from the E&P of petroleum, environmentally significant components, main sources, and type of operations that generate these pollutants are given in Table 2.5.

The type of production (oil and gas), level of activity, and geographical and throughout of lifetime of a field can affect the volumes of produced water (Congress of the United States, Office of Technology Assessment, 1992; E&P Forum/UNEP, 1997;

Table 2.5 Aqueous Effluents From Exploration, Development, and Production of Petroleum (E&P Forum, 1993; Bashat, 2003)

Main Sources	Environmentally Significant Components	Type of Operation
Produced water	Hydrocarbons, inorganic salts, heavy metals, solids, organics, sulfides, corrosion inhibitors, biocides, phenols, BOD, benzene, organohalogens, PAHs, radioactive material	Drilling Production
Process water, e.g., engine cooling water, brake cooling water, wash water	Inorganic salts, heavy metals, solids, organics, BOD, sulfides, corrosion inhibitors, biocides, demulsifiers, wax inhibitors, detergents, hydrocarbons	Seismic Drilling Production Maintenance Abandonment
Ballast water	Hydrocarbons, phenols, PAHs	Production
Hydro-test fluids	Solids, corrosion inhibitors, biocides, BOD, dyes, oxygen scavengers	Construction and commissioning
Contaminated rain/drainage water	Inorganic salts, heavy metals solids, organics, BOD, sulfides, corrosion inhibitors, biocides, emulsifiers, wax inhibitors, scale inhibitors, detergents, hydrocarbons	Construction and commissioning Drilling Production Maintenance Abandonment
Drilling fluid chemicals	Metals, salts, organics, pH, surfactants, biocides, emulsifiers, viscosifiers	Drilling Production
Spent stimulation or fracturing fluids	Inorganic acids (HCL, HF), hydrocarbons, methanol, corrosion inhibitors, oxygen scavengers, formation fluids, naturally occurring radioactive materials (NORM), geling agents	Drilling Production

Table 2.5 **Aqueous Effluents From Exploration, Development, and Production of Petroleum (E&P Forum, 1993; Bashat, 2003)—cont'd**

Main Sources	Environmentally Significant Components	Type of Operation
Spent completion fluids	Hydrocarbons, corrosion inhibitors, inorganic salts	Drilling Production
Waste lubricants	Organics, heavy metals	Seismic Drilling Maintenance
Water-based (include brine) muds and cuttings	High pH, inorganic salts, hydrocarbons, solids/cuttings, drilling fluid chemicals, heavy metals	Drilling
Oil-based muds and cuttings	Hydrocarbons, solids/cuttings, heavy metals, inorganic salts, drilling fluid chemicals	Drilling
Mercury	Mercury	Drilling Production Maintenance Abandonment
Dehydration and sweetening wastes	Amines, glycols, filter sludges, metal sulfides, H_2S, metals, benzene	Production
Domestic sewage	BOD, solids, detergents, coliform bacteria	Seismic Construction and commissioning Drilling Production Maintenance Abandonment

E&P Forum, 1994b). For example, typical values for North Sea fields range from 2400—40,000 m^3/day for oil installations and 2—30 m^3/day for gas installations (E&P Forum/UNEP, 1997; E&P Forum, 1994b). Based on 53 Federal Register 25448 (1988), relative amount of produced waters, drilling fluids, and associated wastes were 98.2%, 1.7%, and 0.1%, respectively (53 Federal Register 25448, 1988; Congress of the United States, Office of Technology Assessment,1992). According to Ahnell and

O'Leary (2008), in 2004, the treated wastewater discharges from BP's E&P and refining operations totaled nearly 260 m^3 a minute.

In 1995, the onshore petroleum E&P industry in the United States generated an estimated 17,900 million barrels of produced water, 149 million barrels of drilling wastes, and 20.5 million barrels of associated wastes. In addition, natural gas processing contributed an estimated 9.5 million barrels of produced water and 0.1 million barrels of dehydration wastes. A decade earlier, in 1985, the E&P industry's generation of produced water, drilling wastes, and associated wastes were 21,000, 361, and 12 million barrels, respectively. The decreased volume of wastes generated by E&P activities in 1995 is consistent with the general decline in E&P industry activity between 1985 and 1995 (lower oil production, fewer producing wells, fewer new wells drilled), which affects the two largest waste streams produced water and drilling wastes (American Petroleum Institute, 2000).

Until the mid-1990s the discharge of oil-based muds and cuttings from drilling were the main source of oil hydrocarbons entering the marine environment from the offshore petroleum industry in some oilfields. For example, for the period 1981–1986, the average annual discharge of oil on cuttings to the Norwegian Continental Shelf (NCS) was 1940 tons (Reiersen et al., 1989; Bakke et al., 2013). This source was gradually eliminated by regulation in 1993 in Norway and in 1996 and 2000 within the OSPAR region (OSPAR Commission, 2000; Bakke et al., 2013). In 2012 about 130 million cubic meters (m^3) of produced water were discharged to the NCS. The highest average daily discharge from a single field was 76,700 m^3. Since 2007 the OSPAR regulation has required that dispersed oil in produced water discharges shall not exceed a performance standard of 30 mg/L (OSPAR Commission, 2001; Bakke et al., 2013). In 2012, the average oil concentration in Norwegian-produced water discharges was 11.7 mg/L. Currently used cleaning equipment seems to be able to reduce the levels to less than 5 mg/L (Voldum et al., 2008; Bakke et al., 2013).

2.2.3 Solid Waste

The main sources of solid wastes from E&P activities are tank/piping sludges, production chemicals, contaminated soils, incinerator ash, oil-based muds and cuttings, pigging sludges, spent catalysts, industrial wastes, medical wastes, domestic refuse, etc. The solid wastes from the E&P of petroleum, environmentally significant components, main sources, and type of operations that generate these pollutants are given in Table 2.6 (E&P Forum, 1993; Bashat, 2003). Control of solid waste can be done by source control, waste treatment, and waste disposal (Orszulik, 2008).

2.3 Wastes From Hydrocarbon Processing

Refineries and petrochemical plants manage huge amounts of raw materials and products, and they are also intensive consumers of energy and water used to carry out the

Table 2.6 Solid Wastes From Exploration, Development, and Production of Petroleum (E&P Forum, 1993; Bashat, 2003)

Main Sources	**Environmentally Significant Components**	**Type of Operation**
Tank/piping sludges, induced gas floatation unit/dissolved gas floatation unit (IGF/DGF) sludge, waxes	Inorganic salts, heavy metals, solids, organics, BOD, sulphides, corrosion inhibitors, biocides, demulsifiers, wax inhibitors, scale inhibitors, phenols, PAHs, hydrocarbons	Production
Production chemicals	Demulsifiers, corrosions inhibitors, wax inhibitors, scale inhibitors, antifoaming agents, biocides, oxygen scavengers, flocculants	Production
Industrial refuse	Heavy metals, metals, plastics, paints	Construction and commissioning Production Abandonment
Soil movements due to e.g., abandonment and construction	Hydrocarbons, heavy metals, metals, plastic, paints, glass	Construction and commissioning abandonment
Cement slurries, cement mix water, cement returns	Thinners, viscosifiers, heavy metals, pH, salts	Drilling Production
Contaminated soils	Hydrocarbons, heavy metals, salts, treating chemicals	Seismic Construction and commissioning Drilling Production Maintenance Abandonment
Absorbents, e.g., spill clean-up	Hydrocarbons, solvents, production chemicals	Seismic Construction and commissioning Drilling Production Maintenance Abandonment

Continued

Table 2.6 Solid Wastes From Exploration, Development, and Production of Petroleum (E&P Forum, 1993; Bashat, 2003)—cont'd

Main Sources	Environmentally Significant Components	Type of Operation
Incinerator ash	Ash, heavy metals, salts	Drilling Production Abandonment
Industrial waste, e.g., batteries, transformers, and capacitors	Acid, alkali, heavy metals, polychlorinated biphenyls (PCBs)	Construction and commissioning Maintenance Abandonment
Maintenance waste, e.g., sandblast (grits), greases, and filters	Hydrocarbons, solvents, heavy metals, solids	Maintenance
Paint materials	Heavy metals, solvents, hydrocarbon	Construction and commissioning Maintenance
Pigging sludges	Inorganic salts, hydrocarbons, heavy metals, solids, production chemicals, NORM, phenols, aromatics	Production
Produced sand, e.g., from drilling/production operations	Hydrocarbons, heavy metals, NORM	Drilling Production
Scrap materials, e.g., abandoned platforms, used pipelines, used process equipment, used tanks, electrical cables, empty drums, used tubulars, used casings	Heavy metals, NORM scales	Seismic Construction and commissioning Maintenance Abandonment
Spent catalysts, e.g., catalyst beds, molecular sieve	Hydrocarbons, heavy metals, inorganic salts	Production Maintenance
Consolidation materials, e.g., epoxy resins	Excess chemicals	Production

Table 2.6 Solid Wastes From Exploration, Development, and Production of Petroleum (E&P Forum, 1993; Bashat, 2003)—cont'd

Main Sources	Environmentally Significant Components	Type of Operation
Medical wastes	Pathogenic organisms, plastics, glass, medicines, needles	Construction and commissioning Drilling Production Maintenance Abandonment
Domestic refuse	Plastics, glass, organic waste	Seismic Construction and commissioning Drilling Production Maintenance Abandonment

processes. In their storage and hydrocarbon processes, refineries and petrochemical plants generate emissions to the air, to water, and to the soil (Faustine, 2008; European Commission and Joint Research Center, 2013; Jafarinejad, 2014a,b, 2015a,b,c,d,e,f, 2016). Environmental management has become a major issue for refineries and petrochemical plants. The petroleum industry is a mature industry, and pollution abatement programs have been carried out in most refineries for a long time to different extents. As a result, the emissions generated by refineries have declined per ton of crude processed and are continuing to decline (European Commission and Joint Research Center, 2013).

It is necessary to note, with respect to the quality and quantity of refinery emissions, which on a macroscale the crude oils vary only to a limited extent in their composition. In addition, refineries are often restricted to a comparatively narrow range of crude-oil diets. Generally, large changes in refinery emissions are not expected when switching from one crude oil to another within this range. Therefore the type and quantity of refinery emissions to the environment are well known during usual operations. However, from time to time, processing of crude oils previously unknown to the refinery can have unforeseen impacts on the performance of refinery processes, leading to an increase in emissions (especially likely to affect water emissions and to a lesser extent air emissions) (European Commission and Joint Research Center, 2013).

2.3.1 Air Emissions and Estimation

The main sources of air emissions from a refinery include flares, combustion emissions associated with the burning of fuels in the refinery, including fuels used in the generation of electricity, equipment-leak emissions (fugitive emissions or nonpoint source emissions) released through leaking valves, pumps, or other process devices, process vent emissions (point-source emissions) released from process vents during manufacturing (e.g., venting, chemical reactions), storage-tank emissions released when product is transferred to and from storage tanks, and wastewater system emissions from tanks, ponds, and sewer-system drains (Orszulik, 2008, Draft Technology Roadmap for the US Petroleum Industry, 2000). The air emissions from refinery and petrochemical plants, environmentally significant components, and the processes that generate these pollutants are given in Tables 2.7 and 2.8, respectively. Refinery

Table 2.7 Main Air Emissions and Their Sources in Refineries (US EPA, 1995c, 2004; Speight, 2005; European Commission and Joint Research Center, 2013)

Air Emissions	Sources and/or Processes
Carbon monoxide (CO)	Process furnaces and boilers, fluidized catalytic cracking regenerators, CO boilers, sulfur recovery units (SRU), flare systems, incinerators, or in processes such as crude-oil desalting, atmospheric distillation, vacuum distillation, thermal cracking/visbreaking, coking, catalytic cracking, catalytic hydrocracking, hydrotreating/hydroprocessing, alkylation, isomerization, catalytic reforming, and propane deasphalting
Carbon dioxide (CO_2)	Process furnaces, boilers, gas turbines, fluidized catalytic cracking regenerators, CO boilers, flare systems, incinerators, LNG plant CO_2 separation
Nitrogen oxides (NO, NO_2)	Process furnaces, boilers, gas turbines, fluidised catalytic cracking regenerators, CO boilers, coke calciners, incinerators, flare systems, or in processes such as crude-oil desalting, atmospheric distillation, vacuum distillation, thermal cracking/visbreaking, coking, catalytic cracking, catalytic hydrocracking, hydrotreating/hydroprocessing, alkylation, isomerization, catalytic reforming, and propane deasphalting
Nitrous oxide (N_2O)	Fluidized catalytic cracking regenerators
Particulates (including metals)	Process furnaces and boilers, particularly when firing liquid refinery fuels, fluidized catalytic cracking regenerators, CO boilers, coke plants, incinerators, or in processes such as crude-oil desalting, atmospheric distillation, vacuum distillation, thermal cracking/visbreaking, coking, catalytic cracking, catalytic hydrocracking, hydrotreating/hydroprocessing, alkylation, isomerization, catalytic reforming, and propane deasphalting

Table 2.7 **Main Air Emissions and Their Sources in Refineries (US EPA, 1995c, 2004; Speight, 2005; European Commission and Joint Research Center, 2013)—cont'd**

Air Emissions	Sources and/or Processes
Sulfur oxides (SO_x)	Process furnaces and boilers, fluidized catalytic cracking regenerators, CO boilers, sulfur recovery units, flare systems, incinerators, or in processes such as crude-oil desalting, atmospheric distillation, vacuum distillation, thermal cracking/visbreaking, coking, catalytic cracking, catalytic hydrocracking, hydrotreating/hydroprocessing, alkylation, isomerization, catalytic reforming, and propane deasphalting
Volatile organic compounds (VOCs)	Storage and handling facilities, as separation units, oil/water separation systems, fugitive emissions (valves, flanges, etc.), vents, flare systems
Fugitive hydrocarbons	Crude-oil desalting, atmospheric distillation, vacuum distillation, thermal cracking/visbreaking, coking, catalytic cracking, catalytic hydrocracking, hydrotreating/hydroprocessing, alkylation, isomerization, catalytic reforming, propane deasphalting, and wastewater treatment
Catalyst dust	Catalytic hydrocracking
HCl (potentially in light ends)	Isomerization
H_2S	From caustic washing in polymerization and wastewater treatment
NH_3	Wastewater treatment
Fugitive solvents	Solvent extraction and dewaxing
Fugitive propane	Propane deasphalting

processes need a lot of energy; according to the European Commission and Joint Research Center (2013), the production of energy for the various refinery processes generates typically more than 60% of refinery air emissions.

As Table 2.7 illustrates, carbon monoxide (CO), carbon dioxide (CO_2) (the greenhouse gas), nitrogen oxides (NO_x), sulfur oxides (SO_x), particulate matter (PM), volatile organic compounds such as benzene, toluene, and xylene (BTX), fugitive hydrocarbons, fugitive solvents, HCL, H_2S, NH_3, carbon disulfide (CS_2), carbonyl sulfide (COS), hydrogen fluoride (HF), and metals as constituents of the particulates (V, Ni, and others) are emissions to the atmosphere in a typical refinery (Faustine, 2008; European Commission and Joint Research Center, 2013; Jafarinejad, 2015d). For example, for each ton of crude processed, emissions from refineries may be approximately as follows:

- Particulate matter: 0.8 kg, ranging from less than 0.1−3 kg.
- Sulfur oxides: 1.3 kg, ranging 0.2−06 kg; 0.1 kg with the Claus sulfur recovery process.
- Nitrogen oxides: 0.3 kg, ranging 0.06−0.5 kg.

Table 2.8 **Main Air Emissions and Their Sources in Petrochemical Plants (Department of Environment (DOE) of Malaysia, 2014; Iranian Ministry of Petroleum, 2007; IL & FS Ecosmart Limited Hyderabad, 2010)**

Air Emissions	Sources and/or Processes
VOCs	Cracker unit, fugitive sources and intermittent vents, process vents, storage and transfer of liquids and gases, distillation units, aromatic unit, process units, opening of vessel manholes, wastewater treatment facilities
Particulate matter (PM)	Drying of solid products (e.g., synthetic rubber, plastics), conditioning of solid raw materials, boilers, catalyst regeneration, waste handling, powder handling, cracker unit, aromatic unit, process heaters
Combustion gases: NO_x, CO_x, SO_x, C_xH_y, metals, soot	Furnaces, steam boilers, incinerators and flares, cracker unit, aromatic unit, process heaters
Acid gases (HCL, HF)	Halogenation reactions
Dioxins	Production processes that use chlorine incinerators
Solvent	Drying of synthetic rubber, plastics (emission of dry air-containing solvent and monomer)

- Benzene, toluene, and xylene (BTX): 2.5 g (g), ranging 0.75−6 g; 1 g with the Claus sulfur recovery process. Of this, about 0.14 g benzene, 0.55 g toluene, and 1.8 g xylene may be released per ton of crude processed.
- VOC emissions depend on the production techniques, emissions-control techniques, equipment maintenance, and climate conditions and may be 1 kg per ton of crude processed (ranging from 0.5 to 6 kg per tons of crude) (World Bank Group, 1998).

It is obvious that a significant amount of emissions can be generated from equipment leaks in refinery processes. Even if an individual leak is generally small, according to the EPA, individual leaks are the largest source of emissions of volatile organic compounds and volatile hazardous air pollutants (HAPs) from petroleum refineries and chemical manufacturing facilities (Faustine, 2008; US EPA, 1995b).

Sulfur oxides (SO_2, SO_3) and other sulfur compounds (H_2S, CS_2, COS), nitrogen oxides (NO_x, N_2O) and other nitrogen compounds (NH_3, HCN), halogens and their compounds (Cl_2, Br_2, HF, HCl, HBr), incomplete combustion compounds, such as CO and C_xH_y, VOCs that might encompass compounds with carcinogenic potential, particulate matter (such as dust, soot, alkali, heavy metals) with possible carcinogenic properties, and acid gases may be found in air emissions from petrochemical processes and energy supplies (IL & FS Ecosmart Limited Hyderabad, 2010). In petrochemical plants, air emissions from pumps, valves, flanges, storage tanks, loading and unloading operations, and wastewater treatment are of greatest concern. Some of the compounds emitted to air from petrochemical plants are carcinogenic or toxic. Ethylene and propylene emissions are of concern because of their fate processes that lead to the formation of oxides that are extremely toxic. Carcinogenic compounds that may be present in air emissions include benzene, butadiene, 1,2-dichloroethane, and vinyl chloride. A normal naphtha cracker at a petrochemical complex may annually release about 2500 metric tons of alkenes (such as propylenes and ethylene), when producing 500,000 metric tons of ethylene. A petrochemical plant may also release 200 metric tons per year nitrogen oxides and 600 metric tons per year sulfur oxides based on 500,000 metric tons per year of ethylene capacity. VOC emissions depend on the products handled at the plant and may include acetaldehyde, acetone, benzene, toluene, trichloroethylene, trichlorotoluene, and xylene. VOC emissions are mostly fugitive and depend on production processes, material handling and effluent treatment procedures, equipment maintenance, and climatic conditions. According to the MIGA (2004), VOC emissions from a naphtha cracker range from 0.6−10 kilograms (kg) (75% are alkanes, 20% unsaturated hydrocarbons about half of these is ethylene, and remaining 5% are aromatics) per metric ton of ethylene; 0.02−2.5 kg (45% of these being ethylene dichloride, 20% being vinyl chloride, and 15% being chlorinated organics) per metric ton of product in a vinyl chloride plant; 3−10 kg per metric ton of product in a styrene butadiene rubber (SBR) plant; 0.1−2 kg per metric ton of product in ethyl benzene plant; 1.4−27 kg per metric ton of product in acrylonitrile butadiene styrene (ABS) plant; 0.25−18 kg per metric ton of product in a styrene plant; and 0.2−5 kg per metric ton of product in a polystyrene plant (MIGA, 2004).

Similar to air emissions from equipment leaks in E&P operations, mass emissions from equipment leaks in SOCMI process units and refineries can be estimated by using the average EF approach, screening ranges approach, EPA correlation approach, and unit-specific correlation approach (US EPA, 1995b; RTI International, 2015). The average EFs for SOCMI process units and refineries are presented in Table 2.9. The SOCMI average EFs estimate TOC emission rates, whereas the refinery average factors estimate nonmethane organic compound emission rates. The emission rate of TOC from all equipment can be calculated from Eq. (2.2). For refineries only, the emission factor "F_A" must be adjusted to account for all organic compounds in the stream because the refinery factors are only valid for nonmethane organic compounds (percents up to a maximum of 10% by weight methane are permitted). The formula is:

$$F_A = F_A \times \left(\frac{\mathrm{WF_{TOC}}}{\mathrm{WF_{TOC}} - \mathrm{WF_{methane}}} \right) \tag{2.5}$$

where $\mathrm{WF_{methane}}$ is the average weight fraction of methane in the stream. Thus Eq. (2.2) for refineries can be rewritten as follows (US EPA, 1995b):

$$E_{TOC} = F_A \times \left(\frac{\mathrm{WF_{TOC}}}{\mathrm{WF_{TOC}} - \mathrm{WF_{methane}}} \right) \times \mathrm{WF_{TOC}} \times N \tag{2.6}$$

Refinery screening range EFs (for nonmethane organic compound emission rates) and SOCMI screening range emission factors (for TOC emission rates) are given in

Table 2.9 **SOCMI and Refinery Average Emission Factors (The Light Liquid Pump Seal Factor Can Be Used to Predict the Leak Rate From Agitator Seals) (US EPA, 1995b)**

Equipment Type	Service	SOCMI Emission Factor (kg/h/source)	Refinery Emission Factor (kg/h/source)
Valve	Gas	5.97×10^{-3}	2.68×10^{-3}
	Light liquid	4.03×10^{-3}	1.09×10^{-2}
	Heavy liquid	2.3×10^{-4}	2.3×10^{-4}
Pump seals	Light liquid	1.99×10^{-2}	1.14×10^{-1}
	Heavy liquid	8.62×10^{-3}	2.1×10^{-2}
Compressor seals	Gas	2.28×10^{-1}	6.36×10^{-1}
Pressure relief valves	Gas	1.04×10^{-1}	1.6×10^{-1}
Connectors	All	1.83×10^{-3}	2.5×10^{-4}
Open-ended lines	All	1.7×10^{-3}	2.3×10^{-3}
Sampling connections	All	1.5×10^{-2}	1.5×10^{-1}

Tables 2.10 and 2.11, respectively. To calculate TOC emissions using the screening ranges approach, Eq. (2.4) can be used. For refineries only, the emission factors "F_G" and "F_L" must be adjusted to account for all organic compounds in the stream because the refinery factors are only valid for nonmethane organic compounds. The equations are:

$$F_G = F_G \times \left(\frac{\mathrm{WF}_{\mathrm{TOC}}}{\mathrm{WF}_{\mathrm{TOC}} - \mathrm{WF}_{\mathrm{methane}}}\right) \tag{2.7}$$

$$F_L = F_L \times \left(\frac{\mathrm{WF}_{\mathrm{TOC}}}{\mathrm{WF}_{\mathrm{TOC}} - \mathrm{WF}_{\mathrm{methane}}}\right) \tag{2.8}$$

Thus Eq. (2.4) for refineries can be rewritten as follows (US EPA, 1995b):

$$\begin{aligned} E_{\mathrm{TOC}} = &\left(\left[F_G \times \left(\frac{\mathrm{WF}_{\mathrm{TOC}}}{\mathrm{WF}_{\mathrm{TOC}} - \mathrm{WF}_{\mathrm{methane}}}\right) \times N_G\right]\right. \\ &\left. + \left[F_L \times \left(\frac{\mathrm{WF}_{\mathrm{TOC}}}{\mathrm{WF}_{\mathrm{TOC}} - \mathrm{WF}_{\mathrm{methane}}}\right)\right]\right) \end{aligned} \tag{2.9}$$

Table 2.10 **Refinery Screening Range Emission Factors (For Nonmethane Organic Compound Emission Rates) (The Light Liquid Pump Seal Factor Can Be Used to Predict the Leak Rate From Agitator Seals) (US EPA, 1995b)**

Equipment Type	Service	≥10,000 ppmv Emission Factor (kg/h/source)	<10,000 ppmv Emission Factor (kg/h/source)
Valves	Gas	0.2626	6×10^{-4}
	Light liquid	0.0852	1.7×10^{-3}
	Heavy liquid	0.00023	2.3×10^{-4}
Pump seals	Light liquid	0.437	1.2×10^{-2}
	Heavy liquid	0.3885	1.35×10^{-2}
Compressor seals	Gas	1.608	8.94×10^{-2}
Pressure relief valves	Gas	1.691	4.47×10^{-2}
Connectors	All	0.0375	6×10^{-5}
Open-ended line	All	0.01195	1.5×10^{-3}

Table 2.11 **SOCMI Screening Range EFs (For TOC Emission Rates) (The Light Liquid Pump Seal Factor Can Be Used to Predict the Leak Rate From Agitator Seals) (US EPA, 1995b)**

Equipment Type	Service	≥10,000 ppmv Emission Factor (kg/h/source)	<10,000 ppmv Emission Factor (kg/h/source)
Valves	Gas	0.0782	1.31×10^{-4}
	Light liquid	0.0892	1.65×10^{-4}
	Heavy liquid	0.00023	2.3×10^{-4}
Pump seals	Light liquid	0.243	1.87×10^{-3}
	Heavy liquid	0.216	2.1×10^{-3}
Compressor seals	Gas	1.608	8.94×10^{-2}
Pressure relief valves	Gas	1.691	4.47×10^{-2}
Connectors	All	0.113	8.1×10^{-5}
Open-ended line	All	0.01195	1.5×10^{-3}

Table 2.12 Equipment-Leak Rate for SOCMI Equipment Components (US EPA, 1995b; RTI International, 2015)

Equipment Type (All Services)	Default Zero Emission Rate (kg/h/source)	Pegged Emission Rate (kg/h/source)		Correlation Equation (kg/h/source)
		10,000 ppmv	100,000 ppmv	
Gas valve	6.6×10^{-7}	0.024	0.11	$1.87 \times 10^{-6}C^{0.873}$
Light liquid valve	4.9×10^{-7}	0.036	0.15	$6.41 \times 10^{-6}C^{0.797}$
Light liquid pump	7.5×10^{-6}	0.140	0.62	$1.90 \times 10^{-5}C^{0.824}$
Connectors	6.1×10^{-7}	0.044	0.22	$3.05 \times 10^{-6}C^{0.885}$

The equipment-leak rate for petroleum refinery equipment components was given in Table 2.4, but the equipment-leak rate for SOCMI equipment components is given in Table 2.12. In this table, emission rates are for TOC including non-VOCs such as methane and ethane and C is the screening value in ppmv measured by the monitoring device. In addition, the correlation for light liquid pumps can be applied to compressor seals, pressure relief valves, agitator seals, and heavy liquid pumps. The light liquid pump default zero value can also be applied to compressors, pressure relief valves, agitators, and heavy liquid pumps. In addition, the light liquid pump seal pegged emission rates can be applied to compressors, pressure relief valves, and agitators (US EPA, 1995b).

Example 2.1

At a refinery, assume there are 100 gas valves in a stream that, on average, contain 80 wt% nonmethane organic compounds, 10 wt% water vapor, 10 wt% methane, and no ethane (thus the TOC wt% would be 90). If the process operates 8000 h per year (h/year), what are the hourly and annual TOC and VOC emissions from the 100 gas valves?

Solution

The average hourly TOC emissions from the gas valves in the stream can be calculated using the applicable EF from Table 2.9 and Eq. (2.6):

$$
\begin{aligned}
E_{\mathrm{TOC}} &= F_{\mathrm{A}} \times \left(\frac{\mathrm{WF}_{\mathrm{TOC}}}{\mathrm{WF}_{\mathrm{TOC}} - \mathrm{WF}_{\mathrm{methane}}}\right) \times \mathrm{WF}_{\mathrm{TOC}} \times N \\
&= 0.0268 \times \left(\frac{0.9}{0.9 - 0.1}\right) \times 0.9 \times 100 = 2.71\ \mathrm{kg\ TOC/h}
\end{aligned}
$$

The average annual TOC emissions from the gas valves in the stream can also be calculated as follows:

$$E_{\mathrm{TOC,\ annual}} = 2.71\ \mathrm{kg\ TOC/h} \times 8000\ \mathrm{h/year} = 21680\ \mathrm{kg\ TOC/year}$$

The average hourly VOC emissions from the gas valves in the stream can be calculated using Eq. (2.3):

$$E_{\mathrm{VOC}} = E_{\mathrm{TOC}} \times \left(\frac{\mathrm{WF_{VOC}}}{\mathrm{WF_{TOC}}}\right) = 2.71 \times \left(\frac{0.8}{0.9}\right) = 2.41\ \mathrm{kg\ VOC/h}$$

The average annual VOC emissions from the gas valves in the stream can also be calculated as follows:

$E_{\mathrm{VOC,\ annual}} = 2.41\ \mathrm{kg\ TOC/h} \times 8000\ \mathrm{h/year} = 19280\ \mathrm{kg\ VOC/year}$ (US EPA, 1995b; RTI International, 2015).

Example 2.2

At an SOCMI process unit, assume there are 100 gas valves in a stream that, on average, contain 80 wt% nonmethane organic compounds, 10 wt% water vapor, 10 wt% methane, and no ethane (thus the TOC wt% would be 90). If the process operates 7900 h per year, what are the hourly and annual TOC emissions from the 100 gas valves?

Solution

The average hourly TOC emissions from the gas valves in the stream can be calculated using the applicable EF from Table 2.9 and Eq. (2.2):

$$E_{\mathrm{TOC}} = F_{\mathrm{A}} \times \mathrm{WF_{TOC}} \times N = 0.00597 \times 0.9 \times 100 = 0.5373\ \mathrm{kg\ TOC/h}$$

The average annual TOC emissions from the gas valves in the stream can also be calculated as follows:

$$E_{\mathrm{TOC,\ annual}} = 0.5373\ \mathrm{kg\ TOC/h} \times 7900\ \mathrm{h/year} = 4244.67\ \mathrm{kg\ TOC/year}$$

(US EPA, 1995b; RTI International, 2015).

Example 2.3

A refinery catalytic reforming unit (CRU) operating 8000 h per year (h/year) has 600 valves. Assume that the number of valves in gas, light liquid, and heavy liquid services for screening value $< 10{,}000$ ppmv are 236, 293, and 65, respectively, and these data for screening value $\geq 10{,}000$ ppmv are 3, 3, and 0, respectively. In addition, assume the average wt% of methane and ethane in all streams are known or estimated to be equal to 3% and 1% of the TOC, respectively. Also assume the TOC content of each stream is 100%. What are the cumulative hourly TOC and VOC emission rates from the valves in this process unit? What are the annual TOC and VOC emissions?

Solution

Hourly TOC emissions for valves in gas, light liquid, and heavy liquid services can be calculated using the applicable EFs from Table 2.10 and Eq. (2.9):

Hourly TOC emissions for valves in gas service:

$$E_{\mathrm{TOC}} = \left(\left[0.2626 \times \left(\frac{100}{100-3}\right) \times 3\right] + \left[0.0006 \times \left(\frac{100}{100-3}\right) \times 236\right]\right)$$
$$= 0.9581 \text{ kg TOC/h}$$

Hourly TOC emissions for valves in light liquid service:

$$E_{\mathrm{TOC}} = \left(\left[0.0852 \times \left(\frac{100}{100-3}\right) \times 3\right] + \left[0.0017 \times \left(\frac{100}{100-3}\right) \times 293\right]\right)$$
$$= 0.7770 \text{ kg TOC/h}$$

Hourly TOC emissions for valves in heavy liquid service:

$$E_{\mathrm{TOC}} = \left(\left[0.00023 \times \left(\frac{100}{100-3}\right) \times 0\right] + \left[0.00023 \times \left(\frac{100}{100-3}\right) \times 65\right]\right)$$
$$= 0.0154 \text{ kg TOC/h}$$

Thus the total hourly TOC emissions for all valves are $0.9581 + 0.7770 + 0.0154 = 1.7505$ kg TOC/h. The hourly VOC emissions from all valves can be calculated using Eq. (2.3):

$$E_{\mathrm{VOC}} = E_{\mathrm{TOC}} \times \left(\frac{\mathrm{WF_{VOC}}}{\mathrm{WF_{TOC}}}\right) = 1.7505 \times \left(\frac{96}{100}\right) = 1.6804 \text{ kg VOC/h}$$

The annual TOC and VOC emissions from all valves can be calculated as follows:

$$E_{\mathrm{TOC,\ annual}} = 1.7505 \text{ kg TOC/h} \times 8000 \text{ h/year} = 14004 \text{ kg TOC/year}$$
$$E_{\mathrm{VOC,\ annual}} = 1.6804 \text{ kg TOC/h} \times 8000 \text{ h/year} = 13443.93 \text{ kg VOC/year}$$

(US EPA, 1995b; RTI International, 2015).

Example 2.4

For the valves in the same reforming unit described in Example 2.3, assume monitoring registers the screening value readings in Table 2.13. What are the cumulative hourly TOC and VOC emission rates from the valves in this process unit at the time the monitoring is conducted?

Solution

To calculate the emissions, the default zero value for valves given in Table 2.4 (7.8×10^{-6}) is used to estimate the TOC emissions from the 580 valves with a

Table 2.13 **Number of Valves, the Screening Value, and Hourly TOC and VOC Emission Rates From the Valves in Example 2.4 (US EPA, 1995b; RTI International, 2015)**

Number of Valves	Screening Value (ppmv)	Emissions (kg/h)	
		TOC	VOC
580	0	0.00452	0.00434
5	200	0.00012	0.00011
5	400	0.00020	0.00019
2	1,500	0.00054	0.00051
2	7,000	0.00169	0.00162
2	20,000	0.00370	0.00355
2	50,000	0.00733	0.00704
2	Pegged at 100,000	0.28000	0.26880
	Total	0.30	0.29

screening value of 0 ppmv. The pegged emission rate for the valves in Table 2.4 (0.140) is used to estimate the TOC emission rate for the two valves with pegged readings. The correlation equation for the valves in Table 2.4 ($2.29 \times 10^{-6}C^{0.746}$) is used to estimate the emissions for each of the valves with a measured screening value. In each case, the calculated TOC emissions are multiplied by $(100 - 4)/100$ to calculate the VOC emissions (US EPA, 1995b; RTI International, 2015).

2.3.2 *Wastewater*

Water is used in petroleum refineries on a continuous basis to maintain the water balances in the steam, cooling water, utility service water, and emergency firewater supply circuits. It is also consumed for process and maintenance use purposes (European Commission and Joint Research Center, 2013). Since water does not enter into the final product, it can be expected that 80–90% of the water supplied to the refinery comes out as wastewater (Siddiqui, 2015).

Sources of wastewater in refineries include, but are not limited to, water used for process purposes or washwater in direct contact with either crude oil or other various fractions of hydrocarbons and substances; washwater and/or steam used to clean and purge systems for maintenance activities in direct contact with these substances; water separated and removed from crude oil, intermediates, and product tanks; stormwater, utility service water, steam condensate, and/or emergency firefighting water that comes in contact with crude oil, intermediates, products, additives, chemicals, and/or lubricating oils in the drainage area; routine and/or special waste solid–liquid separation activities; water originating from ballast water tanks of vessels off-loading or lading petroleum-based materials, routine and/or special groundwater extraction activities; water discarded from periodic tank and piping system hydro test and metal-passivation activities; water for sanitary usage; and rainwater falling onto site that comes into contact with crude oil and other various fractions of hydrocarbons and substances (European Commission and Joint Research Center, 2013).

A collective mix of wastewater streams containing soluble and insoluble pollutants can be generated in refineries. Total hydrocarbon content (THC), total petroleum hydrocarbon index (TPH-index), biochemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), ammoniacal nitrogen, total nitrogen, total suspended solids (TSS), total metals, cyanides, fluorides phenols, phosphates, special metals such as Cd, Ni, Hg, Pb, and vanadium, benzene, toluene, ethylbenzene, and xylene (BTEX), pH (acids, alkalis), taste and odor producers, heat, sulfides, and other micropollutants are water-pollutant parameters in refineries (Orszulik, 2008; European Commission and Joint Research Center, 2013; Jafarinejad, 2015e). The major water pollutants and their sources in refineries are listed in Table 2.14.

The quantity of wastewaters generated and their characteristics depend on the process configuration. As a general guide, approximately 3.5–5 cubic meters (m^3) of wastewater per ton of crude are generated when cooling water is recycled. According to the World Bank Group (1998), refineries generate polluted wastewaters containing BOD and COD levels of approximately 150–250 mg per liter (mg/L) and

Table 2.14 **Major Water Pollutants and Their Sources in Refineries (CONCAWE, 1999; European Commission and Joint Research Center, 2013)**

Water Pollutant	Sources
Oil	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain)
H_2S (RSH)	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, spent caustic
NH_3 (NH_4^+)	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, sanitary blocks
Phenols	Distillation units, visbreaking, catalytic cracking, spent caustic, ballast water
Organic chemicals (BOD, COD, TOC)	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain), sanitary blocks
CN^-(CNS^-)	Visbreaking, catalytic cracking, spent caustic, ballast water
TSS	Distillation units, hydrotreating, visbreaking, catalytic cracking, spent caustic, ballast water, sanitary blocks
Amines compounds	CO_2 removal in LNG plants

300—600 mg/L, respectively; phenol levels of 20—200 mg/L; oil levels of 100—300 mg/L in desalter water and up to 5000 mg/L in tank bottoms; benzene levels of 1—100 mg/L; benzo(a)pyrene levels of less than 1—100 mg/L; heavy metals levels of 0.1—100 mg/L for chrome and 0.2—10 mg/L for lead; and other pollutants (World Bank Group, 1998).

Wastewater generation in petrochemical plants is from process operations (e.g., vapor condensation, process water, and spent caustic in crackers and aromatic plants), cooling tower blow down, pump and compressor cooling, paved utility area drains, cooling water, and stormwater run-off (IL & FS Ecosmart Limited Hyderabad, 2010; MIGA, 2004). According to the MIGA (2004), process wastewaters are generated at a rate of about 15 cubic meters per hour (m^3/h) based on a 500,000 metric tons per year ethylene production and may contain BOD_5 levels of 100 mg/L; COD levels of 1500—6000 mg/L; suspended solids levels of 100—400 mg/L; oil and grease levels of 30—600 mg/L; phenol levels of up to 200 mg/L and benzene levels of up to 100 mg/L (MIGA, 2004).

The details of refinery and petrochemical wastewater characteristics have been collected from some references and are listed in Table 2.15. As shown, refineries and petrochemicals generate polluted wastewaters containing BOD and COD levels of approximately 90—685 and 300—600 mg/L, respectively; phenol levels of 0.2—200 mg/L; oil and grease levels of 12.5—20,223 mg/L; turbidity levels of 10.5—159.4 Nephelometric Turbidity Unit (NTU); TSS levels of 28.9—950 mg/L; BTEX levels of 1—100 mg/L; heavy metals levels of 0.01—100 mg/L; pH levels of 6.7—10.8, etc.

According to the European Commission and Joint Research Center (2013) and EC (2010), 6475 (from 42 sites), 7951 (from 42 sites), and 6074 (from 41 sites) tons/year of TOC were released from refineries in 2004, 2007, and 2009, respectively. Also 45 (from 56 sites), 59 (from 59 sites), and 42 (from 59 sites) tons/year of phenols were released from refineries in 2004, 2007, and 2009, respectively. In addition, 2769 (from 25 sites), 2245 (from 20 sites), and 2103 (from 21 sites) tons/year of total nitrogen were released from refineries in 2004, 2007, and 2009, respectively. In addition, 133 (from 10 sites), 201 (from 12 sites), and 99 (from 11 sites) tons/year of total phosphorus were released from refineries in 2004, 2007, and 2009, respectively. All countries have legislation in place to control the level of pollutants in refinery and petrochemical wastewater. The application of advanced wastewater treatment techniques and plants has led to continuing reductions in pollutant levels. According to Orszulik (2008), this is reflected in the fact that 747 tons of oil was discharged with aqueous effluents from 84 European refineries in 2000 compared with 3340 tons from 95 refineries in 1990 (Orszulik, 2008).

2.3.3 Solid Wastes

Generally, refinery solid wastes include three categories of materials: (1) sludge, both oily (e.g., desalter sludges) and nonoily (e.g., boiler feedwater sludge); (2) other refinery wastes, including miscellaneous liquid, semiliquid, or solid wastes (e.g., contaminated soil, spent catalysts from conversion processes, oily wastes, incinerator

Table 2.15 Details of Refinery and Petrochemical Wastewaters From Different References

	Refinery and Petrochemical Wastewaters From Different References												
Parameters	**Almasi et al. (2014)**	**Gasim et al. (2012)**	**Zhidong et al. (2009)**	**Xianling et al. (2005)**	**Nkwocha et al. (2013)**	**Coelho et al. (2006)**	**Dold (1989)**	**Ma and Guo (2009)**	**Khaing et al. (2010)**	**Amin et al. (2012)**	**Mohr et al. (1998)**	**Benyahia et al. (2006)**	**Shabir et al. (2013)**
BOD (mg/L)	204	3378	90–188		138	570	150–350	150–350					685
SBOD (mg/L)	126												
COD (mg/L)	622	7896	72.1–296.1	250–613	350	850–1020	300–800	300–600	330–556	1200			1965
SCOD (mg/L)	495												
pH	7.9	8.48		7.80–8.79	8	8–8.2		7–9	7.5–10.3	6.7		9.25–10.8	8.31
T (°C)					39.7								
Oil & grease (mg/L)			20–87	35–55	14.75	12.7	3000	50	40–91		20,223	466–3428	1057
Ammonia (mg/L)	13.1	13.5	12.05–19.79	56–125		2.1–5.1		10–30	4.1–33.4	9.3		0.76–4.96	
Nitrate (mg/L)		2.23								9.3			
Total Kjeldahl nitrogen (TKN)		40.6											
Total phosphorus (mg/L)		10.2	0.82–2.96	<0.5	16.25					3.7			0.67
Total alkalinity (mg/L)		990											

Turbidity (NTU)						22–52			10.5–159.4				
TSS (mg/L)	56		245–950	108–159	60		100	150	130–250			28.9–372	315
Volatile suspended solids (VSS) (mg/L)	44												
Total dissolved solids (TDS) (mg/L)					2100							3272	6267
Phenol (mg/L)	69.6				7.35	98–128	20–200					0.2	18.32
BTEX (mg/L)						23.9	1–100						
Volatile fatty acids (VFA) (mg/L)		198											
Heavy metals (mg/L)							0.1–100					0.01–11.7	4.3–6.48

ash, spent caustic, spent clay, spent chemicals, acid tar); (3) nonrefining wastes (e.g., domestic, demolition, and construction) (European Commission and Joint Research Center, 2013). The major solid wastes that generate in a typical petroleum refinery and their sources are listed in Table 2.16.

According to the World Bank Group (1998), refineries generate solid wastes and sludges (ranging from 3 to 5 kg per ton of crude processed), 80% of which may be considered hazardous because of the presence of toxic organics and heavy metals.

Table 2.16 Major Solid Wastes Generated in a Typical Petroleum Refinery and Their Sources (European Commission and Joint Research Center, 2013; US EPA, 1995c, 2004; Speight, 2005; Hu et al., 2013)

Type of Waste	Category	Sources
Oiled materials	Oily sludges	Tank bottoms, biological treatment sludges, residues from oil/water separator, such as the American Petroleum Institute (API) separator, parallel plate interceptor, and corrugated plate interceptor (CPI), sludge from flocculation–flotation unit (FFU), dissolved air flotation (DAF), or induced air flotation (IAF) units, contaminated oiled materials soils, desalter sludges
	Solid materials	Contaminated soils, oil spill debris, filter clay acid, tar rags, filter materials, packing, lagging, activated carbon, calcium chloride sludge from neutralized HCl gas in isomerization process, coke dust (carbon particles and hydrocarbons)
Nonoiled materials	Spent catalyst (excluding precious metals)	Catalytic cracking unit, catalytic hydrocracking, hydrotreating/hydroprocessing, polymerization, residue conversion, catalytic reforming
	Other materials	Boiler feedwater sludge, resins, desicants and absorbents, neutral sludge from alkylation plants, flue-gas desulphurization (FGD) wastes
Drums and containers		Glass, metal, plastic, paint
Radioactive waste (if used)		Catalysts, laboratory waste

Table 2.16 Major Solid Wastes Generated in a Typical Petroleum Refinery and Their Sources (European Commission and Joint Research Center, 2013; US EPA, 1995c, 2004; Speight, 2005; Hu et al., 2013)—cont'd

Type of Waste	Category	Sources
Scales		Leaded/unleaded scales, rust, e.g., from crude-oil desalting
Construction/ demolition debris		Scrap metal, concrete, asphalt, soil, asbestos, mineral fibers, plastic/wood
Spent chemicals		Laboratory, caustic, acid, additives, sodium carbonate, solvents, MEA/DEA (mono/ diethanol amine), TML/TEL (tetra methyl/ ethyl lead)
Pyrophoric wastes		Scale from tanks/process units
Mixed wastes		Domestic refuse, vegetation
Waste oils		Lube oils, cut oils, transformer oils, recovered oils, engine oils
Metals		Crude-oil/desalter sludge, spent catalyst fines in catalytic hydrocracking, hydrotreating/ hydroprocessing, catalytic reforming, API separator sludge, and biological sludge in wastewater treatment

Several factors such as crude-oil properties (e.g., density and viscosity), refinery processing scheme, oil storage method, and most importantly, the refining capacity, can affect the sludge quantity generated from petroleum-refining processes. According to the US EPA (1991), each refinery in the United States generates an annual average of 30,000 tons of oily sludge. Furthermore, according to an investigation conducted by the European Commission and Joint Research Center (2013), waste generation from refineries worldwide was 1547 thousands tons per year (from 357 sites) and 1562 thousands tons per year (from 357 sites) in 2007 and 2009, respectively. According to Hu et al. (2013), it was estimated that 1 ton of oily sludge waste was generated for every 500 tons of crude oil processed. Normally, a higher refining capacity is associated with a larger amount of oily sludge generation. The global refining throughputs in recent years are shown in Fig. 2.1, and it is predicted that more than 60 million tons of oily sludge is generated every year and more than 1 billion tons of oily sludge has accumulated worldwide. The total oily sludge production amount is still increasing as a result of the ascending demand on refined petroleum products worldwide (Hu et al., 2013).

Petrochemical plants also produce a wide variety of solid wastes and sludges, some of which may be considered hazardous because of the presence of toxic organics and

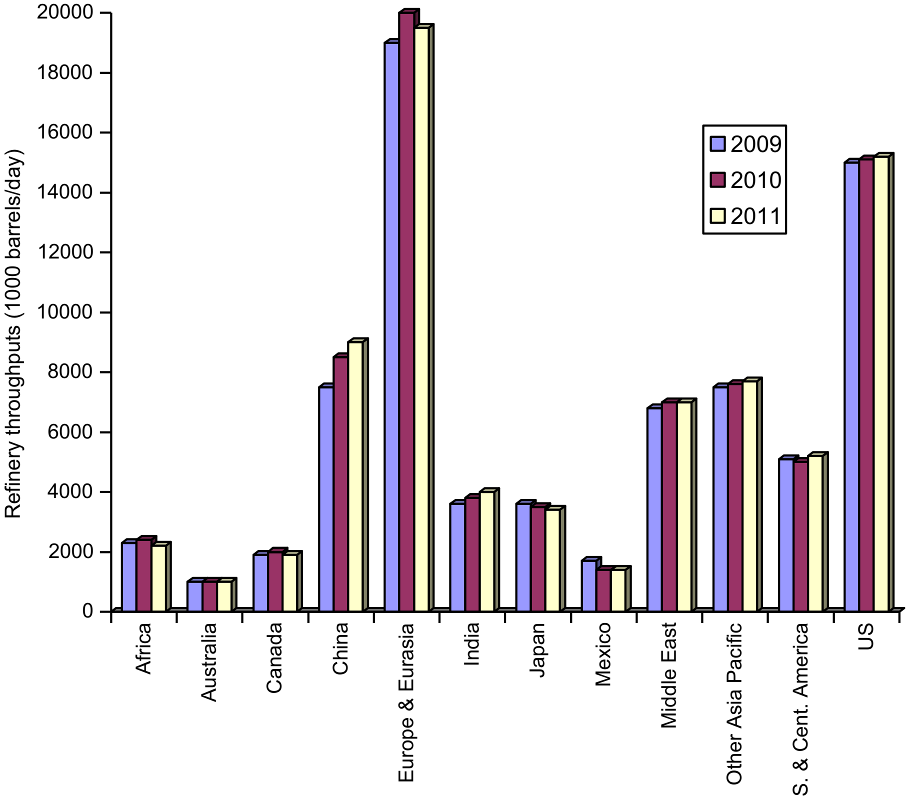

Figure 2.1 Global daily refining throughputs in recent years.
According to Hu, G., Li, J., Zeng, G., 2013. Recent development in the treatment of oily sludge from petroleumindustry: a review. Journal of Hazardous Materials 261, 470–490.

heavy metals. Spent caustic and other hazardous wastes such as distillation residues associated with units handling acetaldehyde, acetonitrile, benzyl chloride, carbon tetrachloride, cumene, phthalic anhydride, nitrobenzene, methyl ethyl pyridine, toluene diisocyanate, trichloroethane, trichloroethylene, perchloroethylene, aniline, chlorobenzenes, dimethyl hydrazine, ethylene dibromide, toluenediamine, epichlorohydrin, ethyl chloride, ethylene dichloride, and vinyl chloride may be generated in significant quantities (MIGA, 2004). Intermittently generated wastes and continuously generated wastes are two main groups of petrochemical solid-waste streams. Intermittent wastes are generally those that result from cleaning within the process areas and off-site facilities such as spent catalysts from certain processing units and product-treatment wastes such as spent filter clay, process-vessel sludge, storage-tank sediments, vessel scale, and other deposits generally removed during turnarounds. Annual volume of intermittent wastes is related to the individual plant waste management and housekeeping practices. Continuous wastes are those that require disposal at less than 2 weeks' interval such as process-unit wastes and wastewater treatment wastes. Steam cracking process when running on gas or naphtha; generate little solid wastes such as organic sludge, coke, spent catalyst, spent adsorbents, oil filters/cartridges and air-drying adsorbents. Catalysts, clay, adsorbents, sludge/solid polymerization material, oil contaminated materials and oily sludge are the major categories of solid waste generations in aromatics plants (IL & FS Ecosmart Limited Hyderabad, 2010). According to Hu et al. (2013), in China, the annual generation of oily sludge from petrochemical industry is estimated to be 3 million tons.

2.3.4 Odor Emissions

An odor is created by one or more volatilized chemical substances, generally at a very low concentration, that humans or other animals perceive by the sense of olfaction. Odors in a petroleum refinery are mainly created by sulfur compounds (e.g., hydrogen sulfide, mercaptans, sulfides, disulfides); nitrogen compounds (e.g., ammonia, amines); and hydrocarbons (e.g., aromatics). The main sources of odor in refineries are storage (such as sour crudes), bitumen production, desalter water, sewers, uncovered DAF, oil/water/solid separation, and biological treatment units and flaring (European Commission and Joint Research Center, 2013; Jafarinejad, 2015f, 2016). Some typical refinery odors, their possible sources, and the most probable compounds contributing to the odors are listed in Table 2.17.

Different approaches can be applied to refinery odor problems such as instrumental measurements [e.g., gas chromatography (GC) and gas chromatography—mass spectrometry (GC—MS)], sensory methods (e.g., olfactometry dilution technique), odor panels, and hybrid instrumentation (CONCAWE, 1975; Brattoli et al., 2011; Jafarinejad, 2016). Generally, odor measurement is necessary for odor regulation

Table 2.17 **Refinery Odors and Their Possible Sources (CONCAWE, 1975; Iranian Ministry of Petroleum, 2007; Jafarinejad, 2016)**

Type of Smell	Odor Compounds	Sources
Bad eggs	H_2S + trace of disulfides	Crude storage, distillation of gases, sulfur removal, flare stacks (cold flare)
Sewer smell	Dimethyl sulfide, ethyl and methyl mercaptans	Effluent water, biological treatment plants, LPG odorizing spent caustic loading and transfer
Burnt oil	Unsaturated hydrocarbons	Catalytic cracking unit, coking asphalt blowing, asphalt storage
Gasoline	Hydrocarbons	Product storage, API and CPI separators
Aromatics (benzene)	Benzene, toluene	Aromatic plants, naphtha reformers
Hot tar	H_2S, mercaptans, hydrocarbons	Asphalt storage

and control. Odor detectability or threshold or concentration, odor intensity, odor persistence, hedonic tone, odor character or quality, and annoyance are the terms associated with odor measurement. A sensory property referring to the minimum concentration that produces an olfactory response or sensation is called odor detectability or threshold or concentration. Odor concentration is measured as dilution ratios and given as dilution to threshold (D/T) (a measure of the number of dilutions needed to make the odorous air nondetectable) and sometimes assigned the pseudodimension of odor units per cubic meter (m^3). Odor unit (OU) is the concentration divided by the threshold. Odor intensity is the strength of the perceived odor sensation. The relationship between intensity and concentration can be explained by Stevens' power law:

$$I = k(C)^n \tag{2.10}$$

where I, k, C, and n are intensity (parts per million of butanol), concentration, constant, and exponent ranges from about 0.2 to 0.8, depending on the odorant, respectively. Odor intensity scales of 1, 2, 3, 4, and 5 depict barely perceptible, slight, moderate, strong, very strong, respectively. Odor persistence describes the rate at which an odor's perceived intensity decreases as the odor is diluted. Hedonic tone is a measure of the pleasantness or unpleasantness of an odor. Odor character or quality refers to the property used to identify an odor that differentiates it from another odor of equal intensity. Annoyance is defined as interference with comfortable enjoyment of life and property. Odor measurement can be done by several ways such as by instrumental methods/chemical analysis, electronic methods, and sensory test methods/olfactometry. Odor sensory methods are normally used. Odor sensory methods are available to monitor odor both from source emissions and in the ambient air (Ministry of

Table 2.18 Odor Threshold of Some Compounds That May Be Found in Refinery Emissions (Iranian Ministry of Petroleum, 2007; European Commission and Joint Research Center, 2013; Jafarinejad, 2016)

Compound	Odor Threshold	Odor Description
Acetic acid	1,000 ppb by volume	Sour
Acetone	100,000 ppb by volume	Chemical, sweet
Monomethyl amine	21 ppb by volume	Fishy, pungent
Dimethyl amine	47 ppb by volume	Fishy
Trimethyl amine	0.2 ppb by volume	Fishy, pungent
Ammonia	46,800 ppb by volume	Pungent
Benzene	4,700 ppb by volume	Solvent
Benzyl sulfide	2 ppb by volume	Sulfidy

Table 2.18 Odor Threshold of Some Compounds That May Be Found in Refinery Emissions (Iranian Ministry of Petroleum, 2007; European Commission and Joint Research Center, 2013; Jafarinejad, 2016)—cont'd

Compound	Odor Threshold	Odor Description
Carbon disulfide	210 ppb by volume	Vegetable-like, sulfidy
Chlorine	314 ppb by volume	Bleach, pungent
Chlorophenol	0.03 ppb by volume	Medicinal
Dimethyl sulfide	1–2 ppb by volume	Vegetable-like, sulfidy
Diphenyl sulfide	5 ppb by volume	Burnt, rubbery
Diethyl sulfide	6 ppb by volume	Garlic-like, foul
Hydrogen sulfide	5 ppb by volume	Rotten eggs
Methyl ethyl ketone	10,000 ppb by volume	Sweet
Methyl mercaptan	1–2 ppb by volume	Sulfidy, decayed cabbage
Ethyl mercaptan	0.4–1 ppb by volume	Sulfidy, decayed cabbage
n-propyl mercaptan	0.7 ppb by volume	Sulfidy
n-butyl mercaptan	0.7 ppb by volume	Strong, sulfidy
Paracresol	1 ppb by volume	Tarry, pungent
Paraxylene	470 ppb by volume	Sweet
Phenol	47 ppb by volume	Medicinal
Phosphine	21 ppb by volume	Oniony, mustard
Sulfur dioxide	470 ppb by volume	Sharp, pungent
Toluene	2,000–4,700 ppb by volume	Solvent, moth balls
Butane	6,000 ppb by volume	
Heptane	18,000 ppb by volume	
Amylenes and pentenes	170–2,100 ppb by volume	
Ethyl benzene	0.17–2.3 ppm by weight	
0-, m-, p-Xylene	0.08–3.7 ppm by weight	Sweet
Lighter alkanes (from C_2H_6 to C_4H_{10})	>50 ppm by weight	
Mid range alkanes (from C_5H_{12} to C_8H_{18})	>2 ppm by weight	
Heavier alkanes (from C_9H_{20})	<2 ppm by weight	

Environment & Forests, Government of India, 2008; Jafarinejad, 2016). The odor threshold of some compounds that may be found in refinery emissions are given in Table 2.18.

Odor emission factors (OEF) have been developed in analogy with the EFs defined by the US EPA (1995a) and can be used to estimate the odor emission rate (OER) associated with an industrial plant, odor impact assessment, etc. (Sironi et al., 2005; Capelli et al., 2014). The odor emission rate can be estimated as follows:

$$\mathrm{OER} = A \times \mathrm{OEF} \times \left(1 - \frac{\mathrm{ORE}}{100}\right) \tag{2.11}$$

where OER is the odor emission rate (in $\mathrm{ou_E/s}$), A denotes the activity index, and ORE is the overall odor reduction efficiency (%) that can be calculated using the following equation:

$$\mathrm{ORE} = 100 \times \left(\frac{C_{\mathrm{od,IN}} - C_{\mathrm{od,OUT}}}{C_{\mathrm{od,IN}}}\right) \tag{2.12}$$

where $C_{\mathrm{od,IN}}$ and $C_{\mathrm{od,OUT}}$ are the odor concentrations at the inlet and at the outlet of the abatement system, respectively (Sironi et al., 2007; Capelli et al., 2014; Jafarinejad, 2016).

2.4 Wastes From Storage, Transportation, Distribution, and Marketing

Storage, manipulation, distribution, and transportation are operations that are integrated with all sectors of the petroleum industry. Production sites and transportation terminals keep considerable amounts of crude oil and/or natural gas. Considerable amounts of crude oil and/or natural gas as well as finished products and finished products are also stored at the processing facilities and marketing terminals, respectively (Cholakov, 2009). Air emissions, wastewater, and solid wastes can be generated in storage, transportation, distribution, and marketing terminals.

2.4.1 Air Emissions and Estimation

Evaporative hydrocarbon emissions from loading/unloading and transit (breathing) losses from the storage tanks (e.g., large storage tanks as mentioned in Chapter 1 and storage tanks at service stations) and the tanks of the transporting vehicle (e.g., rail tank cars, tank trucks, marine vessels, and motor vehicle tanks) include air emission from storage, transportation, distribution, and marketing terminals (Cholakov, 2009). Transportation of crude oil from production operations to a refinery, refined products from a refinery to fuel marketing terminals and petrochemical plants, and fuels from fuel-marketing terminals to service stations, commercial accounts, and local bulk storage plants are potential sources of evaporation losses

(US EPA, 2008). As the volume of the liquid phase in a tank increases or decreases, the volume of the gas phase also changes. Emission of vapors in the atmosphere or sucking in of air during loading/unloading result from this phenomenon. Changing of temperature and pressure outside of the tank, e.g., in transit, leads to breathing (Cholakov, 2009). Moreover, fugitive emissions are mainly from imperfect seals or tank fittings of storage systems and different leaks of relevant equipment include those from pressurize pipelines (Cholakov, 2009; European Commission and Joint Research Center, 2013). The amount of emissions from a particular tank will directly depend on the vapor pressure of the product stored (European Commission and Joint Research Center, 2013). In reality, storage tanks may emit significant levels of VOC and HAP during typical operation, venting, and tank filling or dispensing depending on the specific design and construction of the tank and the characteristics of the petroleum liquids (RTI International, 2015).

There are three primary estimation methods for storage-tank emissions. These methods according to anticipated accuracy are as follows:

- Direct measurement
- Tank-specific modeling
- Default tank emission factors

The direct measurement method can only be used for storage tanks that are covered and vented to a control device. For example, emissions from fixed-roof storage tanks may be depleted and vented to a control device; these emissions can be measured directly at the outlet of the control device using direct measurement methods such as continuous emission monitoring systems (CEMS) for both constituent concentration and flow rate. Note that the control device can serve a group of tanks. If the emissions from the tank during degassing, cleaning, or drained idle periods are routed to the same control device as used during normal operations, the measured emissions will account for these periods. Differential absorption LIDAR (light detection and rating) (DIAL) techniques are direct measurement techniques even when the emissions from the tank are not vented; but these techniques are not recommended as primary methods for annual emission estimation because they do not provide continuous monitoring and have additional limitations (requiring consistent wind direction, etc.) (RTI International, 2015).

Tank-specific modeling is applicable for all petroleum liquid storage tanks except for the limited number of storage tanks whose emissions are collected and controlled external to the storage tank. This method uses the emission estimation procedures and equations detailed in Chapter 1, Section 7.1 of AP—42 (US EPA, 2006) or computer-based models designed to implement these equations such as TANKS v4.09D emission estimation software (US EPA, 2006). For example, total losses from fixed-roof tanks can be calculated as follows:

$$L_{\mathrm{T}} = L_{\mathrm{S}} + L_{\mathrm{W}} \tag{2.13}$$

where L_{T} is the total losses (lb/year), L_{S} denotes the standing storage losses (lb/year), and L_{W} is the working losses (lb/h). The standing storage loss refers to the loss of stock vapors as a result of tank vapor space breathing. Standing storage losses for these tanks can be predicted from the following equation:

$$L_S = 365 V_V W_V K_E K_S \tag{2.14}$$

where 365 is the number of daily events in a year (year^{-1}), V_V denotes the vapor space volume (ft^3), W_W is the stock vapor density (lb/ft^3), K_E is the vapor space expansion factor (dimensionless), and K_S denotes the vented vapor saturation factor (dimensionless) (for more information about these parameters see US EPA, 2006).

The working loss refers to the loss of stock vapors as a result of tank filling or emptying operations. Working losses for these tanks can be predicted from the following equation:

$$L_S = 0.0010 M_V P_{VA} Q K_N K_P \tag{2.15}$$

where M_V is the vapor molecular weight (lb/lb-mole), P_{VA} denotes the vapor pressure at daily average liquid-surface temperature (psia), Q depicts the annual net throughput [tank capacity (bbl) times annual turnover rate] (bbl/year), K_N is the working loss turnover (saturation) factor (dimensionless), and K_P denotes the working loss product factor (dimensionless). For crude oils and all other organic liquids, K_P are 0.75 and 1, respectively (for more information about these parameters and also for the total losses from the other types of tanks see US EPA, 2006).

For fixed-roof tanks that are vented to a control device, the precontrol emissions from these tanks can be predicted using AP—42 equations (Eqs. (2.11), (2.12), and (2.13)). The postcontrol device emissions can be calculated from the precontrol emission estimates and the control device efficiency using the following formula:

$$E_i = E_{unc,i} \times \left(1 - \frac{CD_{eff}}{100\%}\right) \tag{2.16}$$

where E_i is the emission rate of pollutant i (tons/year), $E_{unc,i}$ denotes the projected emission rate of pollutant i assuming the storage tank or unit does not have an add-on control device (tons/year), and $CD_{eff,i}$ is the control device efficiency for pollutant i (wt%). The default control efficiencies for control devices such as thermal oxidizer for all VOC constituents, catalytic oxidizer for all VOC constituents, carbon adsorption for VOC constituents other than acetaldehyde, acetonitrile, acetylene, bromomethane, chloroethane, chloromethane, ethylene, formaldehyde, methanol, and vinyl chloride, and carbon adsorption for constituents listed above are 98%, 98%, 95%, and 0, respectively, although the default control efficiency for the refrigerated condenser for all VOC constituents is variable based on constituents and operating temperature (RTI International, 2015).

In emission estimation from storage tanks using both AP—42 equations and software packages, each tank should be modeled individually using site-specific conditions, vapor pressure, and composition of the material stored in the tank, and emission estimates should be reported for individual pollutants. These tanks should also be modeled using monthly parameters, including average monthly measured tank liquid temperatures, when available. In addition, maximum hourly average emission rates for each tank should be estimated based on the reasonable worst-case (high emission rate) situation for a given storage tank, which will generally correspond to the emissions while the tank is actively filling. For the internal floating-roof tank, the external floating-roof tank, and the domed external floating-roof tank, the tank fittings should be selected to represent the specific characteristics of each individual storage tank. Special computations should be performed to account for tank-roof landings, tank degassing, and tank cleaning, and these predictions should be included in the final annual emissions reported for each tank (RTI International, 2015).

If tank-specific information is not available, default EFs can be used for estimation of storage-tank emissions. The default emissions factors for petroleum refinery storage tanks are presented in Table 2.19. The details regarding the assumptions used to develop these emissions factors can be found in RTI (2002, 2015) and Lucas (2007). Note that if most of the tanks are internal floating-roof tanks and/or external floating-roof tanks with domed covers, emission estimates using these emissions factors will be less accurate. Facility-specific production data is used with the default emissions factors to predict emissions. When these data are not available, crude distillation capacity and production capacities can be used for estimation. The crude distillation capacity can be assumed to be the atmospheric crude-oil distillation capacity. If there is not an atmospheric crude distillation column in a refinery, the crude distillation capacity can be estimated as the sum of the vacuum distillation and coking capacities. The sum of lube-oil production, asphalt production, and coke production can also be used as the heavy distillate production. In addition, light distillate production can be predicted as 60% of the difference of the crude-oil processing rate minus the aromatics and heavy distillate production. In addition, 40% of the difference of the crude-oil processing rate minus the aromatics and heavy distillate production can be assumed as middle distillate production (RTI International, 2015).

Emission factors for petroleum liquids in storage tanks based on tank types are presented in Table 2.20. According to Brooke and Crookes (2007), breathing losses (as mentioned before, changes in ambient temperatures, and atmospheric pressure can cause displacement of overlying vapors from the expansion and contraction of the liquid) is the major source of emissions. In addition, the method used to fill the tank (such as splash filling, submerged filling, or vapor balanced filling) affects the emission.

According to the US EPA (1995c), the majority of tank losses occur through tank seals on gasoline storage tanks in a refinery. According to the European Commission and Joint Research Center (2013), VOC emissions from storage can represent more than 40% of the total VOC emissions in a refinery.

As noted, transportation and marketing of petroleum products using rail tank cars, tank trucks, marine vessels, service stations, and motor vehicle tanks can generate evaporative emissions. Emissions from rail tank cars, tank trucks, and marine vessels are from loading losses, ballasting losses, and transit losses. When the petroleum liquids are loaded into a tank, organic vapors in empty tanks are displaced to the

Table 2.19 **Default Emissions Factors for Petroleum Refinery Storage Tanks (RTI International, 2015)**

	Emissions Factors for Petroleum Liquid Storage Tanks (pounds per million barrels)				
Chemical Name	**Crude Oil**	**Gasoline and Other Light Distillates**	**Diesel Fuel and Other Middle Distillates**	**Asphalt Lube Oils and Heavy Distillates**	**Aromatics**
Benzene	10	70	54	40	Apply sum VOC emission factor to the production of each aromatic produced
Toluene	7.5	180	100	29	Apply sum VOC emission factor to the production of each aromatic produced
Xylene	6.2	140	70	26	Apply sum VOC emission factor to the production of each aromatic produced
Ethylbenzene	1.6	31	18	5.3	
Styrene	0	66	0		
Cumene	0.5	15	10	0.4	
1,2,4-Trimethyl benzene	0.7	0	0	5.9	
Methyl tertiary-butyl ether	0	310	0	0	
1,3 Butadiene	0	1.8	0	0	
Hexane	84	420	480	13	
2,2,4-Trimethylpentane	3.4	140	22	0	
Methyl ethyl ketone		0.3	33	0	

Methyl isobutyl ketone		320	320	0	
Methanol		3.8	3.8	0	
Phenol	0.9	0.9	0.67	0	
Cresol	0.6	13	0.19	0	
Naphthalene	0.6	7.6	4	5.77	
2-Methyl naphthalene		3.5	3.5	0	
Biphenyl	0.2	0.17	0	0.7	
Polycyclic organic matter/ polynuclear aromatics/PAH		0	0	17	
Anthracene		0.24	0.24	0	
Chrysene		0.21	0.21	0	
Fluorene		0.36	0.36	0	
Phenanthrene		1.5	1.5	0	
Pyrene		0.39	0.39	0	
Sum VOC	1350	8800	5300	120	15,000

Table 2.20 Emission Factors for Petroleum Liquids in Storage Tanks Based on Tank Type (Brooke and Crookes, 2007; World Health Organization (WHO), 1993; National Atmospheric Emission Inventory (NAEI), 2000)

Tank Type	Chemical Name	Emission Factor	Comment
Underground tanks	Gasoline	1.5 kg VOC/m^3 2.03 kg VOC/ton	Splash filling
	Gasoline	1.0 kg VOC/m^3 1.353 kg VOC/ton	Submerged filling
	Gasoline	0.16 kg VOC/m^3 0.217 kg VOC/ton	Balanced vapor filling
	Gasoline-unleaded	0.34 kg nonmethane VOC/ton	Delivery at petrol stations
	Gasoline-leaded	0.34 kg nonmethane VOC/ton	Delivery at petrol stations
Floating-roof tank	Gasoline	1.14 kg VOC/m^3 storage capacity year	Factor gives yearly emission. Not clear if this also includes filling losses.
	Crude oil	0.435 kg VOC/m^3 storage capacity year	Factor gives yearly emission. Not clear if this also includes filling losses.
	Jet naphtha	0.415 kg VOC/m^3 storage capacity year	Factor gives yearly emission. Not clear if this also includes filling losses.
	Jet kerosene	0.019 kg VOC/m^3 storage capacity year	Factor gives yearly emission. Not clear if this also includes filling losses.
	Distillate oil	0.015 kg VOC/m^3 storage capacity year	Factor gives yearly emission. Not clear if this also includes filling losses.

Fixed-roof tanks	Gasoline	13.1 kg VOC/m^3 storage capacity year	Factor gives yearly emission. Not clear if this also includes filling losses.
	Crude oil	2.8 kg VOC/m^3 storage capacity year	Factor gives yearly emission. Not clear if this also includes filling losses.
	Jet naphtha	3.8 kg VOC/m^3 storage capacity year	Factor gives yearly emission. Not clear if this also includes filling losses.
	Jet kerosene	0.19 kg VOC/m^3 storage capacity year	Factor gives yearly emission. Not clear if this also includes filling losses.
	Distillate oil	0.17 kg VOC/m^3 storage capacity year	Factor gives yearly emission. Not clear if this also includes filling losses.
Car fuel tanks	Gasoline-unleaded	2.61 kg nonmethane VOC/ton	Factor for vehicle refueling.
	Gasoline-leaded	2.62 kg nonmethane VOC/ton	Factor for vehicle refueling.

Table 2.21 Saturation Factors for Petroleum Liquids (US EPA, 2008)

Cargo Carrier	Mode of Operation	Saturation Factor
Tank trucks and rail tank cars	Submerged loading of a clean cargo tank	0.50
	Submerged loading: dedicated normal service	0.60
	Submerged loading: dedicated vapor balance service	1.00
	Splash loading of a clean cargo tank	1.45
	Splash loading: dedicated normal service	1.45
	Splash loading: dedicated vapor balance service	1.00
Marine vessels (for products other than gasoline and crude oil)	Submerged loading: ships	0.20
	Submerged loading: barges	0.50

atmosphere, which is called loading losses. Splash loading and submerged loading (submerged fill pipe and bottom loading) are the major methods of cargo carrier loading. Emission estimation from uncontrolled loading petroleum liquid can be done using the following equation:

$$L_{\mathrm{L}} = 12.46\frac{SPM}{T} \tag{2.17}$$

where L_{L} is the loading loss [pounds per 1000 gallons (lb/103 gal) of liquid loaded], P denotes the true vapor pressure of liquid loaded (psia), M is the molecular weight of vapors (lb/lb−mole), T denotes the temperature of bulk liquid loaded [°R (°F + 460)], and S is a saturation factor (see Table 2.21). For gasoline-loading operations at marine terminals, the factors presented in Table 2.22 should be used. Emissions from controlled loading operations can be estimated using the following formula:

$$L_{\mathrm{L}} = 12.46\frac{SPM}{T}\left(1 - \frac{\mathrm{eff}}{100}\right) \tag{2.18}$$

where $\left(1 - \frac{\mathrm{eff}}{100}\right)$ is the overall reduction efficiency term. Selection of alternate loading techniques and usage of vapor recovery equipment can reduce loading emissions. Vapors (emissions) can be controlled by the application of refrigeration, absorption, adsorption, and/or compression, with product recovery, and through combustion in a thermal oxidation unit, with no product recovery. Control efficiencies for the recovery units range from 90% to over 99%, depending on both the nature of the vapors and the type of control equipment used.

Table 2.22 Emission Factors for Gasoline-Loading Operations at Marine Terminals (US EPA, 2008)

Vessel Tank Condition	Previous Cargo	Ships/Ocean Barges		Barges	
		mg/L Transferred	lb/10^3 gal Transferred	mg/L Transferred	Lb/10^3 gal Transferred
Uncleaned	Volatile (true vapor pressure greater than 1.5 psia)	315	2.6	465	
Ballasted	Volatile (true vapor pressure greater than 1.5 psia)	205	1.7	Not ballasted	Not ballasted
Cleaned	Volatile (true vapor pressure greater than 1.5 psia)	180	1.5	No data	No data
Gas-freed	Volatile (true vapor pressure greater than 1.5 psia)	85	0.7	No data	No data
Any condition	Nonvolatile	85	0.7	No data	No data
Gas-freed	Any cargo	No data	No data	245	2.0
Typical overall situation	Any cargo	215	1.8	410	3.4

Emissions from loading crude oil into ships and ocean barges can be calculated using the following formula:

$$C_L = C_A + C_G \tag{2.19}$$

where C_L is the total loading loss (lb/10^3 gal of crude oil loaded), C_A denotes the arrival EF, contributed by vapors in the empty tank compartment before loading (lb/10^3 gal loaded) [average arrival TOC emission factors for uncleaned (previous volatile cargo), ballasted (previous volatile cargo), cleaned or gas-freed (previous volatile cargo), and any condition (previous nonvolatile cargo) ships and ocean barge tanks are 0.86, 0.46, 0.33, and 0.33, respectively], and C_G is the generated EF, contributed by evaporation during loading (lb/10^3 gal loaded). The following equation has been proposed for calculation of C_G:

$$C_G = 1.84(0.44P - 0.42)\frac{MG}{T} \tag{2.20}$$

where P is the true vapor pressure of loaded crude oil (psia), M denotes the molecular weight of vapors (lb/lb−mole), G is the vapor growth factor equal to 1.02 (dimensionless), and T denotes the temperature of vapors [°R (°F + 460)]. Eq. (2.20) gives the TOC emission factors and VOC emission factors for crude-oil vapors ranging from approximately 55−100 wt% (usually 85%) of these TOC factors.

Ballasting emission (when the ballast water is loaded into a tank, vapors in empty tank are displaced to the atmosphere) from crude-oil ships and ocean barges can be calculated using the following equation:

$$L_B = 0.31 + 0.20P + 0.01PU_A \tag{2.21}$$

where L_B is the ballasting emission factor (lb/10^3 gal of ballast water) (e.g., TOC emission factors for crude-oil ballasting for fully loaded and lightered or previously short-loaded compartment before cargo discharge are 0.9 and 1.4 lb/10^3 gal of ballast water, respectively), P denotes the true vapor pressure of discharged crude oil (psia), and U_A is the arrival cargo true ullage (the distance between the cargo surface level and the deck level), before dockside discharge, measured from the deck in feet.

Transit losses (similar to breathing losses) from ships and barges can be estimated using the following equation:

$$L_T = 0.1PW \tag{2.22}$$

where L_T is the transit loss from ships and barges (lb/week-10^3 gal transported), P denotes the true vapor pressure of the transported liquid (psia), and W is the density of the condensed vapors (lb/gal). Typical (and extreme) total uncontrolled organic EFs for gasoline rail tank cars and tank trucks during transit in loaded with product condition and in return with vapor condition are 0−0.01 (and 0−0.08) and 0−0.11 (and 0−0.37) lb/10^3 gal transported, respectively.

Filling of underground gasoline storage tanks at service stations is another main source of evaporative emissions. Method and rate of filling, the tank configuration, the gasoline temperature, vapor pressure, and composition can affect the emissions from this operation. Emissions from these tanks can be reduced using a vapor-balance system (with control efficiency from 93–100%). Emission rates from filling underground gasoline tank at service stations using submerged filling, splash filling, and balanced submerged filling are 7.3, 11.5, and 0.3 lb/10^3 gal throughput, respectively. In addition, underground tank breathing and emptying can generate evaporative emissions. Emission rate from underground tank breathing and emptying at service station is 1 lb/10^3 gal throughput.

Uncontrolled displacement losses from vehicle refueling for a particular set of conditions can be calculated using the following equation:

$$E_R = 264.2[(-5.909) - 0.0949(\Delta T) + 0.0884T_D + 0.485(\mathrm{RVP})] \tag{2.23}$$

where E_R is the refueling emissions (mg/L), ΔT denotes the difference between temperature of fuel in vehicle tank and temperature of dispensed fuel (°F), T_D is the temperature of dispensed fuel (°F), and RVP refers to the Reid vapor pressure (psia). Average uncontrolled emissions from vapors displaced during vehicle refueling and average spillage loss are 11 and 0.7 lb/10^3 gal of dispensed gasoline, respectively. Service station business characteristics, tank configuration, and operator techniques can affect the quantity of spillage loss. Vehicle-refueling emissions can be controlled by conveying the vapors displaced from the vehicle fuel tank to the underground storage-tank vapor space through the application of a special hose and nozzle (with control efficiencies in the range of 88–92%). Natural pressure differentials and a vacuum pump are used in balance vapor control systems and vacuum assist systems for conveying, respectively. The average controlled emissions from vapors displaced during vehicle refueling is 1.1 lb/10^3 gal of dispensed gasoline (US EPA, 2008).

Example 2.5

Assume that vessel, cargo description, and compartment conditions in a crude-oil cargo ship are as follows: 80,000 dead-weight-ton tanker, crude-oil capacity 500,000 barrels (bbl); 20% of the cargo capacity is filled with ballast water after cargo discharge; the crude oil has an RVP of 6 psia and is discharged at 75°F; 70% of the ballast water is loaded into compartments that had been fully loaded to 2 ft ullage, and 30% is loaded into compartments that had been lightered to 15 ft ullage before arrival at dockside; and true vapor pressure of crude oil is 4.6 psia. What are the total ballasting emissions and VOC emissions?

Solution

U_A or true cargo ullage for the full compartments is 2 ft and this parameter for the lightered compartments is 15 ft. Thus ballasting emissions can be estimated using Eq (2.21) as follows:

$$\begin{aligned} L_B &= 0.31 + 0.20P + 0.01PU_A \\ &= 0.7[0.31 + (0.20)(4.6) + (0.01)(4.6)(2)] + 0.3[0.31 + (0.20)(4.6) \\ &\quad + (0.01)(4.6)(15)] \\ &= 1.5\ \mathrm{lb}/10^3\ \mathrm{gal} \end{aligned}$$

$$\text{Total ballasting emissions} = \left(1.5\text{lb}/10^3\text{gal}\right)(0.20)(500,000\text{bbl})(42\text{gal}/\text{bbl}) = 6300\text{lb}$$

$$\text{VOC emissions} = (0.85)(6300) = 5360\text{lb}$$

(US EPA, 2008).

2.4.2 Wastewater

Depending on maintenance service, leaking flanges and valves in storage tanks may pollute rainwater (European Commission and Joint Research Center, 2013). Leaking liquids from tanks and pipelines can also be the source polluting underground water (Cholakov, 2009). Liquid tank bottoms (water and oil emulsions with oil level up to 5 g/L) are the wastewater source from refinery storage tanks. Depending on the solidity of the rock and how carefully the fractures in the rock are sealed by injection of concrete in underground storage systems (caverns), groundwater leaking into them should be pumped out that generate wastewater. The quality of wastewater depends on stored product or crude in these systems and usually contains hydrocarbons as emulsion and water-soluble components of stored liquid. For example, the amounts of seeping water removed and hydrocarbon discharged after oil separation from light fuel oil stored in 40,000 m^3 caverns are 22,300 m^3/year and 49 kg/year, respectively (European Commission and Joint Research Center, 2013). Ballast water from transporting vessels and specially tankers is the other wastewater that can be the main source of marine water pollution (Cholakov, 2009).

2.4.3 Solid Wastes

Solid waste generated in storage, transportation, and distribution is mainly sludge from the storage and transportation tanks (Cholakov, 2009). Storage-tank bottom sludge may contain iron rust, clay, sand, water, emulsified oil and wax, phenols, benzene, toluene, xylene, sulfide, sulfate, nitrate, carbonate, ethylbenzene, naphthalene, pyrene, fluorine, cyanide, metals (iron, nickel, chromium, vanadium, antimony, mercury, arsenic, selenium, lead for leaded gasoline storage tanks, etc.), etc. The quality and quantity of sludge can vary in different sites. For example, the composition of oil in gasoline tank field sewer and distillate tank field sewer may be 19% and 3%, respectively (European Commission and Joint Research Center, 2013).

2.5 Oil Spills

According to the Glossary of Environment Statistics (1997), an oil spill refers to oil, discharged accidentally or intentionally, that floats on the surface of water bodies as a discrete mass that is carried by the wind, currents, and tides. Oil spills can be partially controlled by chemical dispersion, combustion, mechanical containment, and adsorption. They have destructive effects on coastal ecosystems. In other words, the release of a liquid petroleum hydrocarbon into the environment, especially marine areas, due to human activity is called an oil spill. It is a form of pollution. This term is usually applied to marine oil spills (release of oil into the ocean and coastal waters), but spills may also occur on land (Fingas, 2011).

2.5.1 Major Oil Spills

The major oil spills since 1967 are listed in Table 2.23. It is obvious that the Gulf of Mexico (1979, 2010), Southern Kuwait (1991), Tobago (1979), Uzbekistan (1992), Persian Gulf (1983), Angola (1991), South Africa (1983), Porstall, France (1978), and Russia (1994) oil spills were the largest oil spills in the world. The Nowruz oilfield spill in the Persian Gulf (Iran) and the Amoco Cadiz oil spill (off Porstall, France) are shown in Figs. 2.2 and 2.3, respectively.

2.5.2 Sources and Occurrences of Oil Spills

The release of crude oil from tankers, offshore platforms, drilling rigs, and wells, as well as spills of refined petroleum products (e.g., gasoline, diesel) and their byproducts, heavier fuels used by large ships such as bunker fuel, or the spill of any oily refuse or waste oil may be the source of oil spills.

The volume of oil spills in US waters from different sources in 1990 and 1998 are shown in Fig. 2.4. Oil tankers are only one source of oil spills. According to the US Census Bureau (2000), 75.4% of the volume of oil spilled in the United States in 1990 came from tank vessels (ships/barges), 5.3% from all other vessels, 13.4% from facilities, 4.0% from pipelines, 0.4% from all other nonvessels, and 1.5% from unknown. On the other hand, 34.4% of the volume of oil spilled in that country in 1998 came from tank vessels (ships/barges), 35.7% from all other vessels, 18.8% from facilities, 5.4% from pipelines, 3.7% from all other nonvessels, and 2% from unknown. In addition, the total volume of oil spills has decreased by 68.5% from 1990 to 1994% and 88.8% from 1990 to 1998.

The ITOPF (2015) has tracked accidental spills that have occurred since 1970. The number of medium (7—700 tons) and large (>700 tons) spills per decade from 1970 to 2014 (only 5 years of data for the period 2010 to 2014) is shown in Fig. 2.5. It is clear from Fig. 2.3 that the number of medium and large spills has decreased significantly in the past 45 years. Furthemore, 54% of the large spills recorded occurred in the 1970s, and this percentage has decreased each decade up to 8% in the 2000s. In addition, approximately 5.74 million tons of oil was lost as a result of tanker incidents from 1970 to 2014. Consistent with the reduction in the number of oil spills from tankers, the volume of oil spilt also shows a marked decrease. For example,the percentage of oil spilled per decade between 1970 and 2009 were 56%, 20.6%, 19.8%, and 3.6% for 1970, 1980, 1990, and 2000s, respectively. In addition, the incidence of spills <7 tons, spills 7—700 tons, and spills >700 tons by operation at time of incident [at anchor (inland/restricted), at anchor (open water), underway (inland/restricted), loading/discharging, bunkering, other operations (activities such as ballasting, deballasting, tank cleaning), and unknown] and primary cause of spill [allision/collision, grounding, hull failure, equipment failure, fire/explosion, other (events such as heavy weather damage and human error), and unknown] during 1970—2014 are given in Table 2.24. This table shows that spills resulting from accidents like allision/collisions, grounding, hull failure, and fire/explosion are much larger, with 87% of these involving losses of over 700 tons.

Table 2.23 **Major Oil Spills Since 1967 (Infoplease, 2015; International Tanker Owners Pollution Federation (ITOPF), 2015)**

Location	Date	Amount of Oil Spill	Circumstance and Source of Oil Spill
Cornwall, England	March 18, 1967	38 million gallons	Torrey Canyon ran aground, spilling crude oil off the Scilly Islands.
Buzzards Bay, Massachusetts, United States	December 15, 1976	7.7 million gallons	Argo merchant ran aground and broke apart southeast of Nantucket Island, spilling its fuel oil.
North Sea	April, 1977	81 million gallons	Blowout of well in Ekofisk oil field.
Off Porstall, France	March 16, 1978	68 million gallons	Wrecked supertanker Amoco Cadiz spilled 68 million gallons, causing widespread environmental damage over 100 mi of Brittany coast.
Gulf of Mexico, United States	June 3, 1979	140 million gallons	Exploratory oil well Ixtoc 1 blew out, spilling crude oil into the open sea.
Tobago	July 19, 1979	46 + 41 million gallons	The Atlantic Empress and the Aegean captain collided, spilling 46 million gallons of crude. While being towed, the Atlantic Empress spilled an additional 41 million gallons off Barbados on August 2.
Stavanger, Norway	Mrch 30, 1980	No data	Floating hotel in North Sea collapsed, killing 123 oil workers.
Persian Gulf, Iran	February 4, 1983	80 million gallons	Nowruz field platform spilled oil.
Cape Town, South Africa	August 6, 1983	78 million gallons	The Spanish tanker Castillo de Bellver caught fire, spilling oil off the coast.
North Sea off Scotland	July 6, 1988	No data	166 workers killed in explosion and fire on Occidental Petroleum's Piper Alpha rig in North sea; 64 survivors. It is the world's worst offshore oil disaster.

Saint John's, Newfoundland	November 10, 1988	43 million gallons	Odyssey spilled oil.
Prince William Sound, United States	March 24, 1989	10 million gallons	Tanker Exxon Valdez hit an undersea reef and spilled 10 million—plus gallons of oil into the water.
Off Las Palmas, the Canary Islands	December 19, 1989	19 million gallons	Explosion in Iranian supertanker, the Kharg-5, caused crude oil to spill into Atlantic ocean about 400 mi north of Las Palmas, forming a 100-square-mile oil slick.
Off Galveston, Texas, United States	June 8, 1990	5.1 million gallons	Mega Borg released oil some 60 nautical miles south-southeast of Galveston as a result of an explosion and subsequent fire in the pump room.
Southern Kuwait	January 23—27, 1991	240—460 million gallons	During the Persian Gulf War, Iraq deliberately released crude oil into the Persian Gulf from tankers 10 mi off Kuwait.
Genoa, Italy	April 11, 1991	42 million gallons	Haven spilled oil in Genoa port.
Angola	May 28, 1991	15—78 million gallons	ABT Summer exploded and leaked 15—78 million gallons of oil off the coast of Angola. It's not clear how much sank or burned.
Fergana Valley, Uzbekistan	March 2, 1992	80 million gallons	Oil spilled from an oil well.
Tampa Bay, Florida, United States	August 10, 1993	336,000 gallons	Three ships collided, the barge Bouchard B155, the freighter Balsa 37, and the barge ocean 255. The Bouchard spilled an estimated 336,000 gallons of no. 6 fuel oil into Tampa Bay.
Russia	September 8, 1994	2 million barrels or 102,000 barrels	Dam built to contain oil burst and spilled oil into Kolva River tributary. US Energy Department estimated spill at 2 million barrels. Russian state-owned oil company claimed spill was only 102,000 barrels.
Off Welsh coast	February 15, 1996	70,000 tons	Supertanker sea Empress ran aground at port of Milford Haven, Wales, spewed out 70,000 tons of crude oil, and created a 25-mile slick.

Continued

Table 2.23 **Major Oil Spills Since 1967 (Infoplease, 2015; International Tanker Owners Pollution Federation (ITOPF), 2015)—cont'd**

Location	Date	Amount of Oil Spill	Circumstance and Source of Oil Spill
French Atlantic coast	December 12, 1999	3 million gallons	Maltese-registered tanker Erika broke apart and sank off Britanny, spilling heavy oil into the sea.
Off Rio de Janeiro	January 18, 2000	343,200 gallons	Ruptured pipeline owned by government oil company, Petrobras, spewed heavy oil into Guanabara Bay.
Mississippi River south of New Orleans	November 28, 2000	567,000 gallons	Oil tanker Westchester lost power and ran aground near Port Sulfur, LA, dumping crude oil into lower Mississippi.
Spain	November 13, 2002	20 million gallons	Prestige suffered a damaged hull and was towed to sea and sank. Much of the 20 million gallons of oil remains underwater.
Pakistan	July 28, 2003	28,000 tons	The Tasman Spirit, a tanker, ran aground near the Karachi port, and eventually cracked into two pieces. One of its four oil tanks burst open, leaking crude oil into the sea.
Unalaska, Aleutian Islands, Alaska, United States	December 7, 2004	337,000 gallons	A major storm pushed the M/V Selendang Ayu up onto a rocky shore, breaking it in two. Oil was released, most of which was driven onto the shoreline of Makushin and Skan bays.
New Orleans, Louisiana, United States	August–September, 2005	7 million gallons	Oil was spilled during Hurricane Katrina from various sources, including pipelines, storage tanks, and industrial plants.
Calcasieu River, Louisiana, United States	June 19, 2006	71,000 barrels	Waste oil was released from a tank at the CITGO refinery on the Calcasieu River during a violent rainstorm.
Beirut, Lebanon	July 15, 2006	Between 3 and 10 million gallons	The Israeli navy bombs the Jieh coast power station, and oil leaks into the sea, affecting nearly 100 miles of coastline.

Guimaras island, The Philippines	August 11, 2006	530,000 gallons	A ship carrying oil sinks in deep water, making it virtually unrecoverable, and it continues to emit oil into the ocean as other nations are called in to assist in the massive clean-up effort.
South Korea	December 7, 2007	2.8 million gallons	The Hebei Spirit collides with a steelwire connecting a tug boat and barge five miles off South Korea’s west coast, spilling crude oil.
New Orleans, Louisiana, United States	July 25, 2008	Hundreds of thousands of gallons	A 61-foot barge, carrying 419,000 gallons of heavy fuel, collides with a 600-foot tanker ship in the Mississippi River near New Orleans. Fuel leak from the barge.
Queensland, Australia	March 11, 2009	52,000 gallons	During Cyclone Hamish, unsecured cargo aboard the container ship MV Pacific Adventurer came loose on deck and caused the release of 52,000 gallons of heavy fuel and 620 tons of ammonium nitrate, a fertilizer, into the Coral Sea.
Port Arthur, Texas, United States	January 23, 2010	462,000 gallons	The oil tanker Eagle Otome and a barge collide in the Sabine−Neches waterway, causing the release of crude oil.
Gulf of Mexico, United States	April 24, 2010	60,000 barrels of oil per day	The Deepwater Horizon, a semisubmersible drilling rig, sank on April 22, after an April 20th explosion on the vessel. When the rig sank, the riser—the 5000-foot-long pipe that connects the wellhead to the rig—became detached and began leaking oil. In addition, US Coast Guard investigators discovered a leak in the wellhead itself. It was the largest oil spill in US history.
South China Sea	January, 2014	3,000 tons	A small tanker sank in the South China Sea loaded with a cargo of approximately 3000 tons of bitumen

Figure 2.2 Nowruz oil-field spill in Persian Gulf of Iran (Courtesy of bing copyright free images. From http://envgeology.wikispaces.com/).

Figure 2.3 Amoco Cadiz oil spill in Porstall, France (https://en.wikipedia.org/wiki/Amoco_Cadiz_oil_spill#/media/File:Amoco_Cadiz_2.jpg).

2.5.3 Estimation of Oil-Spill Volume

2.5.3.1 Estimation of Oil-Spill Volume on Water

The quantity (volume) of oil spilled on water can be estimated by the surface area of the spill and the thickness of the oil film. Measuring the area is a fairly straightforward and accurate process with aerial surveillance and/or satellite imagery (Fig. 2.6). A line is simply traced around the visible edges of the oil slick (a very thin layer of oil covering a large area) and the area inside that boundary is computed. The thickness

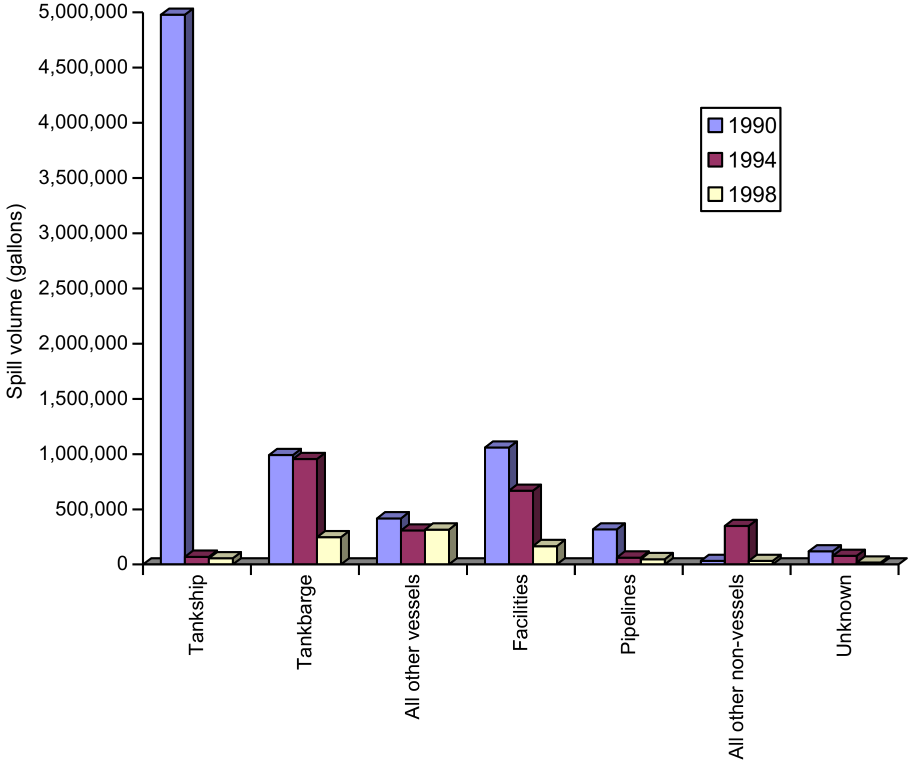

Figure 2.4 Volume of oil spills in US waters from different sources in 1990, 1994, and 1998. According to United States Census Bureau, 2000. 390. Oil Spills in U.S. Water-Number and Volume, U.S. Department of Commerce and Are Subject to Revision by the Census Bureau. [Online] Available from: http://www.allcountries.org/uscensus/390_oil_spills_in_u_s_water.html.

of an oil slick can be estimated by observing its color or appearance and assigning a thickness based on established guidelines for the range of thicknesses. The approximate film thickness and quantity of oil in film based on color observance are given in Table 2.25.

There are also some oil-slick volume estimation equations as follows (National Oceanic and Atmospheric Administration (NOAA), 1992; Washington State Department of Ecology, 1996; Alaska Clean Seas (ACS), 1999):

$$\text{Volume (in US barrels)} = 4.14 \times 10^5 \times \text{Area}\left(\text{miles}^2\right) \times \text{Average thickness (inches)} \tag{2.24}$$

$$\text{Volume (in US gallons)} = 1.74 \times 10^7 \times \text{Area}\left(\text{miles}^2\right) \times \text{Average thickness (inches)} \tag{2.25}$$

$$\text{Volume (in US barrels)} = 647 \times \text{Area (acres)} \times \text{Average thickness (inches)} \tag{2.26}$$

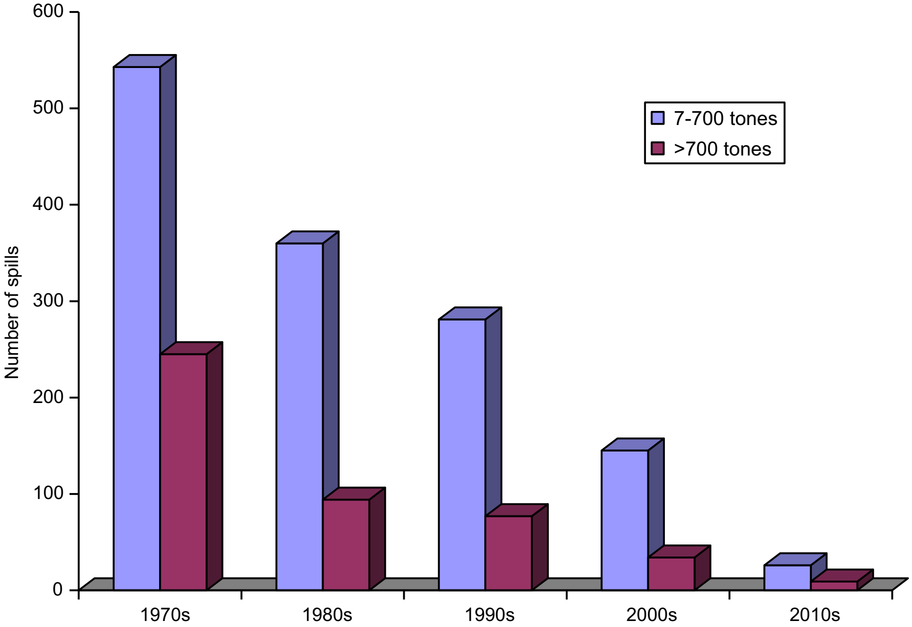

Figure 2.5 Number of medium (7—700 tons) and large (>700 tons) spills per decade from 1970 to 2014.
According to The International Tanker Owners Pollution Federation (ITOPF) Limited, January 2015. Oil Tanker Spill Statistics 2014. [Online] Available from: http://www.itopf.com/fileadmin/data/Documents/Company_Lit/Oil_Spill_Stats_2014FINALlowres.pdf.

$$\text{Volume (in US gallons)} = 2.717 \times 10^4 \times \text{Area (acres)} \times \text{Average thickness (inches)} \tag{2.27}$$

$$\text{Volume (in US gallons)} = 6.85 \times 10^2 \times \text{Area}\left(\text{miles}^2\right) \times \text{Average thickness (microns)} \tag{2.28}$$

$$\text{Volume (in US gallons)} = 1.774 \times 10^3 \times \text{Area}\left(\text{kilometers}^2\right) \times \text{Average thickness (microns)} \tag{2.29}$$

$$\text{Volume (in US barrels)} = 1.48 \times 10^{-2} \times \text{Area}\left(\text{ft}^2\right) \times \text{Average thickness (inches)} \tag{2.30}$$

$$\text{Volume (in US gallons)} = 0.624 \times \text{Area}\left(\text{ft}^2\right) \times \text{Average thickness (inches)} \tag{2.31}$$

Table 2.24 Incidence of Spills <7 tons, Spills 7–700 tons, and Spills >700 tons by Operation at Time of Incident and Primary Cause of Spill During 1970–2014 (ITOPF, 2015)

Group	Item	Incidence of Spills <7 tons	Incidence of Spills 7–700 tons	Incidence of Spills >700 tons
Operations	At anchor (inland/ restricted)			4%
	At anchor (open water)			2%
	Underway (inland/ restricted)			17%
	Underway (open water)			50%
	Loading/discharging	40%	29%	9%
	Bunkering	7%	2%	<1%
	Other operations/ unknown	53%	69%	>17%
Cause	Allision/collision	2%	26%	30%
	Grounding	3%	20%	33%
	Hull failure	7%	7%	13%
	Equipment failure	21%	15%	4%
	Fire/explosion	2%	4%	11%
	Other	23%	13%	6%
	Unknown	41%	15%	3%

Unfortunately, when using satellite imagery, especially synthetic aperture radar (SAR) imagery, we are not able to observe the spectral characteristics that create the apparent color of a typical oil slick and thus cannot use this method. Instead, according to SkyTruth (2015b), it is possible to use a rule of thumb and measure the area of the visible oil slick in an SAR image, and assuming the average thickness of the oil across that area is at least 1 μm, the minimum volume of oil in the slick can be calculated.

Example 2.6

Average thickness and surface area of an oil slick are 1 μm and 7 km^2, respectively. What is the volume of this oil slick in US gallons?

Solution

Eq (2.29) is used for estimation as follows:

Figure 2.6 A suspected oil slick from site 23,051 in the Gulf of Mexico measuring 18 miles long and covering a surface area of 53.7 square miles.
The image was captured on August 11, 2007 by NASA's Terra spacecraft and is available from the MODIS image library. SkyTruth, 2015a. SkyTruth oil spill reports. Oil Slick Site 23051 2007, 08−11. [Online] Available from: http://oil.skytruth.org/site-23051/site-23051-oil-slick-observations/oil-slick-site-23051-2007-08-11.

Table 2.25 Approximate Film Thickness and Quantity of Oil in Film Based on Color (US Coastal Guard, 1995; US EPA, 1971; Washington State Department of Ecology, 1996)

Color/ Appearance	Film Thickness (inches)	Film Thickness (milimeters)	Film Thickness (microns)	Approximate Quantity of Oil in Film
Barely visible	1.5×10^{-6}	4.0×10^{-5}	0.04	25 gallons/mile^2
Silvery	3.0×10^{-6}	8.0×10^{-5}	0.08	50 gallons/mile^2
Slightly colored	6.0×10^{-6}	1.5×10^{-4}	0.15	100 gallons/mile^2
Brightly colored	1.2×10^{-5}	3.0×10^{-4}	0.30	200 gallons/mile^2
Dull	4.0×10^{-5}	1.0×10^{-3}	1.00	666 gallons/mile^2
Dark	8.0×10^{-5}	2.0×10^{-3}	2.00	1332 gallons/mile^2

$$\begin{aligned}\text{Volume (in US gallons)} &= 1.774 \times 10^3 \times \text{Area}\left(\text{kilometers}^2\right)\\ &\quad \times \text{Average thickness (microns)}\\ &= 1.774 \times 10^3 \times 7 \times 1 = 12418 \text{ US gallons}\end{aligned}$$

The volume-estimation methods based on determining thickness of oil on water surface by using visual observations or measurement techniques and determining the spreading area by aerial pictures of the spill are not successful enough or in an acceptable error range for many oil-spill cases (Cekirge, 2013).

Government agencies and companies use oil-spill model systems to assist in oil-spill response decision support, planning, research, training, and contingency planning. The Worldwide Oil Spill Model (WOSM) is a standalone microcomputer-based oil-spill model system for these purposes. The WOSM is designed in a shell architecture in which the only parameters that change are those that describe the area in which the spill model is to be applied. A limited function geographic information system (GIS) is integrated within the model system, and the spill modeling shell includes interfaces to other GIS systems and digital data. The WOSM contains all the databases, data manipulation and graphical display tools, and models to simulate any type of oil spill. The user has control over which weathering processes are to be modeled, and the WOSM data input tools enable continual refinement of model predictions as more refined data is imported (Anderson et al., 1993). Cekirge (2013) has also developed software that can estimate the volume of the spilled oil. The inputs of the software are spreading area and shape of the oil on the water surface and various meteorological and oceanographic conditions of the event. The method is designed for determining initial volume of stray oil spills observed on water surfaces and not for continuous spills.

In settling questions of environmental impact and legal liability, unambiguously identifying spilled oils and petroleum products and linking them to known sources is necessary. Chemical fingerprinting and data-interpretation techniques are used in oil-spill identification studies, including recognition of relative distribution patterns of petroleum hydrocarbons, analysis of “source-specific marker” compounds, determination of diagnostic ratios of specific oil constituents, isotopic analysis, and several other emerging techniques. Some compounds such as PAHs, oxygen, and nitrogen heterocyclic hydrocarbons usually have great potential to supplement the existing suite of hydrocarbon targets to finetune source tracking of petroleum spills. This analysis can also be used to follow weathering and degradation of crude spills (Wang et al., 1999).

2.5.3.2 *Estimation of Oil-Spill Volume on Ice and Snow*

Field experiences and data from actual spills show that the oil-holding capacities of ice and snow range as high as 1600 barrel per acre. The following equations can be used for planning purposes (ACS, 1999):

$$\begin{aligned}\text{Volume (in US barrels)} &= 4.14 \times 10^5 \times \text{Area}\left(\text{mile}^2\right)\\ &\quad \times \text{Average thickness (inches)} \qquad (2.32)\end{aligned}$$

Table 2.26 **Rules of Thumb for Retention Capacity of Soil Types (ACS, 1999)**

Chemical	Retention Capacity for Slit	Retention Capacity for Sand	Retention Capacity for Gravel
Crude oil	12–20%	4–13%	0–5%
Diesel	7–12%	2–8%	0–2%
Gasoline	3–7%	1–5%	0–1%

$$\text{Volume (in US barrels)} = 647 \times \text{Area (acres)} \times \text{Average thickness (inches)} \tag{2.33}$$

$$\text{Volume (in US barrels)} = 1.48 \times 10^{-2} \times \text{Area}\left(\text{ft}^2\right) \times \text{Average thickness (inches)} \tag{2.34}$$

$$\text{Volume (in US gallons)} = 42 \times \text{Volume (in US barrels)} \tag{2.35}$$

2.5.3.3 Estimation of Oil-Spill Volume in or on Soils

Estimating the amount and extent of subsurface pollution from hydrocarbons spilled and trapped in soil is complicated. Hydrocarbons in soil may exist in three phases: (1) as vapors within the pore spaces; (2) as residual liquids attached to or trapped between soil particles; and (3) as dissolved components of oil in moisture surrounding soil particles. Decreasing grain size, poorer sorting of soils, and increasing oil viscosity can increase oil retention. Oil retention of initially dry soils is typically greater than that of initially water-saturated soils. The rules of thumb for retention capacity (an estimate of volume of liquid retained per unit pore volume) of soil types are listed in Table 2.26 (ACS, 1999).

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Environmental Impacts of the Petroleum Industry, Protection Options, and Regulations

3

3.1 Overview of Environmental Impacts of the Petroleum Industry

The term “environmental impacts” generally refers to the effects that activities of people, industries, businesses, projects, plans, etc., have on the receiving environment. These effects can range from very low changes in the chemical composition of air and water to complex changes in the chemical, physical, and biological nature of air, water, sediments, flora, and fauna (Orszulik, 2008). Impact levels can be determined in consideration of intensity or magnitude (low, medium, and high), duration (temporary, interim, and long-term), extent (local, regional, and state-wide), and context (common, important, and unique). In brief, impact levels can be negligible, minor, moderate, and major. Impacts that are extremely low in intensity, temporary, localized, and do not affect unique resources are called negligible impacts. Minor impacts tend to be low in intensity, of short duration, and limited extent, although common resources may experience more intense, longer-term impacts. Moderate impacts can be of any intensity or duration, although common resources may be affected by higher intensity, longer-term, or broader extent impacts while important and/or unique resources may be affected by medium or low intensity, shorter duration, local or regional impacts. Impacts that are typically medium or high intensity, long-term or permanent in duration, a regional or state-wide extent, and affect important or unique resources are called major impacts (U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Marine Fisheries Service, Office of Protected Resources, 2013).

As discussed in Chapter 2, pollution and wastes are associated with all activities and operations throughout all sectors of petroleum industry such as exploration, development, and production; hydrocarbon processing (refineries and petrochemical plants); storage, transportation, and distribution; and marketing. Air emissions, wastewaters, and solid wastes can be generated in these sectors and can have the potential for a variety of impacts on the air, water, soil, and consequently all living being on our planet (Mariano and La Rovere, 2007). At a few sites and areas, naturally occurring radioactive materials can also accumulate to levels where a significant incremental exposure above background is possible that may represent a hazard to employees (Reis, 1996; E&P Forum, 1993). In addition, oil spills (accidentally or intentionally discharged oil) is a form of pollution and can have destructive effects on marine and coastal ecosystems (Fingas, 2011). In addition, some operations in the petroleum industry can generate high noise (acoustic), although the impact of this noise is normally small (Reis, 1996).

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The environmental impacts of the petroleum industry usually depend on the stage of the process in the petroleum industry, the size and complexity of the project, the nature and toxicity of the materials and their concentration after release, the nature and sensitivity of the surrounding environment, and the effectiveness of planning, pollution prevention, mitigation, and control techniques (E&P Forum/UNEP, 1997).

Intensification of the greenhouse effect associated with global warming and climate change, acid rain, photochemical smog, reduced atmospheric visibility, death of forests, ozone depletion (from firefighting agents), soot/heavy metals deposition, poor water quality, surface water/groundwater contamination, soil contamination, disturbance of communities/flora/fauna, and destruction of ecosystems are some of the environmental impacts of the petroleum industry (E&P Forum/UNEP, 1997; Speight, 2005; Mariano and La Rovere, 2007; Orszulik, 2008; Isah, 2012; Jafarinejad, 2015, 2016).

3.1.1 Toxicity

The environmental impacts of petroleum are often negative because it is toxic to almost all forms of life. Crude oil is a mixture of many different kinds of organic compounds, many of which are highly toxic and cancer causing (carcinogenic) (Prasad and Kumari, 1987). The petroleum hydrocarbon mixture poses a challenge in assessing potential health effects associated with environmental exposures through impacted media. Toxicity and environmental fate are two components of risk assessment (the determination of quantitative or qualitative estimate of risk related to a hazard) that must be considered when evaluating these mixtures (Ryer-Powder et al., 1996). In other words, risk is a function of exposure and hazard, and both aspects must be incorporated into sound risk assessment efforts. Information relevant to exposure to and toxicity of petroleum mixtures [especially total petroleum hydrocarbons (TPHs)] is needed in risk assessment for sites contaminated with petroleum products (Heath et al., 1993).

As noted, toxicity is a measure of the potential environmental impact of a material such as petroleum. It is the degree to which a substance can damage an organism. Toxicity can be determined by its effects on the target (organism, organ, tissue, or cell). It can also be measured using bioassay by exposing target animals to different amounts of the substance in question. Dose and concentration are typically two types of toxicity measurements used. Lethal dose$_{50}$ (LD_{50}) (the dose of a substance (milligram of substance per gram of tissue (mg/g)) that causes death in 50% of a defined experimental animal population) is a dose type of toxicity measurement, while lethal concentration$_{50}$ (LC_{50}) (a lethal concentration; parts per million (ppm) or milligram per liter (mg/L)) that kills a 50% of animals within a given period of time) is a concentration type of it (Reis, 1996). The lowest dose of a substance that has been reported to have caused death in humans and animals is called the lethal dose$_{LO}$ (LD_{LO}), similarly, lethal concentration $_{LO}$ (LC_{LO}) refers to the lowest concentration of a substance that has been reported to have caused death in humans and animals within a given period of time (U.S. Department of Health and Human Services, 1999). Acute also refers to exposure that causes an immediate effect, while repeated, long-term exposure is called chronic (Reis, 1996). In addition, an estimate (with uncertainty spanning perhaps an order of magnitude) of the daily exposure of the human population to a potential hazard that is likely to be without risk of deleterious effects during a lifetime is called the reference dose (RfD) (concentration per mass of tissue). The RfD is a human health and safety guideline and is operationally derived from the no-observed-adverse-effect level (NOAEL; from animal and human studies) by consistent application of uncertainty factors that reflect various types of data used to estimate RfDs and an additional modifying factor, which is based on a professional judgment of the entire database on the chemical. Note that RfDs are not applicable to nonthreshold effects such as cancer (U.S. Department of Health and Human Services,1999). The RfDs and toxic effects for some petroleum hydrocarbons are given in Table 3.1.

Identification of components as known, probable, or possible human carcinogens is based on an EPA weight-of-evidence classification scheme in which chemicals are systematically evaluated for their ability to cause cancer in mammalian species from which conclusions are reached about the potential to cause cancer in humans. The EPA classification scheme (U.S. EPA, 1989) contains six classes based on the weight of available evidence, as follows:

A known human carcinogen;
B1 probable human carcinogen, limited evidence in humans;
B2 probable human carcinogen, sufficient evidence in animals and inadequate data in humans;
C possible human carcinogen, limited evidence in animals;
D inadequate evidence to classify; and
E evidence of noncarcinogenicity.

Some components in class D may have the potential to cause cancer, but adequate data are not available to change the classification. The toxicity value used to describe the potency of a class A, B1, B2, or C carcinogen is the cancer slope factor (CSF).

Table 3.1 Reference Dose for Petroleum Hydrocarbons (Ryer-Powder et al., 1996)

Carbon Range	Reference Compound	Toxic Effect	RfD (mg/kg/day)
C_5	n-Pentane	Narcosis, irritation	1.2
C_5 to C_8	n-Hexane	Neurotoxicity	0.06
C_6 to C_{11}	Mineral spirits	Increased liver enzymes in humans	0.015
C_9 to C_{18} (Aliphatics)	n-Nonane	Neurotoxicity	0.38
C_9 to C_{22} (aromatics)	Pyrene	Neurotoxicity	0.03
C_9 to C_{20}	Diesel fuel number 2	Mild histological changes in the liver	0.04
C_{19} to C_{50}	White mineral oil	Diarrhea	4.35

The CSF is generated by the EPA through the use of a mathematical model that extrapolates from the high doses in animal studies to the low doses characterizing human exposures. The CSF represents the 95% upper confidence limit on the slope of the dose—response curve generated by the model. Reference doses, U.S. EPA cancer classifications, and CSF for TPH components are listed in Table 3.2 (Heath et al., 1993).

As discussed in Chapter 2, in the petroleum industry, heavy metals can originate from activities such as exploration, development, production, refineries, etc. Heavy metals are metallic elements with high atomic weights, such as mercury (Hg), chromium (Cr), cadmium (Cd), arsenic (As), lead (Pb), etc. Even at low levels these metals are toxic and can damage living things. They do not break down or decompose and tend to build up in plants, animals, and people causing health concerns (Private Wells Glossary, 2010). In other words, metal that has relatively high density and toxicity at low quantity is referred as heavy metal, e.g., arsenic, lead, mercury, cadmium, chromium, thallium (Tl), etc. Some trace elements are also known as heavy metals, e.g., copper (Cu), selenium (Se), and zinc (Zn). They are essential to maintain the body's metabolism, but they are toxic at higher concentrations. The heavy metals can enter the body to a small extent via food, drinking water, and air. The heavy metals related to environmental science chiefly include Pb, Hg, Cd, Cr, Cu, Zn, manganese (Mn), nickel (Ni), silver (Ag), vanadium (V), etc. Excess quantities of heavy metals is detrimental as they destabilize ecosystems because of their bioaccumulation in organisms and elicit toxic effects on biota and even death in most living organisms (Govind and Madhuri, 2014).

Depending on the type, its concentration, route of exposure, as well as the age, genetics, and nutritional status of exposed targets, heavy metals can raise a variety of environmental and health concerns. There are numerous mechanisms for heavy metals-induced toxicity and carcinogenicity, some of which are complicated. These metals can disrupt metabolic functions in two ways: they can accumulate and thereby disrupt function in vital organs and glands such as the heart, brain, kidneys, bone, liver, etc. They can also displace the vital nutritional minerals from their original place, thereby hindering their biological function (Singh et al., 2011). Maximum contamination levels (MCLs) for some heavy metal in air, soil, and water regulated by the U.S. EPA are given in Table 3.3.

3.1.2 Greenhouse Effect

The term greenhouse gas (GHG) generally refers to any gas that absorbs infrared radiation in the atmosphere. Greenhouse gases include water vapor, carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), hydrochlorofluorocarbons (HCFCs), ozone (O_3), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF_6) (International Petroleum Industry Environmental Conservation Association (IPIECA) and American Petroleum Institute (API), 2007). The three main GHGs relevant to the petroleum industry are methane (CH_4), carbon dioxide

Table 3.2 **Reference Doses, U.S. EPA Cancer Classifications, and Cancer Slope Factors for Total Petroleum Hydrocarbon Components (Heath et al., 1993)**

Components	Inhalation (mg/kg/day)	RfD	Oral (mg/kg/day)	RfD	Cancer Class	Oral CSF	Inhalation CSF
	Subchronic	Chronic	Subchronic	Chronic		(mg/kg/day)$^{A-1}$	(mg/kg/day)$^{A-1}$
t-Butyl alcohol	NA	NA	1.000	0.100	D		
Methyl alcohol	NA	NA	5.000	0.500	D		
Dibromoethane	NA	NA	NA	NA	B2	85.00	0.770
1,1-Dichloroethane	5.000	0.500	1.000	0.100	B2	0.140	NA
Ethylene dibromide	NA	NA	0.200	0.020	C	0.084	NA
Methyl-t-butyl ether	1.400	0.140	NA	NA	D		
Benzene	NA	NA	NA	NA	A	0.029	0.029
Ethylbenzene	0.290	0.290	1.000	0.100	D		
Eip-Isopropylbenzene	0.026	0.0026	0.030	0.040	D		
Toluene	0.570	0.110	2.000	0.200	D		
Xylenes	NA	NA	4.000	2.000	D		
Anthracene	NA	NA	3.000	0.300	D		
Benzo[a] pyrene	NA	NA	NA	NA	B2	7.300	6.100
Fluoranthene	NA	NA	0.400	0.040	D		
Fluorene	NA	NA	0.040	0.040	D		
Naphthalene	NA	NA	0.040	0.040	D		
Pyrene	NA	NA	0.300	0.030	D		
n-Hexane	0.057	0.057	0.600	0.060	D		

Table 3.3 **Maximum Contamination Levels for Some Heavy Metals in Air, Soil, and Water Regulated by the U.S. EPA (Duruibe et al., 2007)**

Heavy Metal	MCLs in Air (mg/m^3)	MCLs in Sludge (Soil) (mg/kg or ppm)	MCLs in Drinking Water (mg/L)	MCLs in Water Supporting Aquatic Life (mg/L or ppm)
Cadmium	0.1–0.2	85	0.005	0.008
Lead	Not available	420	0.01	0.0058
Zinc	1 (chlorine fume), 2 (oxide fume)	7500	5	0.0766
Mercury	Not available	<1	0.002	0.05
Silver	0.01	Not available	0	0.1
Arsenic	Not available	Not available	0.01	Not available

(CO_2), and nitrous oxide (N_2O). The petroleum industry contributes to GHG emissions in three ways:

- Combustion-related emissions
- Equipment leaks and vented emissions
- Emissions from nonemissive uses (asphalt and road oil, distillate fuel oil, lubricants, petroleum coke, special naphtha, waxes, etc.) via several pathways. For example, emissions may occur when producing plastics or rubber from petroleum-derived feedstocks (U.S. EPA, 2010; Bluestein and Rackley, 2010).

According to Bluestein and Rackley (2010), most GHG emissions come from the combustion of petroleum products. For example, 2480 million metric tons of CO_2 equivalent ($MMTCO_2e$) or 36% of total U.S. GHG emissions in 2007 came from the combustion of petroleum products for energy use, either as transportation fuels or as furnace or boiler fuels. The total fugitive CO_2 and CH_4 emissions from petroleum systems were 28.8 $MMTCO_2e$ in 2007, which is equivalent to about 0.4% of total U.S. GHG emissions and 5.2% of total US methane emissions. Some petroleum products are consumed for nonemissive uses. Since this petroleum is not combusted at its point of use, CO_2 is not accounted for in this stage of the process. However, combustion may take place later in the life of the product and can be accounted for at the point where it occurs. Overall, about 62% of the carbon contained in all of the nonemissive petroleum use is stored in the products with the remaining 38% is emitted at various stages. Fig. 3.1 compares emissions from each sector of the petroleum industry as available in the U.S. GHG Inventory and as calculated based on the revised estimates for the four underestimated sources. Total equipment leak and vented CH_4 and CO_2 emissions from the petroleum industry were 317 $MMTCO_2e$ in 2006. Of this total, the natural gas activities emitted 261 $MMTCO_2e$ of CH_4 and 28.50 $MMTCO_2e$ of CO_2 in 2006. Total

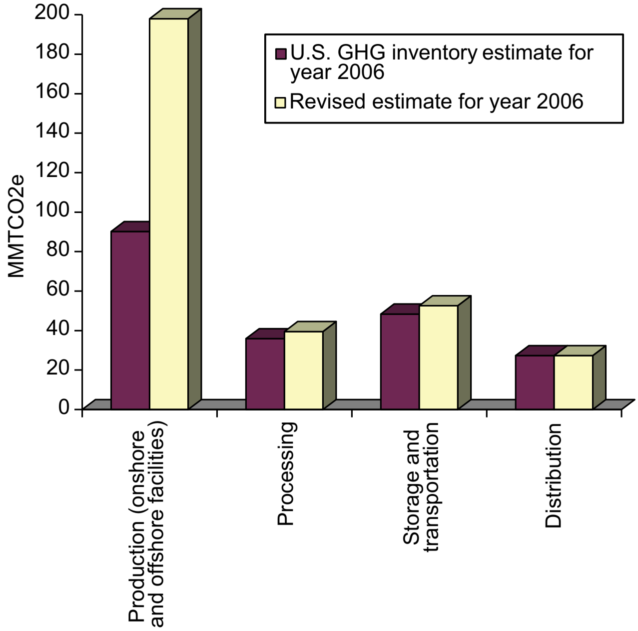

Figure 3.1 Comparison of emissions from each sector of the petroleum industry. According to United States Environmental Protection Agency (U.S. EPA), 2010. Greenhouse Gas Emissions Reporting from the Petroleum and Natural Gas Industry, Background Technical Support Document. U.S. Environmental Protection Agency Climate Change Division, Washington, DC. [Online] Available from: http://www.epa.gov/ghgreporting/documents/pdf/2010/Subpart-W_TSD.pdf.

CH_4 and CO_2 emissions from the oil industry in 2006 were 27.74 $MMTCO_2e$ and 0.29 $MMTCO_2e$, respectively (U.S. EPA, 2010). According to Evans and Bryant (2013), in Canada, emissions from oil and gas production, including extraction, mining, pipelining, and refining, were 163 million tons in 2006, which represented 28% of all GHG emissions.

The greenhouse effect (Fig. 3.2) is a phenomenon in which the atmosphere of a planet traps radiation emitted by its sun, caused by gases such as carbon dioxide, water vapor, and methane that allow incoming sunlight to pass through but retain heat radiated back from the planet's surface (The American Heritage® Dictionary of the English Language, 2013). In other words, the greenhouse effect is the retention of part of the sun's energy in the Earth's atmosphere in the form of heat as a result of the presence of greenhouse gases. Solar energy, mostly in the form of short-wavelength visible radiation, penetrates the atmosphere and is absorbed by the Earth's surface. The heated surface then radiates some of that energy into the atmosphere in the form of longer-wavelength infrared radiation. Although some of this radiation escapes into space, much of it is absorbed by greenhouse gases in the lower atmosphere, which in turn reradiate a portion back to the Earth's surface. The atmosphere thus acts in a manner

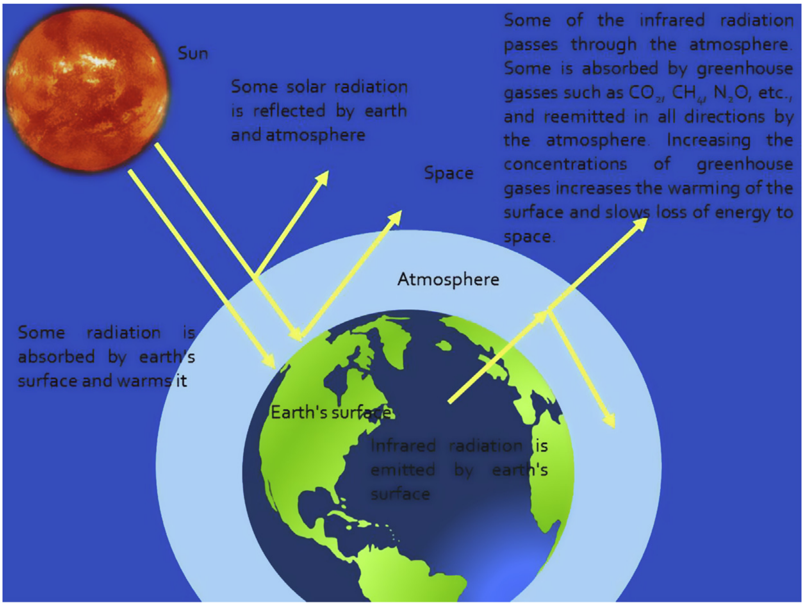

Figure 3.2 Greenhouse effect.

roughly analogous to the glass in a greenhouse, which allows sunlight to penetrate and warm the plants and soil but which traps most of the resulting heat energy inside. The greenhouse effect is essential to life on Earth; however, the intensification of its effect due to increased levels of greenhouse gases in the atmosphere is considered to be the main contributing factor to global warming and climate change. Increasing the concentrations of greenhouse gases increases the warming of the surface and slows the loss of energy to space (The American Heritage® Science Dictionary, 2002).

3.1.3 Acid Rain

Acid deposition, commonly known as acid rain, occurs when emissions from the combustion of fossil fuels and other industrial processes are subjected to complex chemical reactions in the atmosphere and fall to the earth as wet deposition (rain, snow, cloud, fog) or dry deposition (dry particles, gas). Rain and snow are already naturally acidic, but are only considered problematic when less than a pH of 5.0 (Ramadan, 2004). Robert Angus Smith first used the term "acid rain" in 1872 to describe the acidic nature of rain around the industrial town of Manchester, UK in a paper entitled "The Air and Rain Beginning of Chemical Climatology" (Singh and Agrawal, 2008).

Because carbon dioxide is dissolved into rainwater and produce carbonic acid (H_2CO_3), natural rainwater can be slightly acidic. The two principal acids in acid rain are sulfuric acid (H_2SO_4) and nitric acid (HNO_3) that their sources are sulfur dioxide (SO_2) and nitrogen oxides (NO_x). Other emissions that affect acidity are free chlorine, ammonia, volatile organic compounds (VOCs), and alkaline dust

(Ramadan, 2004). As mentioned in Chapter 2, these emissions are generated in the petroleum industry.

The acidity of acid deposition dose is affected by the level of emissions and the chemical reaction of both sulfur dioxide and nitrogen oxides. In fact, sulfur dioxide and nitrogen oxides are released and rise to the upper atmosphere to react with oxygen and water in the presence of sunlight to form acids through many steps which broken into two phases (gas phase and liquid phase) (Ramadan, 2004). The chemical reaction that results in the formation of acid rain involves the interaction of SO_2, $NO_{x,}$ and O_3 (Singh and Agrawal, 2008). A summary of the chemical reactions that cause the acidic deposition phenomenon in the atmosphere are as follows:

$$O_3 \rightarrow O_2 + O^{\bullet} \tag{3.1}$$

$$O^{\bullet} + H_2O \rightarrow 2OH^{\bullet}(\text{hydroxyl radical}) \tag{3.2}$$

Sulfur burns in oxygen to form sulfur dioxide:

$$S + O_2 \rightarrow SO_2 \tag{3.3}$$

Sunlight and hydroxyl radical combine to form sulfuric acid in the gas phase:

$$SO_2 + 2OH^{\bullet} \rightarrow 2H_2SO_4 \tag{3.4}$$

Sulfur dioxide reacts with oxygen in atmosphere to form sulfur trioxide:

$$2SO_2 + O_2 \rightarrow 2SO_3 \tag{3.5}$$

Sulfur trioxide reacts with moisture in the atmosphere to form sulfuric acid in the liquid phase:

$$SO_3 + H_2O \rightarrow H_2SO_4 \tag{3.6}$$

Oxygen and nitrogen mix together:

$$N_2 + O_2 + \text{energy} \rightarrow 2NO \tag{3.7}$$

Nitrous oxide reacts with oxygen diatomic molecule to produce nitrous dioxide:

$$2NO + O_2 \rightarrow 2NO_2 \tag{3.8}$$

Sunlight and hydroxyl radical combine to form nitric acid in the gas phase:

$$NO_2 + OH^{\bullet} \rightarrow HNO_3 \tag{3.9}$$

Nitrogen dioxide reacts with moisture in the atmosphere to form nitric acid in the liquid phase:

$$NO_2 + H_2O \rightarrow HNO_3 \tag{3.10}$$

There are also other gases that form acid such as carbonic acid (Ramadan, 2004; Singh and Agrawal, 2008):

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{3.11}$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{3.12}$$

Acid rain has adverse impacts on surface waters (lakes and streams), aquatic animals and ecosystems, animals, soil, forests (trees) and plants, manmade materials (e.g., building materials, metals, paints, textiles, ceramic, leather, rubber, etc.), visibility, and human health (Ramadan, 2004; Singh and Agrawal, 2008; U.S. EPA, 2008a).

Acidic deposition can usually be controlled by emission control and policy intervention. The damage to lakes and other water bodies may be eliminated or restored by adding lime (Singh and Agrawal, 2008). The national goal to reduce current levels of SO_2 and NO_x production (by implementing and enforcing tough regulations to limit any credit for the height of tall stacks, adopting and implementing penalties for major polluters violating emission standards, establishing a National Air Quality standard for fine particles, such as sulfates and nitrates); clean up smokestacks and exhaust pipes by installing scrubbers in smokestacks (duct injection, wet scrubber or flue gas desulphurization (FGD), and dry scrubber or spray dryers for controlling SO_x emissions, selective noncatalytic reduction (SNCR), and selective catalytic reduction (SCR) for controlling NO_x emissions); the use of alternative ways of producing energy such as hydroelectric power, nuclear power, solar power, and wind power; and conserve resources and energy are methods for acidic deposition control in the petroleum industry (Ramadan, 2004).

3.1.4 Environmental Impacts of Oil Spills

Oil spills can have disastrous social, economical, and environmental consequences. The key factors or variables that influence oil-spill impacts can be identified in several domains: the oil spill itself, disaster management, marine physical environment, marine biology, human health and society, economy, and policy. Oil-spill variables include ship-safety features, location of spill, spill amount and rate, and type of oil. Timing of response, governance, response technology, human capital, natural processes, and local culture and context are disaster-management factors. The marine environment can depend on connecting waterways, tides and currents, wave exposure, temperature and salinity, substrate at site exposed to soil, and weather conditions. Exposure to toxins, exposure quantity, habitat/depth of species, mobility, feeding mode, species identity, other stressors, development stage, and generation time are variables of marine biology. Direct skin contact with carcinogenic compounds, air pollutants from oil spills, ingestion of contaminated food and water, psychological and social costs, and subsistence uses are variables that can affect human health and society. Commercial fisheries and aquaculture, commercial fisheries and aquaculture value chain, tourism industry, waterway usage, other marine-based industries, oil industry, agriculture, pure economic loss, passive use and recreation, real estate, financial sector, legal and research costs, municipal/regional government impacts, economies of scale, recovery boom, expense savings, tax revenues, and conservation benefits should be considered in economy. Policy and decision variables in oil spills include port closure, brand campaigns, compensation payments, and fishing moratoria (Chang et al., 2014).

Spilled oil at water environments such as sea breaks into many different chemical and physical components that spread throughout the system—floating, suspended in the water, sunk to the bottom, buried in sediments and coating organisms and coastal habitats (e.g., rocky shore areas, soft sediment shores, cobble and sandy beaches, tidal flats, salt marshes, etc.). Marine organisms, plants, and animals from the smallest plankton to the largest whales (e.g., birds (Fig. 3.3), mammals, fish, shellfish, invertebrates, sea turtles, etc.) can be affected by both the physical and chemical impacts of oil, tar, and toxic oil compounds (Ross, 2010; Ober, 2010; Mosbech, 2002; ITOPF, 2014a). Oil spill can have impact on human health; health, viability and diversity of coastal ecosystems; commercial fisheries; tourism; etc. (Chang et al., 2014).

Oil spills can impact wildlife directly through ingestion, absorption, and inhalation and indirectly by causing changes in behavior or relocation of home ranges as animals search for new sources of food, increasing the amount of time animals must spend foraging, and disrupting natural lifecycles (Ober, 2010). Oil may impact an environment by one or more of the following mechanisms:

- Physical smothering with an impact on physiological functions;
- Chemical toxicity giving rise to lethal or sublethal effects or causing impairment of cellular functions;
- Ecological changes, primarily the loss of key organisms from a community and the takeover of habitats by opportunistic species; and

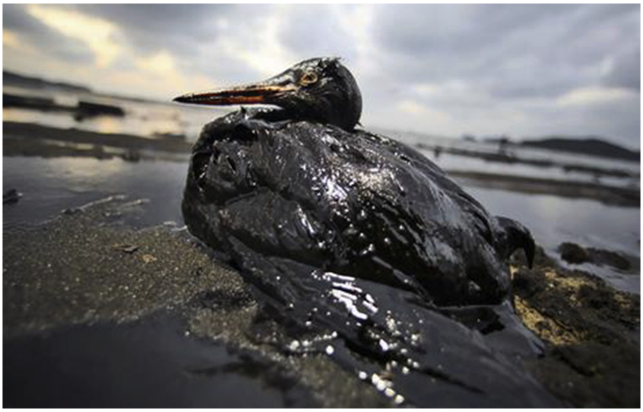

Figure 3.3 A bird covered in oil from oil spill (Bird Education Network (BEN), 2010).

- Indirect effects, such as the loss of habitat or shelter and the consequent elimination of ecologically important species and disruptions to natural lifecycles (ITOPF, 2014a).

As noted, the impacts of an oil spill depend on the size of the spill, the rate of the spill, the type of oil spilled, transportation (e.g., ship) safety features, and the location of the spill (Ramseur, 2012; Chang et al., 2014). Total damages can be enhanced by increased amount of oil spilled. Continued release of oil over several months necessitates multiple waves of response efforts. The chemical composition of oil influences dispersal characteristics (distance, depth, and degradation rate) and toxicity. Double-hulled ships are less accident-prone than single-hulled ships and spills from double-hulled ships may be less costly. Offshore spills have fewer direct economic impacts than near-shore spills in proximity of human populations (Chang et al., 2014). Depending on timing and location, even a relatively minor spill can cause significant harm to individual organisms and entire populations. Oil spills can cause impacts over a range of time scales, from days to years, or even decades for certain spills. Impacts are typically divided into acute (short-term) and chronic (long-term) effects (Ramseur, 2012).

The magnitude of harm caused to wildlife by oil spills varies according to a number of factors:

- The amount of exposure of each animal to oil;
- The pathway through which each animal is exposed to oil;
- The age, reproductive state, and health of each animal; and
- The type of synthetic chemicals used by response teams to clean the spill (Ober, 2010).

3.2 Environmental Protection Options

The term “environmental protection” generally refers to procedures and policies toward protecting the natural environment from destruction or pollution (American Heritage® Dictionary of the English Language, 2011). This practice can be done on individual, organizational, or governmental levels. Environmental audits (EA), waste-management plans, waste-management practices, certification of disposal processes, contingency plans, and employee training are environmental protection options in the petroleum industry (Reis, 1996). Waste-management practices can be done by prevention (improved operations or operating procedures), source reduction or waste minimization (material elimination, inventory control and management, material substitution, process and equipment modifications, and improved housekeeping), reuse, recycling/recovery, treatment, and disposal (E&P Forum, 1993; Reis, 1996; Speight, 2005; Mackenzie Valley Land and Water Board (MVLWB), 2011; European Commission Directorate-General Environment, 2012).

3.2.1 Environmental Audits

Environmental audits have been integrated into a wide variety of activities in environmental protection and management. An environmental audit has been defined by the International Chamber of Commerce (ICC) (1989) as:

"A management tool comprising a systematic, documented periodic and objective evaluation of how well environmental organization, management and equipment are performing with the aim of helping to safeguard the environment by: (i) facilitating management control of environmental practices; and (ii) assessing compliance with company policies, which would include meeting regulatory requirements."

Audits are generally categorized as:

1. Internal audits: using auditors from within the department, unit, or facility being audited.
2. Cross audits: using auditors from within the company but from different plants, facilities, or regions.
3. External audits: using auditors who are wholly independent of the facility to be audited. They would he contractors or consultants, i.e., not part of the company being audited (Smith et al., 1994).

The advantages and disadvantages of different types of environmental audits are listed in Table 3.4.

An environmental audit can be divided into three parts:

A Preaudit activities;
B Activities at the site;
C Postaudit activities (United Nations Environment Programme/Industry and Environment Office (UNEP/IEO), 1990).

Fig. 3.4 shows the basic steps of an environmental audit. According to Ingole (2012), environmental audits can have many benefits such as:

- Preparation of environmental management plan;
- Assessment of environmental input and risks;
- Identifying areas of strength and weakness for improvements;

Table 3.4 **Advantages and Disadvantages of Different Types of Environmental Audits (Smith et al., 1994)**

Audit Type	Advantages	Disadvantages
Internal	Low cost Low organizational disruption Operational familiarity Good opportunities for cross-transfer of information	Least independent Least audit expertise
Cross-audit	More independent Opportunities for cross-transfer of information More audit expertise	Higher cost More disruptive Less operational familiarity
External	Most independent Most audit expertise	Highest cost Most disruptive Low opportunity for information transfer Little operational familiarity

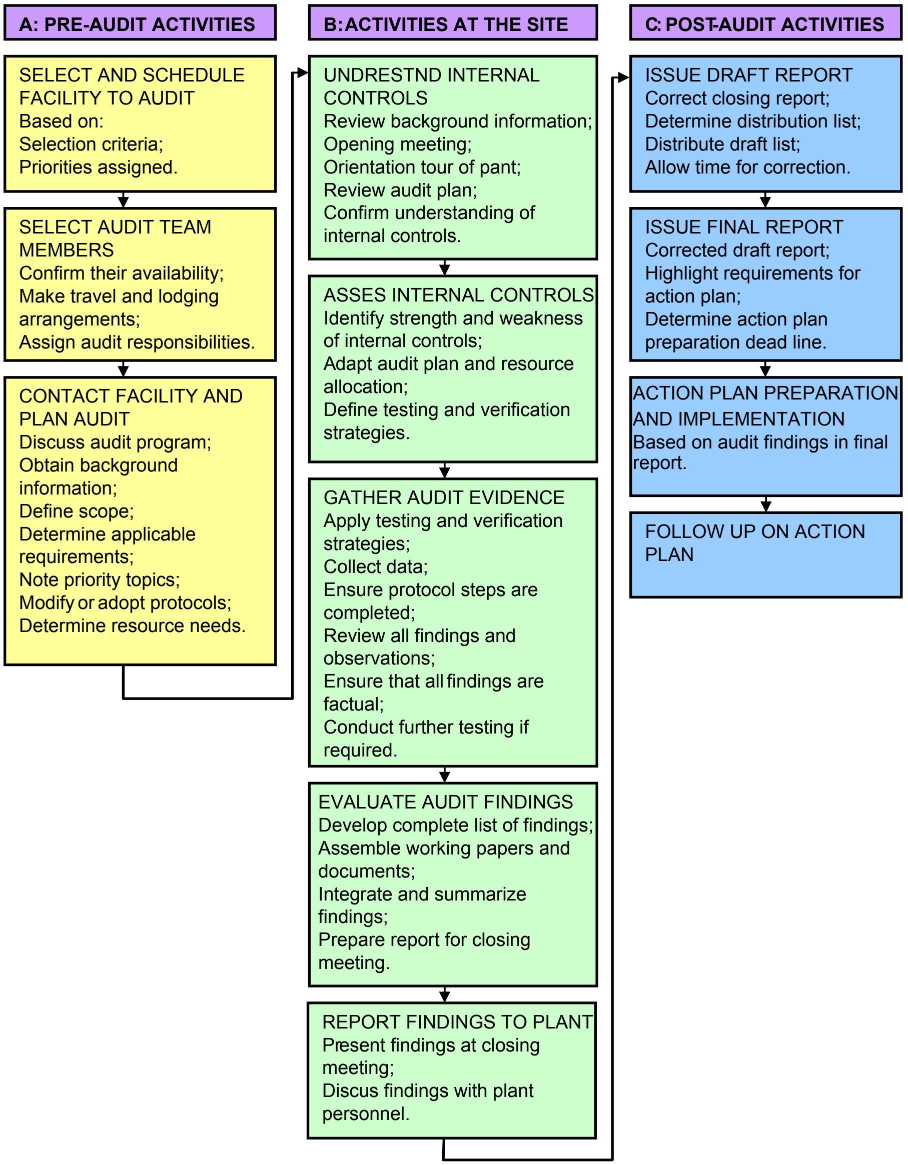

Figure 3.4 Basic steps of an environmental audit.
Modified of United Nations Environment Programme/Industry and Environment Office (UNEP/IEO), 1990. Environmental Auditing, Paris.

- Evaluation of pollution control;
- Verification of compliance with laws;
- Assuring safety of plant, environment and human beings;
- Enhancement of loss prevention, manpower development, and marketing;
- Budgeting for pollution control, waste prevention, reduction, recycling, and reuse;

- Providing an opportunity for management to give credit for good environmental performance; and
- As a whole, the environmental audit plays an important role in minimizing environmental problems locally, regionally, nationally, and internationally.

3.2.2 Waste-Management Plans

Waste-management plans play a major role in attaining sustainable waste management in line with waste legislation. Their key purpose is to give an overview of all waste generated and treatment options for this waste (European Commission Directorate-General Environment, 2012). A waste-management plan is usually a document that outlines the activities and methods of waste management from waste generation to final release to the receiving environment or disposal (MVLWB, 2011).

The waste-management hierarchy is shown in Fig. 3.5. The incorporation of a hierarchy of waste-management practices in the development of waste-management plans is an important part of waste management (E&P Forum, 1993). The waste hierarchy generally lays down a priority order of what constitutes the best overall environmental opinion in waste legislation and policy. The highest priority is given to waste prevention and source reduction, followed by preparing for reuse, recycling, or other recovery (e.g., energy recovery) and treatment. Optimum final disposal is at the bottom of this hierarchy. The goal of implementing the waste hierarchy is to decouple economic growth from negative environmental impacts of the use of natural resources and to become a recycling society (European Commission Directorate-General Environment, 2012).

A waste-management plan can be structured in many ways, but according to the European Commission Directorate-General Environment (2012), the possible elements of a waste-management plan are as follows:

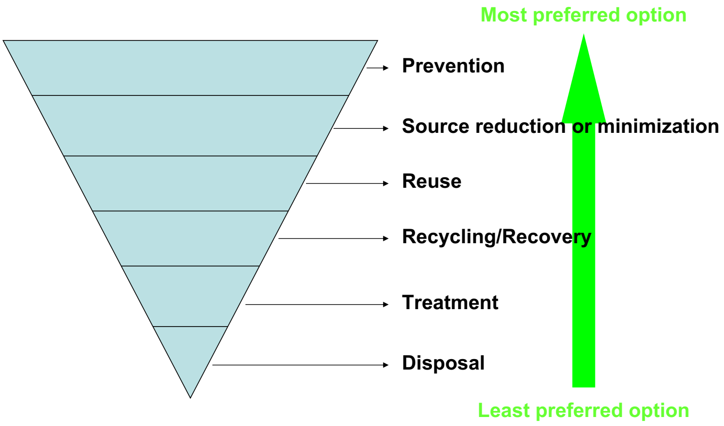

Figure 3.5 Waste-management hierarchy.

- Background:
    - Overall waste problematic in a territory;
    - International and national legislations;
    - Description of national waste policy and prevailing principles to address overall waste problems in a territory, in line with the waste hierarchy (prevention, source reduction or minimization, reuse, recycling/recovery (e.g., energy recovery), treatment, and disposal);
    - Description of objectives set in specific areas;
    - Inputs from the consultation process;
- Status part:
    - Waste amounts (e.g., waste streams, waste sources, and waste-management options);
    - Waste collection and treatment for the above;
    - Waste shipment;
    - Organization and financing;
    - Assessment of previous objectives;
- Planning part:
    - Assumptions for planning;
    - Forecast in terms of waste generation, total and per waste stream;
    - Determination of objectives for forecasted waste streams, waste sources, and waste-management options;

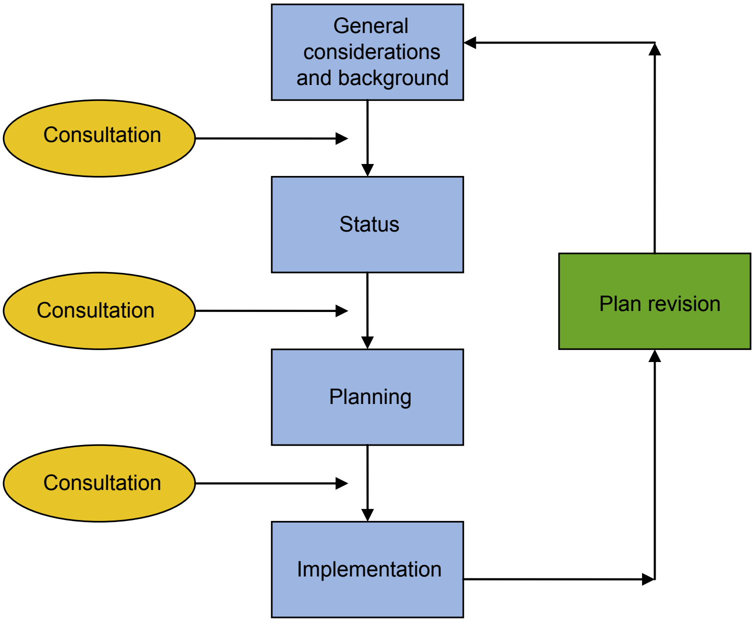

Figure 3.6 Planning process.
Modified of European Commission Directorate-General Environment, 2012. Preparing a Waste Management Plan, a Methodological Guidance Note, Drafted by Members of ETAGIW Consortium (Expert Team for Assessment and Guidance for the Implementation of Waste Legislation) on the Basis of ‘Preparing a Waste Management Plan — a Methodological Guidance Note’ of May 2003 by the European Topic Centre on Waste and Material Flows, Organisations Involved: European Commission, DG Environment, Umweltbundesamt GmbH, Vienna (AEE), BiPRO GmbH, Munich, Ekotoxikologické Centrum, Bratislava (ETC).

- Plan of action, including measures for achieving objectives (collection systems, waste-management facilities, responsibilities, and economy and financing).

The planning process may be divided into six phases: general considerations and background, status part, planning part, consultation process, implementation, and plan revision. The planning process is shown in Fig. 3.6. Note that if a plan already exists, it may have to be reviewed and revised. If, on the other hand, the first waste-management plan has yet to be devised, it is very important that the political level has accepted the need for a plan and allocated sufficient resources to its execution (European Commission Directorate-General Environment, 2012).

3.2.3 Waste-Management Practices

As discussed before, waste-management practices can be done by prevention, source reduction or waste minimization, reuse, recycling/recovery, treatment, and disposal (E&P Forum, 1993; Reis, 1996; Speight, 2005; MVLWB, 2011; European Commission Directorate-General Environment, 2012).

3.2.3.1 Prevention

Proper management of petroleum wastes begins with waste or pollution prevention. Pollution prevention can be done by the elimination, change, or reduction of operating practices in the various sectors of petroleum industry that result in discharges or emissions in the environment (land, air, or water). This principle should be incorporated into the design and management of petroleum industry facilities and the planning of associated activities. Most changes in improvement of operations should be planned in advance (E&P Forum, 1993).

For example, optimizing drilling operations, keeping hazardous and nonhazardous wastes separate, keeping municipal or commercial wastes and other site wastes apart, avoiding unwanted materials such as rig wash, stormwater runoff, etc., from entering the fluid system during drilling (Reis, 1996), supporting research efforts and designing of new or modified operations and processes, developing and implementing a program to improve early detection and reduce impacts of oil spills and other accidental releases from operations, supporting a communication program including sharing of industry experiences and accomplishments, etc., are operational practices options in the E&P sector (E&P Forum/UNEP, 1997). Use of recycled water for desalter, coke fines recovery, collection of catalyst fines during delivery, determination of sludge and water content for feedstock, replacement of desalting with chemical treatment system, keeping the relatively clean rainwater runoff from wastewater in the process streams separate, etc., are operating practices options in the refineries (Speight, 2005).

3.2.3.2 Source Reduction or Waste Minimization

When elimination of petroleum waste is not possible, source reduction or generation of less petroleum waste should be investigated. Source reduction can be done through more efficient practices such as:

- Inventory control and management;
- Material elimination;
- Material substitution;
- Process and equipment modifications; and
- Improved housekeeping and maintenance (E&P Forum, 1993; MVLWB, 2011).

Inventory control and management can be an option for waste minimization. It can be used in the reduction of waste generation, better use of resources and consequently in cost saving. Inventory management includes monitoring and recording of quantities and qualities of discharges and wastes. It should also contain the quantities being discharged and the location of the discharges. As discussed in Chapter 2, data on emissions and discharges in the petroleum industry can be calculated from: direct measurements of contaminant mass flows and application of generic factors for each contaminant and source, e.g., fugitive emission factors derived from petroleum industry standards. Note that the inventory should be renewed and updated whenever there is a change in type, composition, or location of discharge. For example, when there is a change in the chemicals used in the production process, the inventory for production water effluent should be changed (Bashat, 2003).

Material elimination and substitutions are also options for waste minimization. In the petroleum industry, selection and substitution of materials that result in generation of less toxic wastes should be considered. Materials such as corrosion inhibitors, biocides, coagulants, cleaners, solvents, dispersants, emulsion breakers, scale inhibitors, viscosifiers, weighting agents, etc., should be selected with potential environmental impacts and disposal needs in mind. Selection of muds and additives that do not contain significant levels of biologically available heavy metals or toxic compounds and the use of mineral oils in place of diesel oil for stuck drill pump or replacing diesel oil-based mud (DOBM) with mineral oil-based mud (MOBM) are examples of this purpose (E&P Forum, 1993).

In the E&P sector, concerns over the potential toxicity of oil-based drilling fluids has led to the development of synthetic-based drilling muds (SBMs). Synthetic-based drilling muds are more expensive than oil-based muds and have the same desirable properties of oil-based fluids, but have low toxicity because of the elimination of the polynuclear aromatic hydrocarbons (PNAHs), faster biodegradability, lower bioaccumulation potential, and, in some instances, less drilling waste volume (Orszulik, 2008). Using water-based muds containing various low-toxicity polymers and glycols instead of oil-based muds, using potassium acetate or potassium carbonate instead of potassium chloride for shale stability problems to minimize the chlorine content of the drilling mud, replacing petroleum and alcohol-based defoamers with polyglycols, using polyacrylate and/or polyacrylamide polymers instead of chrome lignosulfonate/lignite as deflocculant, replacing sulfites, phosphonates, and amines with sodium chromate for corrosion control, using nonchromium H_2S scavengers instead of zinc chromate for H_2S control, replacing isothiazolins, carbamates, and glutaraldehydes with pentachlorophenol, paraformaldehyde, and arsenic as biocide, using chose barite from sources low in cadmium, mercury, and lead instead of barite as mud densifier, and using lithium-based grease with microsphere ceramic balls instead of pipe dope compounds such as lead, zinc, copper, cadmium, etc., are some examples for material substitutions in the E&P sector for waste minimization (Reis, 1996).

Reduction or elimination of chromate-containing wastes in cooling tower and heat exchanger by replacing chromates with low toxic alternatives such as phosphates, using activated alumina supports instead of ceramic catalyst support with the possibility of recycling the activated alumina supports with the spent alumina catalyst, etc., are examples of material substitutions in refineries for waste minimization (Speight, 2005).

Waste minimization can be accomplished by proper operation of equipment and process modifications. Use of newer and/or efficient equipment is necessary for reduction of waste generation. Process modification may be possible through more effective use of mechanical components rather than chemical additions (E&P Forum, 1993).

All leaks and spills from equipment should be detected, repaired, and controlled. Fugitive emissions can be minimized by the detection and subsequent repair or replacement of leaking components. This is achieved by adopting a structured approach, commonly known as a leak detection and repair (LDAR) program. Identification of the leaking components can be done by the sniffing (EN 15,446) and optical gas imaging (OGI) methods. Repairing of these leaks to minimize losses can be accomplished by tightening bolts to eliminate leaks from valve stems or flanges, installing tight caps on open ends, changing gaskets or packing, and the replacement of equipment (European Commission and Joint Research Center, 2013). Fugitive emissions from loading of tanker barges may be reduced by more than 90% by installing a vapor loss control system that consists of vapor recovery or the destruction of the VOC emissions in a flare (Speight, 2005). Emission of partially burned hydrocarbons and formation of SO_x during combustion can be reduced by control of the fuel/air ratio and using a low-sulfur fuel such as natural gas, respectively (Reis, 1996). Replacing a large number of old boilers in a refinery with a single new cogeneration plant with emission controls can reduce emissions of SO_x, NO_x, and PM (Speight, 2005).

Installation of vapor recovery systems for reduction of VOC emissions, installation of low-volume, high-pressure nozzles and automatic shutoff nozzles on all hoses on the rig floor and wash racks for reduction of wastewater (Reis, 1996), using gravel packs and screening for reduction of volume of solids/sludge generation, minimization of mud changes, engine oil changes, and solvent usage using improved controls (E&P Forum, 1993), development of low NO_x turbines, examining replacements for firefighting systems (E&P Forum/UNEP, 1997), etc., are examples for process and equipment modifications in the E&P sector for waste minimization.

Using hydrotreating instead of clay filtration, adding coking operations for use of certain hazardous wastes as coker feedstock, substitution of electric heaters or ail coolers for water-heat exchangers, using optimum pressures, temperatures, and mixing ratios, segregation of oily wastes (Speight, 2005), etc., can help reduce waste generation in refineries.

Installation of secondary seals on floating-roof tanks, replacing them with fixed roofs in some cases to eliminate the collection of rainwater, contamination of crude oil or finished products, and oxidation of crude oil, minimizing the number of storage tanks that my lead to reduced tank-bottom solids and decanted wastewater, installation of a vapor-loss control systems containing vapor recovery or the destruction of the VOC emissions in a flare for tanker barges operations (Speight, 2005), etc., can minimize wastes in storage and transportation sector.

Improved housekeeping and maintenance are essential for waste reduction. Good housekeeping techniques refer to the proper handling of the day-to-day aspects in the petroleum industry. Many daily petroleum industry activities undertaken in various domains such as maintenance, cleaning, new process and process modification development, production planning (including start-ups, shutdowns), information systems process supervision/control, and training and safety are likely to have an impact on environmental performance and should be managed properly in that respect (European Commission and Joint Research Center, 2013).

3.2.3.3 Reuse

After consideration of all waste-reduction options, it is necessary to evaluate reuse of waste materials. Reuse means reusing materials in their original forms (E&P Forum, 1993; Bashat, 2003). The reuse may be in the same, alternative, or downgraded service, or the return of unused materials for reissue or reuse in other industries. Use of vent gas for fuel, use of drill-cutting waste for brick manufacturer and road-bed material, use of produced water or process water as wash water, return of oil based drilling mud to the vendor for reprocessing and reissue, use of tank bottoms, emulsions, heavy hydrocarbons, and hydrocarbon bearing soil for road oil, road mix, or asphalt (analyze to have density and metals content consistent with road oil or mixes), burning waste oil for energy (E&P Forum, 1993), reuse of rinse waters, use of waste acids to neutralize caustic wastes (Speight, 2005), reuse of waste lubes, reuse of wastewater generated by the overhead reflux drum as a desalter wash water, reuse of spent caustic within the refinery, reuse of certain types of sludge (e.g., oily sludge) in process units (e.g., coking) as part of the feed due to their oil content (European Commission and Joint Research Center, 2013), etc., are examples of reuse of materials to reduce waste in the petroleum industry.

3.2.3.4 Recycling/Recovery

Recycling means converting waste back into a usable material, whereas recovery means extracting materials or energy from a waste for other uses (E&P Forum, 1993; Bashat, 2003). These can be accomplished at either on-site production facilities or off-site commercial facilities (E&P Forum, 1993).

Recycling drilling muds, recycling scrap metal, using cleaned drill cuttings for road construction material, recovering oil from produced water and drilling muds, burning waste lubrication oil for energy recovery, recycling paper and plastic, recycling batteries (E&P Forum, 1993), recycling lubrication and cooling water used by pumps (Reis, 1996), etc., are examples of recycling/recovery in the E&P sector.

In addition, recovery of oil from tank bottoms via centrifuging and filtering and vapor recovery (E&P Forum, 1993; European Commission and Joint Research Center,

2013) are examples of recycling/recovery in the storage and distribution sector. The vapor recovery unit (VRU) can include condensation, absorption, adsorption, membrane separation, and hybrid (combinations of available VRU techniques) systems. A vapor incineration unit may be substituted for a vapor recovery unit if vapor recovery is unsafe or technically impossible because of the volume of return vapor (European Commission and Joint Research Center, 2013).

Regeneration catalysts and recovery of valuable metals from spent catalyst, recycling catalyst and coke fines, residual oil recovery, valuable product recovery from oily sludge with solvent extraction (Speight, 2005), recycling cooling waters, recycling of waste rubber of asphalt grades, recycling, in multistage desalters, part of the brine effluent water of second stage desalters to the first stage, minimizing the wash water quantity, soot recovery, either by washing with naphtha and recycling of the naphtha/soot mixture to the gasification section and/or by filtration, recycling caustics containing phenols on-site by reducing the pH of the caustic until the phenols become insoluble thereby allowing physical separation, recycling of monoethanolamine solutions, solvent recovery, recovery of gas (including the final venting) as a component of refinery fuel gas (RFG), sulfur recovery, etc., are examples of recycling/recovery in refineries. For sulfur recovery, the H_2S gas streams are treated in sulfur recovery unit, which most often consists of a Claus process for bulk sulfur removal and subsequently a tail gas treatment unit (TGTU) for the remaining H_2S removal. In general, the Claus process may remove only about 94–96% (two stages) or 96–98% (three stages) of the hydrogen sulfide in the gas stream, and TGTU processes must be used to recover additional sulfur. According to the principles applied, the most frequently used TGTU processes can be broadly divided into the following four categories:

- Direct oxidation to sulfur (PRO-Claus stands for Parson RedOx Claus and the SUPERCLAUS process);
- Continuation of the Claus reaction (cold-bed absorption (CBA) process, the CLAUSPOL process, and the SULFREEN process (HYDROSULFREEN, DOXOSULFREEN, and MAXISULF));
- Reduction to H_2S and recovering sulfur from this H_2S (the FLEXSORB process, high Claus ratio (HCR) process, reduction, absorption, recycle (RAR) process, the SCOT process (H_2S scrubbing), and the Beavon sulfur removal (BSR) process); and
- Oxidation to SO_2 and recovering sulfur from SO_2 (the Wellman–Lord process, the CLINTOX process, and the LABSORB process) (European Commission and Joint Research Center, 2013).

3.2.3.5 Treatment

Treatment refers to the destruction, detoxification, and/or neutralization of waste though various processes. Common methods of treatment are thermal (e.g., incineration and thermal desorption), physical (e.g., filtration and centrifugation), chemical (neutralization and stabilization), and biological (landspreading and tank-based reactors) processes (E&P Forum, 1993; MVLWB, 2011). Treatment of air pollutants, wastewater, and solid wastes in the petroleum industry are discussed in Chapters 5, 6, and 7, respectively.

3.2.3.6 Disposal

After all prevention, source reduction, reuse, recycling/recovery, and treatment options for minimization of wastes volume and toxicity have been examined, responsible disposal options for residue should be determined. Disposal refers to depositing residue to the receiving environment (on land or in water) using methods appropriate for a given situation. Disposal methods can include surface discharge, incineration, biodegradation, composting, landspreading or landfarming, landfilling, etc. (E&P Forum, 1993). These methods are discussed in Chapter 7.

3.2.4 Disposal Certification

It is essential to consider certification of disposal processes. The relevant laws and regulations of the area, the availability of off-site disposal facilities, transportation of wastes to the facility, the area-wide topographical and geographical features, current and likely future activities around the disposal site, hydrological data, area rainfall or net precipitation conditions, soil conditions, and loading, drainage areas should be considered. In addition, environmental sensitivity features such as wetlands, urban areas, historical or archaeological sites, protected habitats, or the presence of endangered species should be identified. In addition, potential air-quality impact of the waste-management facility must be considered (E&P Forum, 1993).

3.2.5 Contingency Plans

A contingency plan refers to a course of action designed to prepare an organization to respond well to a significant oncoming event or circumstance that may or may not happen. Contingency plans are important in the petroleum industry. Identification of risk, the planning and implementation of actions to manage risks, procedures for reviewing and testing of preparedness, and training of personnel are the goals of contingency planning. Contingency planning should facilitate the rapid mobilization and effective use of manpower and equipment necessary to carry out and support emergency response operations (E&P Forum/UNEP, 1997).

Developing a contingency plan in the petroleum industry involves knowing in advance about risks, resources, the environmental conditions and sensitive environmental zones, communication procedures, and response procedures. The development steps of a contingency plan are as follows:

- Identification of risks and expected consequences (risk assessment);
- Establishment of response strategy;
- Establishment of communication and reporting;
- Determination of resource requirements (personnel, equipment, supplies, and funds);
- Defining roles and responsibilities;

- Determination action plans or response actions;
- Defining of training and exercise requirements;
- Preparation of data directory and supporting information (E&P Forum/UNEP, 1997; ITOPF, 2014b).

Note that a contingency plan should allow modification, if needed. Examples of contingency plans for oil spills are available in these references (International Petroleum Industry Environmental Conservation Association (IPIECA), 1991; ITOPF, 2014b).

3.2.6 Employee Training

Employee training is essential for environmental protection success in the petroleum industry. Environmental training in the petroleum industry should foster, in each person, and ensure that they are able to meet their defined role and job requirements, and to apply environmental operating procedures correctly. Environmental training in the petroleum industry should be concentrated on the following:

- Policy, plans, and management;
- Objectives, targets, and performances;
- Global, national, and local issues;
- Legislations, consents, and compliances;
- Operational procedures;
- Pollution prevention;
- Waste controls;
- Emergency and contingency response; and
- Reporting (E&P Forum/UNEP, 1997).

3.3 Environmental Regulations

3.3.1 Environmental Regulations in the Petroleum Industry

Regulations are mandatory requirements that can apply to individuals, businesses, state or local governments, nonprofit institutions, or others (U.S. EPA, 2015a). Setting and enforcing environmental regulations in the petroleum industry is important for minimizing the potential environmental impacts and protecting human health and the environment. Performance-based regulations, rather than traditional command and control approaches, should be considered since they have potential to stimulate more innovative and effective environmental management in all areas of the world (E&P Forum/UNEP, 1997). Lack of regulatory oversight can be traced to many illnesses and even deaths for people and wildlife around the world (Kosnik, 2007).

Identifying wastes, determining their volumes, properties, potential impacts, assessing the sensitivity of the receiving environment, determining control strategies, and implementing systems for monitoring and control are steps in regulatory development. Regional, local, and national government authorities are responsible for preparing this information. Industry groups, technical societies, various industry organizations, agencies, and environmental groups help identify concerns and supplement the available data (Orszulik, 2008). In other words, in developing meaningful regulations, industry, regulators, and regulatory agencies should communicate (Reis, 1996).

Regulatory control and enforcement is the responsibility of competent national authorities, and international requirements are implemented by national authorities via primary legislation (E&P Forum/UNEP, 1997). Civil penalties (on both companies and individuals for violations) and criminal penalties (on individuals for deliberate violations) with fines and jail terms may be imposed by many environmental regulations (Reis, 1996). According to the E&P Forum/UNEP (1997), effective application of environmental legislation requires the following factors:

- Appropriate national and international laws, regulations, and guidelines;
- Coherent methods for decisions on projects and activities;
- Legislation with clearly defined responsibilities and appropriate liabilities;
- Enforceable standards for activities and operations;
- Appropriate monitoring methods and protocols;
- Performance reporting;
- Adequately funded and motivated enforcement authorities;
- Existence of adequate consultation and appeal procedures; and
- Appropriate sanctions and political will for their enforcement.

The Montreal protocol of the Vienna Convention aimed at the phase-out of ozone-depleting substances, the Basel convention on transfrontier movement of hazardous wastes, convention on migratory species, framework convention on climate change, biodiversity convention, United Nations (UN) law of the sea, marine pollution (MARPOL) or the international convention for the prevention of pollution from ships, and regional sea conventions (Barcelona, Oslo Paris commission (OSPAR), Kuwait, etc.) are some of the important international environmental conventions in the petroleum industry. In addition, the E&P Forum on environmental principles, management systems, waste management, drilling muds, decommissioning, atmospheric emissions, produced water, arctic, mangroves, and tropical rainforests, European Petroleum Industry Association (EUROPIA) on environmental principles, the United Kingdom Offshore Operators Association (UKOOA) on environmental principles, API on management systems and chemical usage, United Nations Environment program (UNEP) on management systems, oil spills, drilling muds, auditing, and cleaner production, International Petroleum Industry Environmental Conservation Association (IPIECA) on oil spills, International Association of Geophysical Contractors (IAGC) on seismic operations, International Maritime Organization (IMO)/IPIECA on oil spills, ITOPF on oil spills, conservation of clean air and water in Europe (CONCAWE) on oil spills, International Union for Conservation of Nature (IUCN) on tropical rainforests, the IUCN/E&P Forum on arctic and mangroves, and International Chamber of Commerce (ICC) related to auditing are some examples of industry guidelines on the environment in the petroleum industry (E&P Forum/UNEP, 1997).

Environmental regulations can vary from locality to locality, state to state, and country to country (Reis, 1996). US regulations, European regulations, and Russian

Table 3.5 Major US Federal Environmental Regulations Relevant to the Petroleum Industry (U.S. EPA, 2015c; Reis, 1996; Speight, 2005)

Regulation	Brief Description
Clean Air Act (CAA)	CAA establishes air-quality standards for activities that emit air pollutants and make provisions for their implementation and enforcement.
Clean Water Act (CWA)	CWA establishes the basic structure for regulating discharges of pollutants into the surface waters.
Safe Drinking Water Act (SDWA)	SDWA or underground injection control regulations sets the limits of contaminants in underground sources of drinking water (USDW) or freshwater aquifers.
Resource Conservation and Recovery Act (RCRA)	RCRA regulates management, treatment, and disposal of hazardous wastes.
Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or Superfund	CERCLA creates a tax on the chemical and petroleum industries and provided broad federal authority to respond directly to releases or threatened releases of hazardous substances that may endanger public health or the environment and regulates clean up of existing hazardous waste sites.
Superfund Amendments and Reauthorization Act (SARA)	SARA regulates reporting of storage and use of hazardous chemicals and addresses closed hazardous waste disposal sites that may release hazardous substances into any environmental medium.
Emergency Planning and Community Right-to-Know Act (EPCRA)	EPCRA Authorized by Title III of the SARA, is designed to help local communities protect public health, safety, and the environment from chemical hazards.
Oil Pollution Act (OPA)	OPA provides emergency response plans for oil discharges or streamlines and strengthens the ability to prevent and respond to catastrophic oil spills.
Toxic Substances Control Act (TSCA)	TSCA regulates testing of new chemicals and provides controls, if necessary, for those chemicals that may threaten human health or the environment.

Continued

Table 3.5 **Major US Federal Environmental Regulations Relevant to the Petroleum Industry (U.S. EPA, 2015c; Reis, 1996; Speight, 2005)—cont'd**

Regulation	Brief Description
Endangered Species Act (ESA)	ESA regulates actions that jeopardize endangered or threatened species.
Hazard Communication Standards (HCS)	HCS informs employees of potentially dangerous substances in the workplace and trains them on how to protect themselves against potential dangers.
National Environmental Policy Act (NEPA)	NEPA regulates actions of federal government that may result in environmental impacts.
Hazardous Materials Transportation Act (HMTA)	HMTA regulates transportation of chemicals and hazardous materials through the nation's highways, railways, and waterways. The act includes a comprehensive assessment of the regulations, information systems, container safety, and training for emergency response and enforcement.
Marine Mammal Protection Act (MMPA)	MMPA regulates the use of explosives for removing offshore platforms and prohibits the taking and harassing marine mammals.
Comprehensive Wetland Conservation and Management Act (CWCMA)	CWCMA regulates activities impacting wetlands.

and former Soviet Republic regulations are three of the major regulatory systems. There are other additional environmental regional and national regulatory systems. Most of these are modeled and developed based on the US and European systems with local modifications (Orszulik, 2008). Petroleum laws, planning laws, environmental assessment, pollution, water and air quality, protection of waterways, health, safety, and environment (HSE), protected areas, nuisance and noise, etc., may be found in these systems (E&P Forum/UNEP, 1997).

The major US federal environmental regulations relevant to the petroleum industry are briefly summarized in Table 3.5. In addition to the federal regulations, there are also state and local regulations in the United States. Considerable knowledge and effort are required to ensure compliance of these regulations (Reis, 1996). In the United States, the EPA works in partnership with state governments, tribal governments, and other federal agencies to assure compliance with the nation's environmental laws to help protect public health and the environment (U.S. EPA, 2015b).

3.3.2 Hazardous Wastes Under the Resource Conservation and Recovery Act

According to the EPA's regulations, there are two ways of identifying a solid waste as hazardous under the RCRA:

- If it is included on a specific list of wastes that the EPA has determined are hazardous due to pose substantial present or potential hazards to human health or the environment. U.S. EPA (2008b) has developed a document for listed hazardous wastes.
- If it exhibits certain hazardous properties (characteristics). An RCRA characteristic hazardous waste is a solid waste that exhibits at least one of four characteristics: ignitability, corrosivity, reactivity, and toxicity.

Ignitable wastes can create fires under certain conditions, are spontaneously combustible, or have a flash point less than 60°C (140°F). Examples include waste oils and used solvents. The Pensky—Martens closed-cup method for determining ignitability, the Setaflash closed-cup method for determining ignitability, the ignitability of solids test method for oxidizing solids, and the test method to determine substances likely to spontaneously combust may be used to determine ignitability.

Corrosive wastes are acids or bases (pH less than or equal to 2, or greater than or equal to 12.5) and/or are capable of corroding metal containers, such as storage tanks, drums, and barrels. Battery acid is an example. The corrosivity toward steel is the test method that may be used to determine the ability of a waste to corrode steel.

Table 3.6 Maximum Concentrations of Contaminants for the Toxicity Characteristic Under the RCRA (U.S. EPA, 2009)

Contaminant	Regulatory Level (mg/L)
Arsenic	0.5
Barium	100.0
Benzene	0.5
Cadmium	1.0
Carbon tetrachloride	0.5
Chlordane	0.03
Chlorobenzene	100.0
Chloroform	6.0
Chromium	5.0
o-Cresol	200.0
m-Cresol	200.0
p-Cresol	200.0

Continued

Table 3.6 **Maximum Concentrations of Contaminants for the Toxicity Characteristic Under the RCRA (U.S. EPA, 2009)—cont'd**

Contaminant	Regulatory Level (mg/L)
Cresol	200.0
2,4-D	10.0
1,4-Dichlorobenzene	7.5
1,2-Dichloroethane	0.5
1,1-Dichloroethylene	0.7
2,4-Dinitrotoluene	0.13
Endrin	0.02
Heptachlor (and its epoxide)	0.008
Hexachlorobenzene	0.13
Hexachlorobutadiene	0.5
Hexachloroethane	3.0
Lead	5.0
Lindane	0.4
Mercury	0.2
Methoxychlor	10.0
Methyl ethyl ketone	200.0
Nitrobenzene	2.0
Pentrachlorophenol	100.0
Pyridine	5.0
Selenium	1.0
Silver	5.0
Tetrachloroethylene	0.7
Toxaphene	0.5
Trichloroethylene	0.5
2,4,5-Trichlorophenol	400.0
2,4,6-Trichlorophenol	2.0
2,4,5-TP (Silvex)	1.0
Vinyl chloride	0.2

Reactive wastes are unstable under normal conditions. They can cause explosions, undergo violent reactions, generate toxic fumes, gases, or vapors or explosive mixtures when heated, compressed, or mixed with water. Examples include lithium-sulfur batteries and explosives. According to the U.S. EPA (2009), there are currently no test methods available.

Toxic wastes are harmful or fatal when ingested or absorbed (e.g., containing mercury, lead, etc.). When toxic wastes are land disposed, contaminated liquid may leach from the waste and pollute ground water. The toxicity characteristic leaching procedure (TCLP) can be used to define toxicity through a laboratory procedure. The TCLP helps identify wastes likely to leach concentrations of contaminants that may be harmful to human health or the environment. Maximum concentrations of contaminants for the toxicity characteristic under the RCRA are listed in Table 3.6 (U.S. EPA, 2009).

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Oil-Spill Response

4

4.1 Fate of Oil in the Marine Environment

Before explaining the facts influencing oil-spill response, it is necessary to discuss the fate of oil in the marine environment. Crude-oil and petroleum distillate products introduced to the marine environment are immediately subject to a variety of changes as follows:

- Abiological (physical and chemical) weathering processes such as evaporation, dissolution, dispersion, photochemical oxidation, water-in-oil emulsification, adsorption onto suspended particulate material, sinking, and sedimentation; and
- Biological processes such as ingestion by organisms as well as natural biodegradation.

Chemical composition and physical properties of the original pollutant are changed by simultaneous occurrence of these processes, which in turn may affect the effectiveness of some oil-spill response methods such as biodegradation, use of dispersants, etc.

Evaporation is usually the most important weathering process during the first 48 h of a spill, by which low- to medium-weight crude-oil components with low boiling points volatilize into the atmosphere. While the evaporative loss rate generally diminishes rapidly over time, evaporation can be responsible for the loss of one- to two-thirds of an oil spill's mass during the first 48 h of a spill. The composition of the oil, its surface area and physical properties, wind velocity, air and sea temperatures, sea state, and the intensity of solar radiation can contribute to the evaporative loss. The material left behind is richer in metals (mainly nickel and vanadium), waxes, and asphaltenes than the original oil. The specific gravity and viscosity of the original oil are also increased by evaporation.

The other abiological weathering processes are much less important processes than evaporation from the perspective of mass lost from a spill. For instance, dissolution of oil in the water column is a much less important process than evaporation. However, due to being acutely toxic some water-soluble fractions of crude oil such as light aromatic compounds to various marine organisms and their greater impact on the marine environment, dissolution can be important. Dispersion or breakup of oil slicks into numerous small droplets and transport from the surface to the water column is an important process in the removal of surface slicks. Sea-surface turbulence can affect the dispersion. Use of chemical dispersants can enhance this process. When seawater, through heavy wave action or in turbulent conditions, becomes entrained with the insoluble components of oil, water-in-oil emulsions can be formed (often termed "mousse") and may contain 30% to 80% water. The most stable mousses can be formed from heavier or weathered crudes with high viscosities. Mousse not only may first sink or become stranded on beaches, but will also eventually disperse in the water column

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and/or be biodegraded. Degradation of a water-in-oil emulsion is more difficult than oil alone by microorganisms probably due to the low surface area of the mousse and the low flux of oxygen and mineral nutrients to the oil-degrading microorganisms within it. It can be a major limiting factor in petroleum biodegradation.

Natural biodegradation is a process whereby microorganisms, especially bacteria, but also yeasts, fungi, and some other organisms, break down and convert organic molecules into other substances, such as fatty acids and carbon dioxide. Although some products can actually be more complex, ideally hydrocarbons would be transformed to carbon dioxide, nontoxic water-soluble materials, and new microbial biomass. Natural biodegradation is ultimately one of the most important processes for removal of oil, especially for nonvolatile components of crude or refined petroleum from the marine environment. Manmade bioremediation methods for oil-spill response are intended to improve the effectiveness of natural biodegradation, which will be discussed in this chapter (Congress of the United States, Office of Technology Assessment (OTA), 1991).

4.2 Overview of Oil-Spill Response

Protection, recovery, and cleanup phases are important in an oil-spill response. The protection phase consists of keeping oil out of a habitat or reducing the amount that enters. Recovery consists of removing floating oil from the water surface. The main objective of cleanup is to remove stranded oil from shoreline habitats. In most oil-spill response situations, protection and oil recovery are the immediate goals. Combinations of protection, recovery, and cleanup methods are commonly used in oil-spill responses (API and NOAA, 1994).

The response methods should be considered before a spill occurs to reduce the ultimate environmental impact and costs resulting from a spill. In addition, these methods must reduce the impact of oil and should have minimal intrinsic ecological impact (API and NOAA, 1994). In addition, environmental sensitivity index (ESI) maps can help responders reduce the environmental consequences of the spill and the cleanup efforts; also planners before a spill happens in identifying vulnerable locations, establishment of protection priorities, and identifying recovery and cleanup strategies (Office of Response and Restoration, NOAA, 2015).

4.2.1 Environmental Sensitivity Index Maps

The ESI maps provide a concise summary of marine and coastal resources that are at risk if an oil spill occurs nearby. Environmental sensitivity index maps are a compilation of information from three main categories:

- Shoreline habitats (e.g., wave-cut rocky platforms, marshes, and tidal flats);
- Sensitive biological resources (e.g., birds, reptiles, amphibians, fish, invertebrates, plants, wetlands, and marine mammals and terrestrial mammals); and
- Human-use resources (e.g., drinking water intake, boat ramp, marina, historic and archaeological sites, public beaches, and parks) (Office of Response and Restoration, NOAA, 2015).

An example ESI map is shown in Fig. 4.1. As noted before, it can be used to identify vulnerable locations, establish protection priorities, and identify recovery and cleanup strategies (Office of Response and Restoration, NOAA, 2015).

4.2.2 Oil-Spill Response Methods

According to the API and NOAA (1994), oil-spill response methods are generally divided into three categories:

- Physical response methods (booming, skimming, sorbents, in situ burning, manual oil removal/cleaning, mechanical oil removal, physical herding, natural recovery, barrier/berm, vacuum, debris removal, sediment reworking, vegetation removal, flooding, low-pressure, cold-water flushing, high pressure, cold-water flushing, low-pressure, hot-water flushing, steam cleaning, and sand blasting);
- Chemical response methods (dispersants, emulsion treating agents, visco-elastic agents, herding agents, solidifiers, chemical shoreline pretreatment, and shoreline cleaning agents) (API and NOAA, 1994); and
- Biological response methods or bioremediation (nutrient enrichment (biostimulation), seeding with naturally occurring microorganisms (bioaugmentation), and seeding with genetically engineered microorganisms (bioaugmentation with GEMs)) (Congress of the United States, OTA, 1991; Zhu et al., 2001; Hassanshahian and Cappello, 2013).

These methods are different depending on habitat type, conditions under which the methods should be used, biological constraints commonly applied to the use of the method to protect sensitive resources, the environmental effects expected from the proper use of the method, and authorization needed for method use during a spill (API and NOAA, 1994).

Response to an oil spill can be difficult and may depend on many factors such as type of oil spilled, temperature of the water (affecting evaporation and biodegradation), types of shorelines and beaches involved, etc. Some of the above methods may be ineffective or inapplicable for an oil type or habitat. Some of the most common and important methods are discussed in this section.

4.2.2.1 Booming

Booms are large floating barriers (Fig. 4.2) that control the movement of floating oil by containment, diversion, deflection, or exclusion. Containment refers to deploying a boom to hold the oil until it can be removed. Deflection involves oil away from sensitive areas. Diversion involves moving oil toward recovery sites that have slower flow, better access, etc. Placing booms to prevent oil from reaching sensitive areas is called exclusion, in which the ultimate goal is to recover the oil.

Booms can be used in all water environments. When the effective current or towing speed exceeds 0.7 knots perpendicular to the most booms irrespective of skirt depth, they begin to fail by entrainment. Nearly all types of response to spills on water involve deploying booms to assist in the recovery of floating oil. Because of both fire and inhalation hazards to responders, containment booming of gasoline spills is usually not done. However, when public health is at risk, booming of gasoline can be attempted

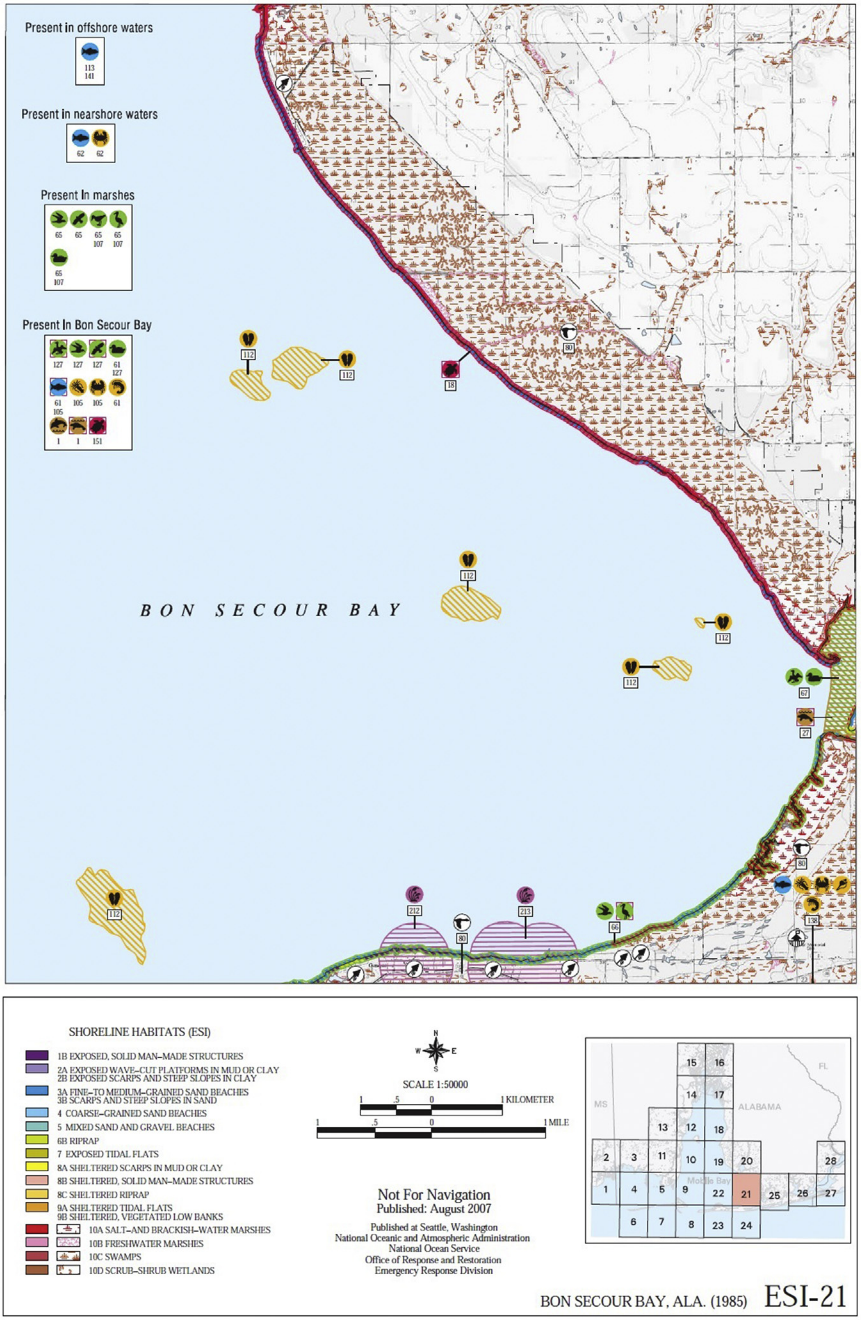

Figure 4.1 ESI map of Bon Secour Bay, Alabama (Emergency Response Division, Office of Response and Restoration, NOAA, 2007).

Figure 4.2 Boom used in the Gulf of Mexico oil spill (https://commons.wikimedia.org/wiki/File:Shrimp_boats_tow_fire-resistant_oil-containment_boom_in_Gulf_of_Mexico_2010-05-03_1.jpg).

with use of foam and extreme safety procedures. Deflection or exclusion booming of sensitive areas to prevent exposure to oil, including gasoline, can be an important protection action. Environmental effects can be minimal if surface disturbance by cleanup work force traffic is controlled (API and NOAA, 1994).

There are two broad categories of boom design:

- Curtain booms (Fig. 4.3) (usually with a circular cross-section continuous subsurface skirt or flexible screen supported by an air or foam-filled flotation chamber); and
- Fence booms (Fig. 4.4) (typically with a flat cross-section held vertically in the water by integral or external buoyancy, ballast, and bracing struts).

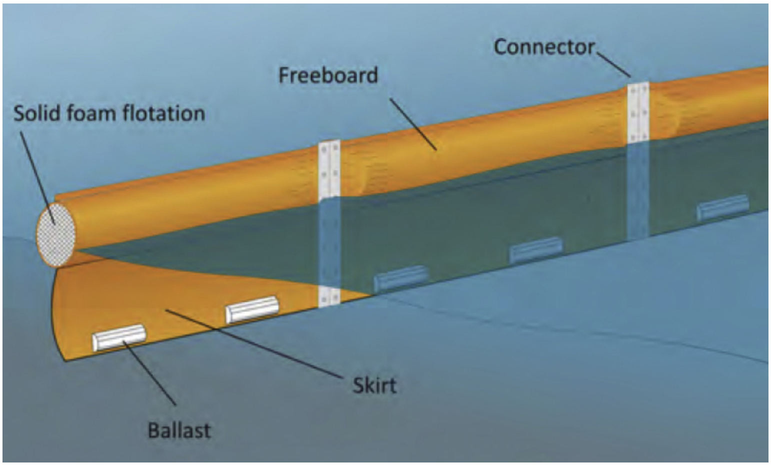

Figure 4.3 Curtain boom with external ballast and solid foam flotation (ITOPF, 2011a).

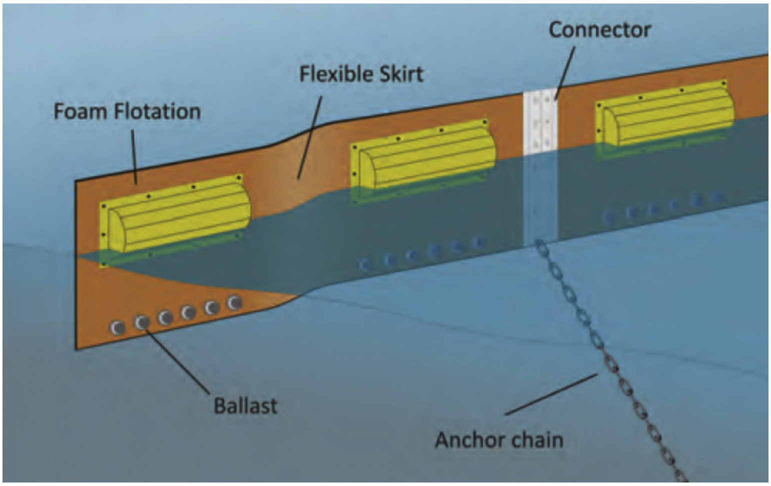

Figure 4.4 Fence boom with external foam flotation and ballast (ITOPF, 2011a).

There is also another boom type whereby the skirt is replaced by water-filled chambers allowing the boom to settle on an exposed shoreline at low tide. This boom is called shore-sealing or beach-sealing boom (Fig. 4.5).

Oil containment or deflection capability is the most important characteristic of a boom. Freeboard to prevent or reduce splash-over, subsurface skirt to prevent or reduce escape of oil under the boom, floatation in the form of air, foam, or other buoyant materials, longitudinal tension member (chain or wire) to withstand forces from winds, waves, and currents, ballast to maintain the vertical aspect of boom are features incorporated into booms to enhance this characteristic. The characteristics of common boom types are listed in Table 4.1 (ITOPF, 2011a).

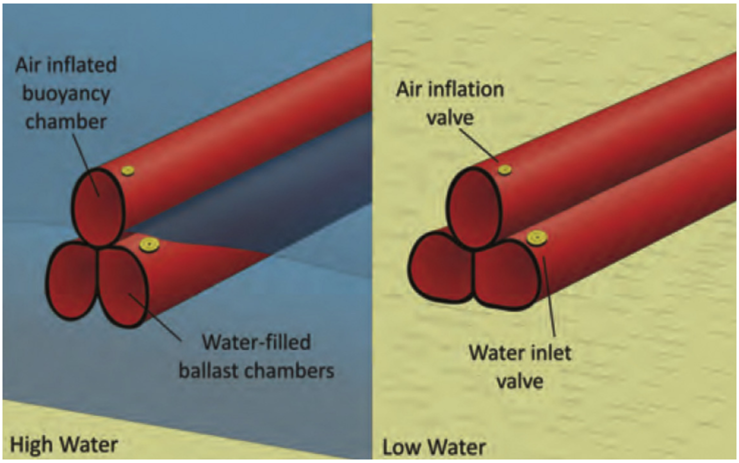

Figure 4.5 Shore-sealing boom (ITOPF, 2011a).

Table 4.1 Characteristics of Common Boom Types (ITOPF, 2011a)

Type of Boom	Flotation Method	Storage	Wave Following Property	Moored or Towed	Ease of Cleaning	Relative Cost	Preferred Use
Curtain boom	Inflatable	Compact when deflated	Good	Both	Straightforward	High	Inshore or offshore
	Solid foam	Bulky	Reasonable	Moored	Easy/straightforward	Midrange to low	Sheltered inshore waters (e.g., harbors)
Fence boom	External foam floats	Bulky	Poor	Moored	Difficult/medium; oil can become trapped behind external flotation or in the junctions of the chambers	Low	Sheltered waters (e.g., ports and marines)
Shore-sealing boom	Inflatable upper chamber, lower chambers water-filled	Compact when deflated	Good	Moored	Medium; oil can become trapped in junctions of the chambers	High	Along sheltered intertidal shores (no breaking waves)

The approximate force F_1 (kg) exerted on a boom with a subsurface area A_1 (m^2) by a current with velocity V (m/s) can be calculated from the following formula:

$$F_1 = 100 \times A \times V_{\text{current}}^2 \tag{4.1}$$

The approximate force F_2 (kg) exerted directly on the freeboard is A_2 (m^2) of the boom by wind can also be considerable. Estimation of this force using the above formula can be done on the basis that roughly equivalent pressures are created by water current and wind speed 40 times greater. Thus:

$$F_2 = 100 \times A_2 \times \left(\frac{V_{\text{wind}}}{40}\right)^2 \tag{4.2}$$

The vectorial summation of these forces is the net force exerted on the boom. These estimations aid in the selection of mooring and towing vessels. In practice, to modify the magnitude and direction of the forces, the boom would be positioned at an angle to the flow forming a curve. For instance, the maximum deployment angles to flow direction at current strengths of 0.35, 0.5, 0.75, 1, and 1.5 m/s are 90, 45, 28, 20, and 13 degrees, respectively (ITOPF, 2011a).

Example 4.1

Assume that the length of a boom with a 0.8 m skirt and a 0.5 m freeboard is 100 m. The water-current velocity and wind speed are 0.35 and 7 m/s, respectively, and are acting in the same direction on this boom. What is the approximate combined force of current and wind?

Solution: The approximate force exerted on the boom by the water current is:

$$F_1 = 100 \times A \times V_{\text{current}}^2 = 100 \times 100 \times 0.8 \times 0.35^2 = 980\,\text{kg}$$

The approximate force exerted on the boom by the wind speed is:

$$F_2 = 100 \times A_2 \times \left(\frac{V_{\text{wind}}}{40}\right)^2 = 100 \times 100 \times 0.5 \times \left(\frac{7}{40}\right)^2 = 153.12\,\text{kg}$$

Therefore the approximate combined force exerted on the boom is $980 + 153.12 = 1133.12$ kg.

4.2.2.2 Skimming

Skimming is a process of recovering floating oil from the water surface. The principles for skimmers' operation are based on the fluidity properties of oil and oil—water mixture, density differences between oil or oil—water mixtures, and water or differences in adhesion to materials (Deepwater Horizon, 2010). Skimmers are usually used in conjunction with booms. Booms are used to collect and concentrate floating oil at the skimmer, and for recovery, the skimmer is placed at the oil—water interface. Large amounts of water are often collected and must be handled, and adequate storage of recovered oil—water mixture is required (API and NOAA, 1994; Deepwater Horizon, 2010). Skimmers are constructed of weather and water-resistant materials such as stainless steel, rubber, aluminum, and polypropylene. The skimming head (the component separating oil from water), transfer system (built-in pump or vacuum unit, discs, brushes, belts or ropes, hoses, and couplings), and containment unit (tank or container for recovered oil) are components of skimmers (Deepwater Horizon, 2010).

According to the API and NOAA (1994), weir, suction, centrifugal, submersion, and oleophilic are the five different types of skimmers. They may operate independently from shore, be mounted on vessels, or be completely self-propelled. They vary considerably in their working principles and construction. Oil-collection methods of skimmers can determine their respective uses. According to Deepwater Horizon (2010) and ITOPF (2012), the types of skimmers include:

- Oleophilic skimmers (disc, rope mop, drum, belt, and brush);
- Vacuum/Suction skimmers;
- Weir skimmers; and
- Other skimmers.

Oil recovery rate, recovery efficiency (the relation between recovered oil and recovered fluids (oil—water mixture)), and throughput efficiency (the relation between recovered oil and encountered oil) are usually used to define the skimmer performance (Deepwater Horizon, 2010).

The viscosity and adhesive properties of the spilt oil with respect to any change in these properties due to the weather conditions over time together with the sea state and levels of debris are important factors in the selection of skimmers (ITOPF, 2012).

4.2.2.2.1 Oleophilic Skimmers

These skimmers employ specific materials that have greater affinity for oil than for water. Such materials are known as oleophilic (mops, rope, drum, belt, brushes, or discs) (Deepwater Horizon, 2010; ITOPF, 2012). Oleophilic materials are usually from some form of polymer, although metal surfaces have also been shown to be effective (ITOPF, 2012). The moving part of the skimmer (rope, belt, drum, and disc) with the oleophilic surface is rotated or drawn through the oil slick. The oil is then scraped or squeezed off and guided into a sump to be pumped or sucked away. These skimmers are divided into subgroups such as disc skimmers, rope-mop skimmers, drum skimmers, belt skimmers, and brush skimmers (Deepwater Horizon, 2010; ITOPF, 2012).

Disk skimmers (Fig. 4.6) can be used for open-sea operation (Deepwater Horizon, 2010), and in low waves and currents can be highly selective with little entrained water, but can be swamped in choppy waters. These skimmers can also be clogged by debris. They are most effective in medium viscosity oils (ITOPF, 2012) and cannot handle emulsified oil. The volume and weight of these discs are large due to the size and number of rotating discs (Deepwater Horizon, 2010). The recovery rate of these skimmers depends on the number and size of the disks. Tests have shown that

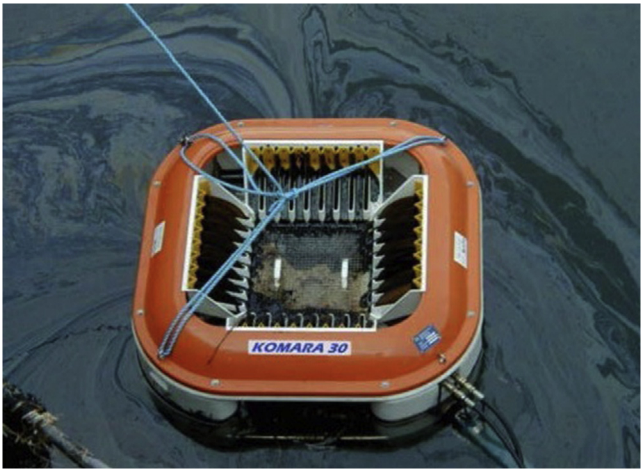

Figure 4.6 Oleophilic disk skimmer (Vikoma International Ltd, 2015).

grooved discs can be highly effective (ITOPF, 2012). The recovery capacities of these skimmers range from 40 to 100 m^3/h (Deepwater Horizon, 2010).

Rope-mop skimmers (Fig. 4.7) can be highly selective with very little and or no entrained water and can operate in choppy waters. They are able to tolerate significant debris, ice, and other obstructions. These skimmers are most effective in medium oils, although can be effective in heavy oils. Their recovery rate depends on the number and velocity of the ropes and is generally low throughput (ITOPF, 2012). Horizontal and vertical are two types of rope-mop skimmers. For instance, vertical rope-mop skimmers are large units launched from a vessel or shore using a crane during the entire operation and used only for single-sweep operations (Deepwater Horizon, 2010).

In low waves and currents drum skimmers (Fig. 4.8) can be highly selective with little entrained water, but can be swamped in choppy waters. These skimmers can also be clogged by debris. They are most effective in medium viscosity oils. The recovery rate of these skimmers depends on the number and size of the drums. Tests have shown that grooved drums are more effective (ITOPF, 2012).

Belt (Fig. 4.9) and brush (Fig. 4.10) skimmers are large and either mounted on a barge (self-floating unit) or on a specially constructed vessel (Deepwater Horizon, 2010). Both of them can be selective with little entrained water and can operate in choppy waters, but some designs of brush skimmers would be swamped in waves. Both are effective in small debris, but can be clogged by large debris. Belt skimmers are most effective in medium to heavy oils, but brush skimmers have different brush sizes for light, medium, and heavy oils. The recovery rate of belt skimmers are low- to midrange, while the throughput of brush skimmers depends on the number and the velocity of brushes and are generally midrange (ITOPF, 2012).

4.2.2.2.2 Vacuum/Suction Skimmers

Vacuum/suction skimmers do not have a pump unified in the actual floating skimmer device (skimmer head (Fig. 4.11)). The recovered oil—water mixture is sucked from

Figure 4.7 Vertical oleophilic rope-mop skimmer. Direct Industry, 2016. Products, Oil Skimmer for Offshore Applications, DESMI Pumping Technology A/S. [online] Available from: http://www.directindustry.com/prod/desmi-pumping-technology-s/product-21088-478363.html.

Figure 4.8 Oleophilic drum skimmer (Elastec, 2015).

the skimmer head by a suction or vacuum pump. The simplest type of vacuum skimmer is a hose directly connected to a vacuum truck, which can easily be employed in harbors or rivers (Deepwater Horizon, 2010). In this operation, high proportions of water may be collected. These skimmers are used in calm waters and small waves can result in collection of excessive water (ITOPF, 2012; Deepwater Horizon, 2010). The addition of a weir may be more selective. These skimmers can be clogged by debris and are most effective in light to medium oils. Their recovery rate depends on the vacuum pump brushes and is generally low- to midrange (ITOPF, 2012).

Figure 4.9 Belt skimmer. International Tanker Owners Pollution Federation (ITOPF) Limited. Belt Skimmer in Operation. [online] Available from: http://www.itopf.com/fileadmin/data/Documents/Image_Library/Belt_skimmer.jpg.

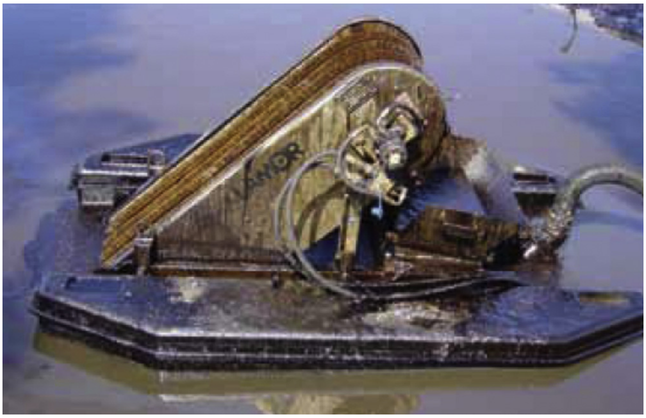

Figure 4.10 Brush skimmer (ITOPF, 2012).

4.2.2.2.3 Weir Skimmers

Weir skimmers (Fig. 4.12) include any device using gravity to drain oil from the water surface. A free floater, a weir is normally launched from a vessel, using a crane, and is guided by ropes. The edge of the weir is positioned just below the upper slick surface allowing oil to flow over the weir edge into a collecting sump and then to be pumped to storage. It is probably the most commonly used skimmer type because of its simple construction. Weir systems can either be remote controlled or self-adjusting. Remote-adjusting systems are based on compressed air (Deepwater Horizon, 2010). Some weir skimmers have an onboard pump for overcoming friction losses along transfer hoses, so that the recovered oil is pushed along the hose rather than relying on suction. These skimmers can be highly selective in calm water with little entrained

Figure 4.11 Skimmer head of a vacuum/suction skimmer (ITOPF, 2012).

Figure 4.12 Weir skimmer (https://en.wikipedia.org/wiki/Skimmer_(machine)#/media/File:Self_adjusting_weir_type_oil_skimmer,_Ultraspin.jpg).

oil and can be easily swamped with an increase in entrained water. They can also be clogged by debris, although some pumps can handle small debris. These skimmers are effective in light to heavy oils and very heavy oils may not flow to the weir. Their recovery rate can be significant and can depend on pump capacity, oil type, etc. (ITOPF, 2012).

4.2.2.2.4 Other Skimmers

Other skimmer designs have been developed to better meet the needs of rougher areas. For example, upward rotating belts can be partially lowered beneath the oil—water interface to reduce the influence of surface waves. Buckets or paddles can also be used on the belt to aid lifting of the oil from the water surface. In addition, as shown in Fig. 4.13, some weir skimmer designs incorporate interchangeable adaptors to prolong their use as the oil weathers and its viscosity increases (ITOPF, 2012).

4.2.2.2.5 Use of Skimmers for Onshore Operations

The best solution for oil spills on soil is digging a pit at a collection point and conducting the oil toward the pit. A vacuum skimmer can be used for recovery of oil from the pit. Note that an excavator or shovels may be used to mechanically remove the topsoil for further treatment.

For oil spills on concrete, asphalt, or other hard surfaces, sorbent booms can be laid out to contain the spill. For fresh oil and nonfresh (solidified) oil, recovery using a vacuum skimmer and high-pressure cleaner combined with chemical treatment can be options, respectively.

For shallow water areas (marsh, swamp, or lagoons), sorbent booms can be applied to guide the oil toward the rope-mop or disc skimmers. When there is a large amount of debris in the water, these skimmers can be useful. If it is not possible to concentrate the spilled oil, rope-mop skimmers can be applied to cover a larger area than the disc skimmer. Due to the damaging effects of heavy equipment on the environment when possible use of any type of mechanical treatment in sensitive areas, such as marsh or shallow water, should be avoided (Deepwater Horizon, 2010).

Figure 4.13 Belt adaptor incorporated to increase the capability of weir skimmers in highly emulsified fuel oil (ITOPF, 2012).

4.2.2.3 Sorbents

Sorbents are generally insoluble materials or mixtures of materials used to recover oil through absorption (the oil is picked up and retained into porous materials), adsorption (the oil sticks to the surface of adsorbent materials), or both. To remove floating oil, sorbents need to be both oleophilic (oil-attracting) and hydrophobic (water-repellent). Sorbents may be applied to spills manually or mechanically using blowers or fans (U.S. EPA, 2015).

The capacity of a particular sorbent, the energy available for lifting oil off the substrate, and the stickiness of the oil can affect the efficacy. Sorbents can be used in any habitat or environment type (API and NOAA, 1994). In small oil spills, they may be used as the sole cleanup method, but they are most often used to remove final traces of oil (secondary treatment), or in sensitive areas where access is restricted (e.g., cannot be reached by skimmers) (U.S. EPA, 2015; API and NOAA, 1994). Overuse of sorbent materials and generating large volumes of waste should be prevented. Recovery of all sorbent materials is mandatory (API and NOAA, 1994). Sorbent materials and any oil that is removed from them must be disposed of in accordance with approved local, state, and federal regulations (U.S. EPA, 2015).

Sorbents come in three basic categories:

- Natural organic sorbents such as peat moss, straw, hay, sawdust, ground corncobs, feathers, and other readily available carbon-based products. These sorbents can adsorb between 3 and 15 times their weight in oil, but there are disadvantages to their use. Their tendency to adsorb water as well as oil, causing some of sorbents to sink, and collection problems of some of them after spreading on the water, are their disadvantages. Adding flotation devices can counterbalance these problems. For instance, empty drums attached to sorbent bales of hay overcome the sinking issue. To aid in collection, mesh can be wrapped around loose particles.
- Natural inorganic sorbents such as clay, perlite, vermiculite, glass wool, sand, or volcanic ash. They can adsorb from 4 to 20 times their weight in oil. These sorbents, like organic sorbents, are inexpensive and readily available in large quantities. These types of sorbents are not used on the water's surface.
- Synthetic sorbents consist of manmade materials that are similar to plastics, such as polyurethane, polyethylene, and polypropylene (adsorption) and other synthetic cross-linked polymers and rubber materials (absorption). Most synthetic sorbents can absorb up 70 times their own weight in oil.

When selecting sorbents for cleaning up oil spills, it is essential to consider the characteristics of both sorbents and oil types. Rate of absorption (the absorption of oil is faster with lighter oil products), rate of adsorption (the thicker oils adhere to the surface of the adsorbent more effectively), oil retention (lighter, less viscous oil is lost through the pores more easily than are heavier, more viscous oils during recovery of adsorbent materials causing secondary contamination), and ease of application (many natural organic sorbents that exist as loose materials, such as clay, are dusty, difficult to apply in windy conditions, and potentially hazardous if inhaled) should be considered when choosing of sorbents (U.S. EPA, 2015).

The sorptivity and effectiveness of oil sorbents may be modeled using the following formula:

$$V = V_{\max}\left(1 - e^{-pt}\right) \tag{4.3}$$

where V is the volume of the sorbent oiled, $V_{\max}$ denotes the estimated volume when the oiled area is stabilized, t is the time of sorption, and p is the sorption parameter. The sorption parameter indicates the activity of the sorbent. For example, Konczewicz et al. (2013) reported that this parameter for Densorb, a mineral sorbent, and peat moss, as an organic sorbent, are 0.025 and 0.017 s^{-1}, respectively.

4.2.2.4 In Situ Burning

The process of burning floating oil on the water surface or habitat is called in situ burning. Oil floating on the water surface is collected into slicks at least 2—3 mm thick and ignited (API and NOAA, 1994). The oil needs to be contained in fire-resistant booms, or by natural barriers such as ice or the shore (API and NOAA, 1994; Royal Dutch Shell plc, 2011). In situ burning has many potential applications for spills in ice. It can also be used on land, where there is heavy oil in sites not amenable or accessible to physical removal and where it is necessary to immobilize the stranded oil quickly. On land, oil in the habitat is burned, usually when it is on a combustible substrate such as vegetation, logs, and other debris. Oil can be burned off nonflammable substrates using a burn promoter. On sedimentary substrates, it may be necessary to dig trenches for oil to accumulate in pools thick enough to burn efficiently (API and NOAA, 1994). The oil condition is also important; as the oil weathers evaporation may cause it to lose its lighter oil fractions and it may begin to form an emulsion (ITOPF, 2015a). In other words, heavy and emulsified oils are more difficult to ignite and sustain an efficient burn, but are still burnable (API and NOAA, 1994).

A variety of devices ranging from a diesel-soaked rag to more sophisticated equipment such as the Helitorch can be used for ignition. This is essentially a flame thrower suspended beneath a helicopter and is generally accepted as one of the safest techniques of ignition in trained hands. However, the device and experience using it are not readily common in many parts of the world (ITOPF, 2015a).

On average, about 80—95% of the oil is eliminated as gas, 1—10% as soot, and 1—10% remains as a residue. Following the burning, this residue can be recovered from the water surface (Royal Dutch Shell plc, 2011). Large volumes of toxic smoke are generated, and may have the potential to impact human health, populated areas, and nesting birds (ITOPF, 2015a; API and NOAA, 1994) therefore it is a more suitable method for use offshore or away from populated areas. In Arctic regions, there is concern about the potential impact of soot deposits on the rate of melting ice (ITOPF, 2015a). Burns can eliminate 1000 barrels of oil per hour. Tests over several decades have proved that in situ burning work well in the Arctic (Royal Dutch Shell plc, 2011).

4.2.2.5 Manual Oil Removal/Cleaning

Removal of oil and debris manually using rakes, shovels, buckets, rags, sorbent pads, etc., and placing it in containers is called manual oil cleaning. This method can be used for light to moderate oiling conditions for stranded oil, or heavy oils on water that have formed semisolid to solid masses that can be picked up manually. It is the most common method of shoreline cleanup and can also be used in all habitat types. Foot traffic over sensitive areas such as wetlands should be restricted (API and NOAA, 1994).

4.2.2.6 Mechanical Oil Removal

Oil removal from water surface, bottom sediments, and shorelines with heavy equipment such as backhoes, graders, dredges, bulldozers, draglines, etc., is called mechanical oil removal. This method can be used on land to push the oiled material into piles for transport offsite for treatment/disposal. On water, the equipment can also operate from shore or barges to recover large amounts of heavy or solidified oil. Heavy equipment may be restricted and prevented in sensitive habitats such as wetlands and soft substrate or areas containing endangered plants and animals (API and NOAA, 1994).

4.2.2.7 Dispersants

Dispersants are chemicals containing surface-active agents (surfactants) designed for use in marine environments (API and NOAA, 1994; Royal Dutch Shell plc, 2011; ITOPF, 2011b). They accelerate the breakup of oil slicks into numerous small droplets that can then disperse and dilute into the water column and subsequently degrade more easily by naturally occurring microorganisms in the sea (API and NOAA, 1994; ITOPF, 2011b). They can be sprayed onto the slicks from fixed-wing aircraft, helicopters, boats, and vessels (API and NOAA, 1994; Royal Dutch Shell plc, 2011).

It is necessary to consider the potential impact of dispersed oil on water intake prior to dispersant use. When the impact of the floating oil is greater than the impact of mixing oil into the water column, the use of dispersants is considered (API and NOAA, 1994). Their use should be considered carefully to take into account oil characteristics, sea and weather conditions, environmental sensitivities, and national regulations on dispersant use (ITOPF, 2011b). Their use offshore is generally recognized as an efficient way to rapidly treat large areas of spilled oil to reduce the impact on marine life and the environment (Royal Dutch Shell plc, 2011), especially when other at-marine response methods are limited by weather conditions or the availability of resources (ITOPF, 2011b).

4.2.2.7.1 Classification of Dispersants

Dispersants are a mixture of surfactants in a solvent. Each surfactant molecule consists of a hydrophilic part (attracted to water) and an oleophilic part (attracted to oil). The solvent can act as a thinner to reduce the viscosity of the surfactant and can also promote the penetration of the surfactant into the oil slick. Dispersants increase natural dispersion by reducing the surface tension at the oil—water surface; therefore many fine oil droplets can be created by wave motion.

According to the ITOPF (2011b), the classification of dispersants based on their generation and types are as follows:

- First-generation dispersants: They were similar to the industrial cleaners and degreasers introduced in the 1960s. Because of toxicity, they are no longer applied in oil-spill response.
- Second-generation or type I dispersants: Containing typically 15–25% surfactant and a hydrocarbon solvent with low or no aromatic content, these are intended to be used undiluted (neat). Predilution with seawater makes them ineffective. Dosage rates range between 1:1 and 1:3 (dispersant to oil). They are less toxic than the first-generation dispersants and less effective and more toxic than the third-generation dispersants. Their usage has been restricted in many countries.
- Third-generation or types II and III dispersants: They typically contain a blend of 25–65% two or three surfactant with glycol and light petroleum distillate solvents that are concentrate dispersants. Nonionics such as fatty acid esters and ethoxylated fatty acid esters and anionics such as sodium alkyl sulfosuccinate are the most common used surfactants. Dosage rates of type II range between 2:1 and 1:5 (dispersant/water mix to oil) and should be diluted with seawater at typically 10% dispersant prior to use. The need for dilution restricts their application from vessels. Type III dispersants require a dosage of 1:5 to 1:50 (neat dispersant to oil) and are used neat, which allows efficient application from aircraft and vessels (ITOPF, 2011b).

4.2.2.7.2 Effective Parameters on Dispersant Use

As noted, oil characteristics, sea and weather conditions, dose rates, environmental sensitivities, and national regulations should be considered in dispersant use (ITOPF, 2011b). In other words, effectiveness is a major issue in oil-spill response using dispersants, i.e., the only thing that is important is effectiveness on real spills at sea. Oil characteristics, sea energy, state of oil weathering, the type of dispersant used and the amount applied, temperature, and salinity of the water affect dispersant effectiveness. Oil characteristics, followed closely by sea energy are the most important of these factors (Fingas, 2008a).

The viscosity and pour point of oil are two properties that indicate how easily the oil is likely to disperse. Increase of oil viscosity decreases dispersant effectiveness. Most dispersants are unlikely to be effective for oils with a viscosity above 5000–10,000 centistokes (cSt) at spill time. Note that the viscosity of the oil spilled will be enhanced due to weathering, evaporation, and emulsification effects. Oils with a pour point close to, or higher than, the sea temperature will also not be dispersible. Use of dispersants on light products or on sheens derived from crude or fuel oil is not advised.

The optimum wind speed for successful use of a dispersant in a marine environment is between 4 and 12 m/s (8 and 25 knots). In addition, a dosage of 1:20 type III concentrate dispersant to oil is usually used for planning purposes (ITOPF, 2011b).

Fingas and Ka'aihue (2005) reviewed the effects of water salinity on chemical dispersion, especially those effects related to effectiveness, and reported that testing of effectiveness with salinity variation consistently shows a decrease in effectiveness at lower salinities and a decrease after a maximum salinity is reached between about 20 and 40 psu (or ‰). They also reviewed the effects of salinity on surfactants and surfactant phenomena and reported that recovery efficiency falls off at both high and low salinities in the use of surfactants for secondary oil recovery. The salinity at which surfactant efficiency peaks is very dependent on the structure of the specific surfactant. The solubility of the hydrocarbon increases with increasing salinity and is low at low salinities. The interfacial tension of water and oil changes with surfactant and salinity. The interfacial tension is higher at lower salinities. The optimal interfacial tension is generally achieved at salinities of between 25‰ and 35‰. In addition, they reported that stability of microemulsions is greater at salinities of 25–35‰ and the stability of systems is very low in freshwater or in water with salinities of <10‰, which this is consistent with findings in oil-spill literature. In addition, Fingas (2008a) reported that there appears to be an interaction between salinity and temperature in oil-spill-dispersant effectiveness. Effectiveness appears to peak at about 15°C and about 25‰.

The use of dispersants in shallow water can affect benthic resources (API and NOAA, 1994). In addition, use of dispersants in the vicinity of fish cages, shellfish beds, or other shallow-water fisheries due to the increased risk of tainting the stock and proximity to industrial water intakes due to increased risk of oil entering water intakes is not advised (ITOPF, 2011b).

Example 4.2

Assume that the volume of oil in a 2 ha slick is 2000 L and a third-generation, type III dispersant is used for oil-spill response. What is the discharge rate from an aircraft traveling at a speed of 40 m/s with a swath of 15 m?

Solution: For a dosage of 1:20 type III concentrate dispersant to oil, the quantity of dispersant, application rate, and discharge rate needed would be:

Dispersant quantity = 2000 L of oil/20 = 100 L.

Application rate = 100 L/20,000 m^2 = 0.005 L/m^2.

Discharge rate = 0.005 L/m^2 × 15 m × 40 m/s = 3 L/s (ITOPF, 2011b).

4.2.2.8 Solidifiers

Most solidifiers are products composed of dry high molecular weight polymers that have a porous matrix and large oleophilic surface area. Solidifiers are available in various forms, including dry powder, granules, semisolid materials (e.g., pucks, cakes, balls, sponge designs), and contained in booms, pillows, pads, and socks. According to the National Response Team (NRT) Science and Technology Committee (2007), solidifiers should meet the following criteria:

- Insoluble in water;
- Specific gravity of less than 1.0;
- Composed primarily of polymers (with few other additives);
- Contain less than 5 ppm of heavy metals and chlorinated hydrocarbons;
- Have a physical reaction with oil whereby at the prescribed application rate, the oil is sorbed by the product in a manner in which the oil is resistant to leaching;
- Do not release solidified liquids under pressure; and
- Product itself is nontoxic to wildlife and other species.

The results of testing solidifiers over 20 years are given in Table 4.2. The results show that the effectiveness of the products varies widely, but the aquatic toxicity

Table 4.2 **Solidifier Testing Results From Canadian Environment (Fingas, 2008b)**

Agent	Percent to Solidify	Toxicity (Aquatic)
A610 Petrobond	13	>5600
Rawflex	16	>5600
Envirobond 403	18	>5600
Norsorex	19	>5600
Jet Gell	19	>5600
Grabber A	21	>5600
Rubberizer	24	>5600
SmartBond HS	25	>5600
Elastol	26	>5600
CI agent	26	>5600
Gelco 200	29	>5600
Oil bond 100	33	>5600
Oil sponge	36	>5600
Petro Lock	44	>5600
SmartBond HO	45	>5600
Molten wax	109	>5600
Powdered wax	278	>5600

(values are LC_{50} to rainbow trout in 96 h) of all products tested is below the threshold of measurement; in other words all products listed were relatively nontoxic to aquatic species (Fingas, 2008b).

The intent of using a solidifier is to change the physical state of the spilled oil from a liquid to a solid to reduce the impact of the oil to shorelines (API and NOAA, 1994). Solidifiers have a physical attraction to oil that is enhanced by van der Waals forces, which are based on the theory that nonpolar hydrocarbon polymers are attracted to nonpolar petroleum hydrocarbons and thus prefer to be oil-wet rather than water-wet. The grain size (and thus surface area) of the product can affect the reaction time. Solidifiers work best with light, low viscosity oils compared to heavy, high viscosity oils (NRT Science and Technology Committee, 2007). The recommended application rates are 10−50% by weight of the liquid to be recovered, and reaction time is usually fast, minutes to hour (hours) (NRT Science and Technology Committee, 2007; Fingas, 2008b; API and NOAA, 1994). Various broadcast systems, such as leaf blowers, water cannons, or fire-suppression systems, can be modified to apply a solidifier over large areas (API and NOAA, 1994), and it can also be done by hand (NRT Science and Technology Committee, 2007).

Solidifiers can be applied to both floating and stranded oil. They can be used in all water environments, bedrock, sediments, and manmade structures. They can be useful when immobilization of the oil is desired, to prevent refloating from a shoreline, penetration into the substrate, or further spreading. However, the oil may not fully solidify unless the product is well mixed with the oil, and may result in a mix of solid and untreated oil (API and NOAA, 1994). Solidifiers work best with light to moderate oils (NRT Science and Technology Committee, 2007; Fingas, 2008b). They are generally not used on heavy oil spills because the product cannot be readily mixed into viscous oils (API and NOAA, 1994). At a spill, preliminary tests should be conducted with the spilled oil to determine overall application rate, effectiveness, and character of the treated oil (e.g., consistency, cohesiveness, stickiness) (NRT Science and Technology Committee, 2007).

Possible sinking of the product or the treated oil over time (it should not sink or cause treated oil to sink initially or after 24 h of floating on the water surface), fate and bioavailability of unreacted product in the environment, and fate and behavior of treated but unrecovered oil are the environmental concerns with solidifiers (NRT Science and Technology Committee, 2007; Fingas, 2008b). Available solidifiers are insoluble and have very low aquatic toxicity (API and NOAA, 1994; NRT Science and Technology Committee, 2007; Fingas, 2008b). Physical disturbance is likely during application and recovery (API and NOAA, 1994).

4.2.2.9 Bioremediation or Biological Response Methods

According to the Congress of the United States, OTA (1991), bioremediation refers to “the act of adding materials to contaminated environments, such as oil-spill sites, to cause an acceleration of the natural biodegradation process.” It is one method that may be useful to remove spilled oil under certain geographic and climatic conditions. For the purpose of oil-spill response, it includes the use of nutrients to increase the activity of indigenous organisms and/or the addition of naturally occurring nonindigenous microorganisms. Bioremediation has emerged as one of the most promising technologies for converting the toxigenic compounds of oil to nontoxic products without further disruption to the local environment and is typically used as a polishing step or a secondary treatment option for oil removal, after conventional cleanup methods have been used (NRT Science and Technology Committee, 2000; Zhu et al., 2001). It is a relatively slow process, requiring weeks to months for effective cleanup. If done properly, it can be very cost-effective, although an in-depth economic analysis has not been conducted to date (NRT Science and Technology Committee, 2013).

In the long run, biodegradation is usually the fate of oil spilled in a marine environment that cannot be collected or burnt (Prince et al., 2003). It is necessary to establish and maintain conditions that favor enhanced oil biodegradation rates in the contaminated environment for the success of oil-spill bioremediation (Zhu et al., 2001). In other words, physical and chemical conditions can affect the success of bioremediation. Temperature, pressure, surface area of the oil, and the energy of the water are physical parameters that affect bioremediation, while chemical parameters include oxygen and nutrient content, pH, salinity, and the composition of the oil (Congress of the United States, OTA, 1991; Zhu et al., 2001).

The two main approaches to oil-spill bioremediation are biostimulation and bioaugmentation (NRT Science and Technology Committee, 2013; Congress of the United States, OTA, 1991; Zhu et al., 2001). For marine oil-spill response purposes, bioremediation technologies can be divided into three discrete categories:

1. Nutrient enrichment (biostimulation);
2. Seeding with naturally occurring microorganisms (bioaugmentation); and
3. Seeding with genetically engineered microorganisms (bioaugmentation with GEMs) (Congress of the United States, OTA, 1991; Zhu et al., 2001; Hassanshahian and Cappello, 2013).

4.2.2.9.1 Summary of Petroleum Biodegradation

Bacteria capable of degrading petroleum hydrocarbons were first isolated almost a century ago (Hassanshahian and Cappello, 2013). Over 200 species of bacteria, yeasts, and fungi have been shown to degrade hydrocarbons ranging from methane to compounds of over 40 carbon atoms and these microorganisms are ubiquitous in marine, freshwater, and soil habitats (Zobell, 1973; Zhu et al., 2001). A recent investigation found 79 bacterial genera that can use hydrocarbons as a sole source of carbon and energy, as well as 9 cyanobacterial genera, 103 fungal genera, and 14 algal genera that are known to degrade or convert hydrocarbons (Hassanshahian and Cappello, 2013). The major oil-degrading microorganisms are listed in Table 4.3.

In the biodegradation of petroleum, progressive or sequential reactions take place in which certain organisms may carry out the initial attack on the petroleum constituent, which produces intermediate substances that are subsequently utilized by a different group of organisms in a process that results in further degradation. Nonhydrocarbon utilizer microorganisms may also play a role in the eventual removal of petroleum from the environment (Karrick, 1977; Zhu et al., 2001).

When petroleum hydrocarbons are broken down by microorganisms the first step is usually the addition of a hydroxyl group to the end of an alkane chain or on to an unsaturated ring of a polycyclic aromatic hydrocarbon (PAH), forming an alcohol. Progressive oxidation to an aldehyde and then a carboxylic acid leads to chain-length reduction and eventually to production of carbon dioxide, water, and biomass. In the case of a PAH, ring fission takes place, again leading eventually to mineralization. When oxygen is added to hydrocarbons, makes the compounds more polar and thus more water-soluble. These compounds are usually more easily biodegradable and thus less toxic. Although the more polar compounds are more likely to enter the water column as biodegradation ensues, they are unlikely to cause environmental damage or toxic effects to nearby biota. Furthermore, the amount of dilution available from the tidal waters is so great that the amounts of benign polar constituents entering the food chain are likely to be negligible. Thus the effect of biochemical end-products from the easily metabolizable compounds in oil are insignificant in the environment (NRT Science and Technology Committee, 2013).

Table 4.3 **Major Oil-Degrading Microorganisms (Congress of the United States, OTA, 1991; Hassanshahian and Cappello, 2013)**

Bacteria	Fungi	Yeast
Achromobacter	*Allescheria*	*Candida*
Acinetobacter	*Aspergillus*	*Cryptococcus*
Actinomyces	*Aureobasidium*	*Debaryomyces*
Aeromonas	*Botrytis*	*Hansenula*
Alcanivorax	*Candida*	*Pichia*
Alcaligenes	*Cephalosporium*	*Rhodotorula*
Arthrobacter	*Cladosporium*	*Saccharomyces*
Bacillus	*Corollasporium*	*Sporobolomyces*
Beneckea	*Cunninghamella*	*Torulopsis*
Brevibacterium	*Debaromyces*	*Trichosporon*
Burkholderia	*Dendryphiella*	*Yarrowia*
Coryneforms	*Fusarium*	
Corynebacterium	*Gliocladium*	
Erwinia	*Gonytrichum*	
Flavobacterium	*Hansenula*	
Klebsiella	*Helminthosporium*	
Lactobacillus	*Luhworthia*	
Leiothrix	*Mucor*	
Moraxella	*Oidiodendron*	
Mycobacterium	*Paecilomyces*	
Nocardia	*Phialophora*	
Peptococcus	*Penicillium*	
Pseudomonas	*Rhodosporidium*	
Rhodococcus	*Rhodotorula*	
Sarcina	*Saccharomyces*	
Spherotilus	*Saccharomycopsis*	
Sphingomonas	*Scopulariopsis*	
Spirillum	*Sporobolomyces*	
Streptomyces	*Torulopsis*	
Vibrio	*Trichoderma*	
Xanthomyces	*Trichosporon*	
	Varicospora	
	Verticillium	

Biodegradation susceptibility of petroleum hydrocarbons may occur in the following order: *n*-alkanes > branched alkanes > low-molecular-weight aromatics > cyclic alkanes (Zhu et al., 2001). Biodegradation rates are typically highest for saturates, followed by the light aromatics, with high-molecular-weight aromatics, asphaltenes, and resins exhibiting extremely low rates of degradation. Weathering an oil-spill changes its composition: the light aromatics and alkanes dissolve or evaporate rapidly and are metabolized by microorganisms. Since they are harder to degrade, the heavier components remain. Crude oil is not completely biodegraded, and claims that all of a light oil or more than 50% of a heavy oil can be biodegraded in days or weeks are not accurate (Congress of the United States, OTA, 1991).

4.2.2.9.2 Effective Parameters on Bioremediation

As noted, bioremediation can be influenced by physical and chemical conditions. Temperature, pressure, surface area of the oil, and the energy of the water are physical parameters that affect bioremediation, while chemical parameters include oxygen and nutrient content, pH, salinity, and the composition of the oil (Congress of the United States, OTA, 1991; Zhu et al., 2001). Factors such as oxygen and nutrient availability can often be manipulated at spill sites to enhance natural biodegradation (i.e., using bioremediation). Other factors, such as salinity, are not usually controllable (Congress of the United States, OTA, 1991).

The properties of spilled oil and the activity or populations of microorganisms can be influenced by the ambient temperature of an environment. At low temperatures, the viscosity of oil is increased, which changes the toxicity (the volatility of toxic low-molecular-weight hydrocarbons is reduced) and solubility of the oil (e.g., short-chain alkanes are more soluble at lower temperatures and some low-molecular-weight aromatics are more soluble at the higher temperature), depending on its composition (Zhu et al., 2001). Most seawater temperature is between −2 and 35°C. Biodegradation has been observed in this entire temperature range (Congress of the United States, OTA, 1991), but the rate of biodegradation generally decreases with decreasing temperature. The highest degradation rates usually occur in the range of 30−40°C in soil environments, 20−30°C in some freshwater environments, and 15−20°C in marine environments. The interaction effects between temperature and other factors (e.g., the composition of the microbial population) can be complicated. In environments where a psychrophilic population has been established, degradation can occur at remarkable rates under cold conditions. Hydrocarbon biodegradation has been seen at temperatures as low as 0−2°C in seawater and −1.1°C in a soil (Zhu et al., 2001).

The rate of biodegradation generally decreases with increasing pressure, which can be important in the deep ocean. Oil reaching great ocean depths degrades very slowly and, although probably of little concern, is likely to persist for a long time. The effects of the surface area of the oil, the energy of the water, and the composition of the oil on biodegradation were discussed earlier. Because microorganism growth takes place at the interface of oil and water, the surface area of the oil plays an important role in biodegradation. An increase of the surface area of the oil can increase the rate of degradation. Sea-surface turbulence or energy of the water can affect dispersion. Turbulent waters will disperse and dilute essential nutrients for the microorganisms and also spread the oil. It is hard for microorganisms to degrade heavy oils compared to light oils (Congress of the United States, OTA, 1991).

Oxygen is required for biodegradation of hydrocarbons. Requirements can be substantial and for complete oxidization of one part of hydrocarbon into carbon dioxide and water, three to four parts of dissolved oxygen are needed (Congress of the United States, OTA, 1991). Conditions of oxygen limitation normally do not exist in the upper levels of the water column in marine and freshwater environments and in the surface layer of most beach environments. Oxygen may become limiting in subsurface sediments, anoxic zones of water columns, and most fine-grained marine shorelines, freshwater wetlands, mudflats, and salt marshes. Wave and water flow, the physical state of the oil, and the amount of available substrates can affect the availability of oxygen (Zhu et al., 2001). Anaerobic degradation of certain hydrocarbons [e.g., some aromatic hydrocarbons such as BTEX (benzene, toluene, ethylbenzene, and xylene)] also occurs, but may be at negligible rates (Congress of the United States, OTA, 1991; Zhu et al., 2001).

Approximately 150 mg of nitrogen and 30 mg of phosphorus are theoretically applied in the conversion of 1 g of hydrocarbon to cell materials (Rosenberg and Ron, 1996; Zhu et al., 2001). In other words, nutrients such as nitrogen, phosphorus, and iron play a much more critical role than oxygen in limiting the rate of biodegradation in marine waters. Due to consumption of these substances by non-oil-degrading microorganisms (including phytoplankton) in competition with the oil-degrading species and precipitation of phosphorus as calcium phosphate at the pH of seawater, marine and other ecosystems are often deficient in these substances (Congress of the United States, OTA, 1991). As nitrogen and phosphorus levels decrease in the summer (probably due to algal productivity), oil biodegradation also decreases (Zhu et al., 2001). Iron is often more limited in clear offshore waters than in sediment-rich coastal waters (Congress of the United States, OTA, 1991).

Degradation of hydrocarbons increases with increasing pH and optimum degradation takes place under slightly alkaline conditions (Dibble and Bartha, 1979; Zhu et al., 2001). In most marine environments, the pH is usually stable and slightly alkaline. However, in salt marshes the pH maybe as low as 5.0, and thus may slow the rate of biodegradation in these habitats (Congress of the United States, OTA, 1991). The pH of freshwater and soil environments can vary widely. Organic soils in wetlands are often acidic, while mineral soils have more neutral and alkaline conditions (Zhu et al., 2001).

Microorganisms are usually well adapted to cope with the range of salinities common in the world's oceans. Estuarine environments may present a special case because salinity values, as well as oxygen and nutrient levels, are quite different from those in coastal or ocean areas (Congress of the United States, OTA, 1991). Hydrocarbons biodegradation may be influenced by changes in salinity via alteration of the microbial population (Zhu et al., 2001). Ward and Brock (1978) investigated hydrocarbon biodegradation in hypersaline environments and reported that rates of hydrocarbon metabolism decreased with increasing salinity in the range of 3.3−28.4%.

4.2.2.9.3 Nutrient Enrichment (Biostimulation)

Biostimulation involves the addition of rate-limiting nutrients such as nitrogen and phosphorus (Congress of the United States, OTA, 1991; API and NOAA, 1994; Zhu et al., 2001; NRT Science and Technology Committee, 2013) or other growth-limiting cosubstrates to a contaminated environment and/or alterations in environmental conditions (e.g., surf-washing, oxygen addition by plant growth, etc.) to stimulate the growth of indigenous oil degraders to accelerate biodegradation. This approach is also called fertilization or nutrient enrichment (Zhu et al., 2001).

Many bench-scale treatability studies have been done to determine the type, concentration, and frequency of the addition of amendments needed for maximum stimulation in the field (Venosa, 1998; Zhu et al., 2001). For instance, studies have shown that nitrate was a better nitrogen source than ammonia for biodegradation of light crude oil in poorly buffered seawater (Wrenn et al., 1994) and addition of ammonia was observed to be more effective than nitrate at stimulating degradation of crude oil in salt-marsh soils (Jackson and Pardue, 1999). In addition, using nitrate as a biostimulation agent, it was found that approximately 1.5−2.0 mg N/L supported near maximal biodegradation of heptadecane immobilized onto sand particles in a microcosm study (Venosa et al., 1994). Results also showed that nitrate concentrations below approximately 10 mg N/L limited the rate of oil biodegradation of Alaska North Slope crude oil in continuous-flow beach microcosms at a loading of 5 g-oil/kg sand (Du et al., 1999; Zhu et al., 2001).

Nutrient enrichment is meant to overcome the rate of natural biodegradation of oil. There is no indication that fertilizer use causes algal blooms or other significant adverse impacts. In Alaska tests, fertilizer use appeared to increase the biodegradation rate by at least a factor of two (Congress of the United States, OTA, 1991). This approach can be applied on moderately to heavily oiled substrates, after other methods have been used to remove as much oil as possible, on lightly oiled shorelines where other methods are destructive or not effective, and where nutrients limit natural degradation. It is most effective on diesel-type and medium oils that do not have large amounts of high molecular weight, slowly degrading components; and less effective where oil residues are thick. In addition, it is not considered for gasoline spills due to complete removal by evaporation at faster timeframes than by microbial degradation. In addition, it is not appropriate in shallow water or restricted waterbodies where nutrient overloading may lead to eutrophication, or where toxicity of nutrients, particularly ammonia, is of concern (API and NOAA, 1994).

4.2.2.9.4 Seeding With Naturally Occurring Microorganisms (Bioaugmentation)

Bioaugmentation is the addition of oil-degrading microorganisms to a polluted environment to supplement the existing microbial population for promotion of increased rates of biodegradation (Congress of the United States, OTA, 1991; API and NOAA, 1994; Zhu et al., 2001; NRT Science and Technology Committee, 2013). A blend of nonindigenous microbes from various polluted environments, specially selected and cultivated for their oil-degrading characteristics, or a mix of oil-degrading microbes selected from the site to be remediated and mass-cultured in the laboratory or in on-site bioreactors, are used as inoculum. The seed culture usually contains nutrients (Congress of the United States, OTA, 1991).

Because indigenous microbial populations may not be capable of degrading the wide range of potential substrates present in complex mixtures such as petroleum, oil-degrading microorganisms are added to a spill site (Leahy and Colwell, 1990; Congress of the United States, OTA, 1991; Zhu et al., 2001). Other conditions under which seed cultures may be most appropriate are when the indigenous hydrocarbon-degrading population is low or unable to degrade a particular hydrocarbon (especially difficult-to-degrade petroleum components such as polynuclear aromatic hydrocarbons), the speed of decontamination is the primary factor, and when seeding may reduce the lag period to start the bioremediation process (Forsyth et al., 1995; Congress of the United States, OTA, 1991; Zhu et al., 2001). Seeding with a culture consisting of indigenous organisms avoids the potential environmental adaptation problems of nonindigenous organisms. In many cases, fertilizers are needed. Bioaugmentation may not be necessary at most sites because there are few locales where oil-degrading microbes do not exist. Requirements for successful seeding are more demanding than those for biostimulation (Congress of the United States, OTA, 1991).

Companies that advocate seeding with microorganisms claim that commercial bacterial blends can be custom-tailored for different types of oil in advance of a spill, that the nutritional needs and limitations of seed cultures are well understood, that microbes can easily be prepared in large quantities for emergency conditions, and that seed cultures can be stored, ready for use, for up to 3 years (Congress of the United States, OTA, 1991). Many successful bioaugmentation bench-scale studies have been done. Bioaugmentation may be effective in bench-scale studies where environmental conditions are well controlled, but this will not guarantee its effectiveness in the field (Zhu et al., 2001).

4.2.2.9.5 Seeding With Genetically Engineered Microorganisms (Bioaugmentation With GEMs)

The reason for creating genetically engineered microorganisms (GEMs) is that they may be more efficient than naturally occurring species or have the ability to degrade fractions of petroleum not degradable by naturally occurring species (Congress of the United States, OTA, 1991). For example, Thibault and Elliot (1980) developed a multiplasmid P. putida strain that can simultaneously degrade some lighter alkanes and aromatics. However, the survival of such a strain in the environment is questionable. There is also the problem of public perception over the release of foreign microorganisms or GEMs into the environment (Zhu et al., 2001). Since the development and use of GEMs are still limited by scientific, economic, regulatory, and public perception obstacles, the imminent use of bioengineered microorganisms for environmental cleanup is unlikely. Many individuals, including EPA officials, believe that we are so far from realizing the potential of naturally occurring microorganisms to degrade marine oil spills that the increased problems associated with GEMs present them unnecessary at this time (Congress of the United States, OTA, 1991).

4.2.2.9.6 Advantages and Disadvantages of Bioremediation

According to the Congress of the United States, OTA (1991), potential advantages and disadvantages of bioremediation include:

Advantages:

- Usually involves only minimal physical disruption of a site;
- No significant adverse effects when used correctly;
- May be helpful in removing some of the toxic components of oil;
- Offers a simpler and more thorough solution than mechanical technologies; and
- Possibly less costly than other approaches.

Disadvantages:

- Of undetermined effectiveness for many types of spills;
- May not be appropriate at sea;
- Takes time to work;
- Approach must be specifically tailored for each polluted site; and
- Optimization requires substantial information about spill site and oil characteristics.

4.2.2.9.7 Methods for Monitoring Oil Bioremediation

Changing of chemistry or microbial populations and environmental conditions, particularly nutrient concentrations, can be useful to demonstrate that biodegradation is taking place in the field. The following methods can be used in monitoring oil bioremediation:

1. Analytical Methods
   - **a.** Microbiological analysis such as enumeration of hydrocarbon-degrading microorganisms: culture-based techniques (e.g., plate count and most-probable-number (MPN) procedures) and culture-independent population/community techniques (e.g., phospholipid fatty acid (PLFA) analysis and nucleic acid-based molecular techniques);
   - **b.** Chemical analysis of nutrients such as automated colorimetric methods for ammonia analysis; ultraviolet spectrophotometric method, automated cadmium reduction method, and nitrate electrode method for nitrate analysis; and conversion of the phosphorus form of interest to dissolved orthophosphate and colorimetric determination of dissolved orthophosphate for phosphorus analysis; and
   - **c.** Chemical analysis of oil and oil constituents such as TPH techniques (e.g., gravimetric and infrared spectroscopic methods); analysis of specific oil constituents (e.g., gas chromatography/flame ionization detection (GC/FID), gas chromatography−mass spectrometry (GC−MS), and thin-layer chromatography−flame ionization detection (TLC−FID)).
2. Use of biomarkers such as pristane and phytane, hopanes, alkylated PAH isomers, phenanthrenes, anthracenes, and chrysenes
3. Sampling in the field
4. Monitoring general site background conditions including dissolved oxygen (e.g., iodometric technique and membrane electrode method), pH, temperature, and salinity (e.g., a conductivity method and density methods)

5. Monitoring of Biological Impacts
   a. Bioassessment
   b. Bioassays (benthic invertebrates, microtox, and fish) and application of bioassays to assess bioremediation in marine environments (Zhu et al., 2001).

4.2.3 Shoreline Response

The methods available for shoreline cleanup are relatively straightforward and do not usually require specialized equipment. Evaluation of the degree and type of contamination, together with the length, nature, and accessibility of the affected coastline, consideration of environmental sensitivity of the shoreline, shoreline type, and generation of minimum waste are crucial in the selection of the most suitable response methods. Because of the oil weathering process and oil sticking more firmly to rocks and sea walls and becoming mixed or buried in sediments with passing time, where possible, it is important to start removing oil from contaminated shorelines as quickly as practicably possible (ITOPF, 2015b). Shoreline-cleaning agents may be used to increase the efficiency of oil removal from contaminated substrates. Special formulations are applied to the substrate, as a presoak and/or flushing solution, to soften or lift weathered or heavy oils to enhance flushing methods (API and NOAA, 1994).

Shoreline-cleanup operations are often conducted in three stages:

Stage 1: Bulk oil is removed from the shore to prevent remobilization using vacuum trucks, pumps, and skimmers on pooled liquid bulk oil, or using mechanical collection by a variety of nonspecialized civil engineering or agricultural machinery to collect and remove stranded oil and contaminated material, or using manpower to collect oil and contaminated shoreline material on sensitive shores and areas inaccessible to vehicles;

Stage 2: Stranded oil and oiled shoreline materials are removed, which is often the most protracted part of shoreline cleanup. This stage may involve flushing, a technique that uses high volumes of low-pressure water to wash stranded or buried oil from shorelines. Similar in principle to flushing is surf washing, whereby the natural cleaning action of the shoreline waves are used to release the oil from within the shore sediment; and

Stage 3: Final cleanup of light contamination and removal of stains, if required. This stage may involve high-pressure washing using either hot or cold water on most hard surfaces, bioremediation, etc.

Note that consideration should be given to the environmental sensitivity of the shoreline to ensure the planned level of cleaning will not cause more harm than leaving the oil in place. In considering the cleanup of a specific shoreline type, the level of amenity use, the environmental sensitivity, and the exposure of the shoreline to natural cleaning action should be considered. For instance, cleanup methods for ports, harbors, sea defenses and similar manmade structures, and natural hard surfaces such as bedrock or boulders may utilize high-pressure washing or flushing with the priority being a high level of oil removal. Flushing and surf-washing methods, together with mechanical washing, are typically the most useful cleanup methods for cobble, pebble, and shingle shores.

A well-designed contingency plan that incorporates a high degree of local knowledge can be helpful in successful management and organization of a shoreline cleanup and could be prepared by those agencies, organizations, and stakeholders that might be involved in a shoreline response (ITOPF, 2015b).

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Control and Treatment of Air Emissions

5

5.1 Overview of Control and Treatment of Air Emissions

As discussed in Chapter 2, a wide variety of air pollutants such as nitrogen oxides (NO_x), sulfur oxides (SO_x), carbon monoxide (CO), volatile organic compounds (VOCs), dust or particulates, etc., are generated and emitted from operations in the petroleum industry (E&P Forum, 1993; U.S. EPA, 1995; European Commission and Joint Research Center, 2013; Jafarinejad, 2015a, 2016a). There are a variety of techniques for minimizing, controlling, preventing, and treating emissions to air including:

1. For nitrogen oxides (NO_x): Reduction of residence time (a design feature) (Orszulik, 2008); reduction of air/fuel ratio (careful control of air used for combustion); staged combustion (air staging and fuel staging); flue-gas recirculation (reinjection of waste gas from the furnace into the flame to reduce the oxygen content and therefore the temperature of the flame); low NO_x burners (LNBs) (based on reducing peak flame temperatures, delaying but completing the combustion and increasing the heat transfer; the design of ultralow-NO_x burners (ULNB) including combustion staging (air/fuel) and flue-gas recirculation); optimization of combustion (monitoring and controlling of combustion parameters such as O_2, CO content, fuel/air or (oxygen) ratio, unburnt components); diluent injection (addition of inert diluents such as flue gas, steam, water, nitrogen to combustion equipment can reduce the flame temperature and consequently the concentration of NO_x in the flue gases); low-temperature NO_x oxidation; selective noncatalytic reduction (SNCR); and selective catalytic reduction (SCR) (European Commission and Joint Research Center, 2013).
2. For sulfur oxides (SO_x): Use of low-sulfur crude; liquid-fuel desulfurization (hydrogenation reactions take place by hydrotreatment process and lead to reducing sulfur content); treatment of refinery fuel gas (RFG), e.g., by acid-gas removal to remove H_2S; use of gas such as onsite liquefied petroleum gas (LPG) or RFG or externally supplied gaseous fuel (e.g., natural gas) with a low level of sulfur and other undesirable substances to replace liquid fuel; use of SO_x-reducing catalyst additives (note that SO_x-reducing catalyst additives might have a detrimental effect on dust emissions by increasing catalyst losses due to attrition, and on NO_x emissions by participating in CO promotion, together with the oxidation of SO_2 to SO_3); use of a hydrotreatment process that reduces sulfur, nitrogen, and metal content of the feed; acid gas (mainly H_2S) removal from the fuel gases, e.g., by amine-treating (absorption); use of sulfur-recovery unit (SRU); use of tail-gas treatment unit (TGTU); use of flue-gas desulfurization (FGD) (European Commission and Joint Research Center, 2013); and use of scrubbing systems (wet scrubbing and dry or semidry scrubbing in combination with a filtration system) (Joseph and Beachler, 1998; Boamah et al., 2012; European Commission and Joint Research Center, 2013; Jafarinejad, 2016a).
3. For carbon monoxide (CO): Combustion operation control by careful control of the operational parameters; use of substances (catalysts) that selectively promote the oxidation of CO into CO_2 (combustion); and use of CO boiler where CO present in the flue gas is consumed downstream of the catalyst regenerator to recover the energy. Note that the CO

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boiler is usually used only with partial-combustion fluidized-bed catalytic cracking (FCC) units (European Commission and Joint Research Center, 2013).

4. For VOCs: Use of leak-detection and repair (LDAR) program to minimize fugitive VOC emissions by detection and subsequent repair or replacement of leaking components; use of VOC diffuse emissions monitoring by solar occultation flux (SOF) or differential absorption lidar (DIAL); use of vapor balancing to prevent emissions to atmosphere from loading operations (vapor can be stored prior to vapor recovery or destruction) (European Commission and Joint Research Center, 2013); use of vapor recovery (U.S. EPA, 2006a, 2008; European Commission and Joint Research Center, 2013); use of vapor destruction; and use of high-integrity equipment including valves with double-packing seals, magnetically driven pumps/compressors/agitators, pumps/compressors/agitators fitted with mechanical seals instead of packing, and high-integrity gaskets (such as spiral wound, ring joints) for critical applications (European Commission and Joint Research Center, 2013).
5. For dust or particulates: Use of electrostatic precipitator (ESP) (Turner et al., 1999; Mizuno, 2000; Boamah et al., 2012); use of bag filters constructed from porous woven or felted fabric that are suitable to the characteristics of the waste gases and the maximum operating temperature; use of multistage cyclone separators; use of centrifugal washers that combine the cyclone principle and an intensive contact with water, e.g., venturi washer; and use of third-stage blowback (reverse flow) ceramic or sintered metal filters (European Commission and Joint Research Center, 2013).
6. For combined air-pollutant emissions: Use of wet scrubbing and SNO_x combined method to remove SO_x, NO_x, and dust where a first dust-removal stage (ESP) takes place followed by specific catalytic processes. The sulfur compounds are recovered as commercial-grade concentrated sulfuric acid, while NO_x is reduced to N_2. Overall, SO_x and NO_x removal are in the range 94–96.6% and 87–90%, respectively (European Commission and Joint Research Center, 2013).
7. Other air-emissions control: Methods to prevent or reduce emissions from flaring (Indriani, 2005); choice of the catalyst promoter such as chlorinated compound for effective reforming catalyst performance to avoid dioxins formation and emissions of dioxins and furans; and solvent recovery for base oil-production processes, e.g., 1,2-dichloroethane (DCE) and dichloromethane (DCM) in a distillation step and a stripping step in a fractionator or DCE recovery in wax-processing units (European Commission and Joint Research Center, 2013).

Some of the emissions levels that should be achieved are listed in Table 5.1. Air emissions from stacks should be monitored once every shift, if not continuously, for opacity (maximum level, 10%). Air emissions of H_2S from an SRU should be monitored on a continuous basis. Annual emissions monitoring of combustion sources should be carried out for SO_x (sulfur content of the fuel monitored on a supply-tank basis) and for NO_x (World Bank Group, 1998).

5.1.1 Low-Temperature NO_x Oxidation Process

The low-temperature oxidation (LTO) process can be used to remove NO_x and other pollutants from waste-gas streams and consequently to control NO_x emission to air (The Linde Group, 2015). In the LTO process (Fig. 5.1), ozone is injected into a flue-gas stream at optimal temperatures below 150°C to oxidize insoluble NO and NO_2 to highly soluble N_2O_5 (European Commission and Joint Research Center, 2013), which can be effectively removed by a variety of air-pollution control (APC)

Table 5.1 **Maximum Effluent Level From the Petroleum Industry (World Bank Group, 1998)**

Parameter	Maximum Value
Nitrogen oxides (mg/m^3) (excludes NO_x emissions from catalytic units)	460
Sulfur oxides (mg/m^3)	150 for SRUs and 500 for other units.
PM (mg/m^3)	50
Nickel and vanadium (combined) (mg/m^3)	2
Hydrogen sulfide (mg/m^3)	152

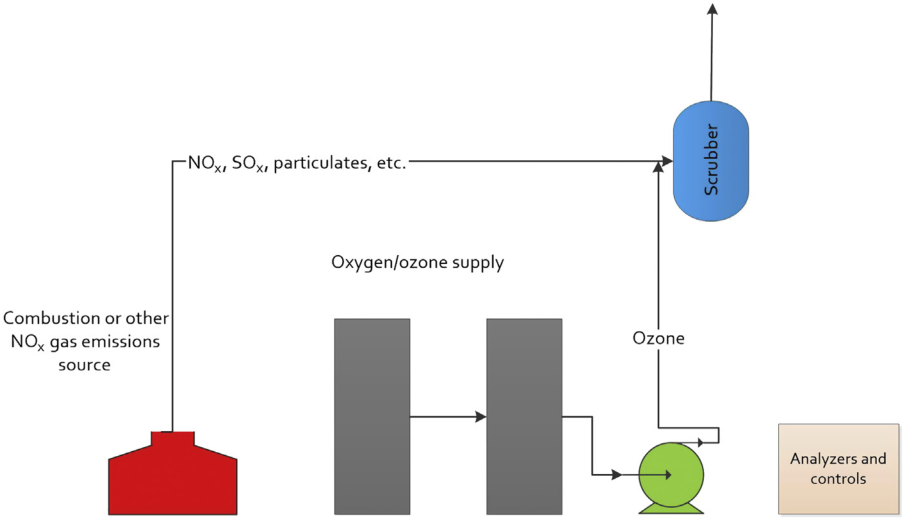

Figure 5.1 Schematic of low-temperature NO_x oxidation process.
Modified from The Linde Group, 2015. LoTOx™ System, Low Temperature Oxidation for NO_x Control. Gases Division, Seitnerstrasse 70, 82049 Pullach, Germany, pp. 1–2. [Online] Available from: http://www.linde-gas.com/internet.global.lindegas.global/en/images/LOTOX%20datasheet17_130449.pdf.

equipment, such as wet or semidry scrubbers or wet electrostatic precipitators (WESP) (The Linde Group, 2015). The N_2O_5 is removed in a wet scrubber by forming dilute nitric acid-waste water that can be used in plant processes or neutralized for release and may need additional nitrogen removal (European Commission and Joint Research Center, 2013). Calcium nitrate, a valuable commercial fertilizer, can be produced as a saleable product in systems using lime scrubbers. NO_x capture in a dry or semidry scrubber can result in a waste stream of nitrates mixed with other solids such as PM, sulfides, chlorides, etc. (The Linde Group, 2015).

5.1.2 Selective Noncatalytic Reduction

Selective noncatalytic reduction (SNCR) is based on the chemical reduction of NO_x into nitrogen (N_2) and water vapor (H_2O) by injection of a nitrogen-based reducing agent (reagent) such as ammonia (NH_3) or urea (CH_2CONH_2) into the postcombustion flue gas (U.S. EPA, 2003a; Ramadan, 2004; European Commission and Joint Research Center, 2013). A schematic of an SNCR process is shown in Fig. 5.2. Urea is more expensive than ammonia, but urea-based systems have advantages over ammonia-based systems such as nontoxicity, less volatility, safe handling, and further penetration of urea solution droplets into the flue gas, enhancing mixing with the flue gas, which is difficult in large boilers. The NO_x-reduction reaction occurs at temperatures between 870 and 1150°C (U.S. EPA, 2003a), and operating temperature range must be maintained between 900 and 1050°C for optimal reaction (European Commission and Joint Research Center, 2013).

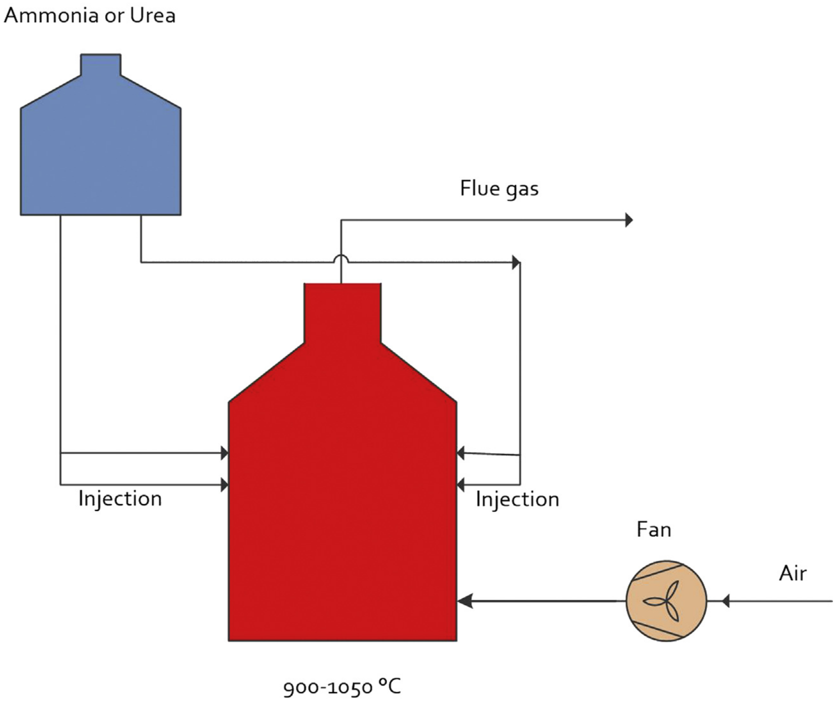

Figure 5.2 Schematic of a selective noncatalytic reduction (SNCR) process.
Modified from Energie- en milieu-informatiesysteem (EMIS), VITO, 2015a. Selective Non-catalytic Reduction. VITO, Boeretang 200, B-2400 Mol, Belgium. [Online] Available from: http://emis.vito.be/techniekfiche/selective-non-catalytic-reduction?language=en.

Selective noncatalytic reduction can reduce NO_x emissions by 30–50% (U.S. EPA, 2003a) or 35–60% (Ramadan, 2004) that can be used in new and retrofit installations. NO_x-reduction levels range from 65% to 75% for SNCR applied in conjunction with combustion controls such as low-NO_x burners (U.S. EPA, 2003a).

Having the lowest capital and operating costs among all NO_x reduction methods, relatively simple retrofitting, cost-effective for seasonal and variable load applications, accepting waste-gas streams with high levels of PM, and applicable with combustion controls to provide higher NO_x reductions are some of the advantages of SNCR. The specified temperature-range requirement for waste-gas stream, not applicable to sources with low NO_x concentrations such as gas turbines, lower NO_x reduction than SCR, probable downstream equipment cleaning requirement, possible ammonia contamination of fly ash (ammonia can cause odor problems), release of unreacted ammonia into the environment with treated flue gases, and production of (N_2O), a potent greenhouse gas, during the reaction of flue-gas NO_x with the injected reagents are some of the disadvantages of SNCR (Ramadan, 2004).

5.1.3 Selective Catalytic Reduction

Selective catalytic reduction (SCR) is based on the reduction of NO_x into nitrogen and water vapor in a catalytic bed by reaction with ammonia (in general aqueous solution) or urea (U.S. EPA, 2003b; Ramadan, 2004; European Commission and Joint Research Center, 2013). A reagent is injected into the downstream of the combustion unit that is mixed with the waste gas and is entered a reactor module congaing catalyst. The reagent reacts selectively with the NO_x in the presence of catalyst and oxygen. An example schematic of a SCR process is shown in Fig. 5.3. Temperature, the amount of reducing agent, injection grid design, and catalyst activity can affect the actual removal efficiency. Optimum operating temperatures range from 250–427°C (U.S. EPA, 2003b) or 300–450°C depending on the catalyst (European Commission and Joint Research Center, 2013).

The catalysts used in SCR are oxides of metals, typically vanadium and titanium (Ramadan, 2004). The catalyst is generally composed of active metals or ceramics with highly porous structures. Ceramic honeycomb and pleated metal plate (monolith) designs are general configurations of catalysts (U.S. EPA, 2003b). One or two layers of catalyst may be applied and higher NO_x reduction can be achieved with the use of higher amounts of catalyst (two layers) (European Commission and Joint Research Center, 2013). Catalyst activity plays a major role in the NO_x-reduction reaction rate. Poisoning of active sites by flue-gas constituents, thermal sintering of active sites due to high temperatures within reactor, blinding/plugging/fouling of active sites by ammonia-sulfur salts and PM, and erosion due to high gas velocities can deactivate catalysts. A decrease in catalyst activity can reduce NO_x removal and increase ammonia slip (U.S. EPA, 2003b).

There are several different installation configurations for SCR systems downstream of the combustion unit. In most applications, the reactor is located downstream of the economizer and upstream of the air heater and particulate control devices (hot side). Selective catalytic reduction may be located after PM and sulfur-removal equipment

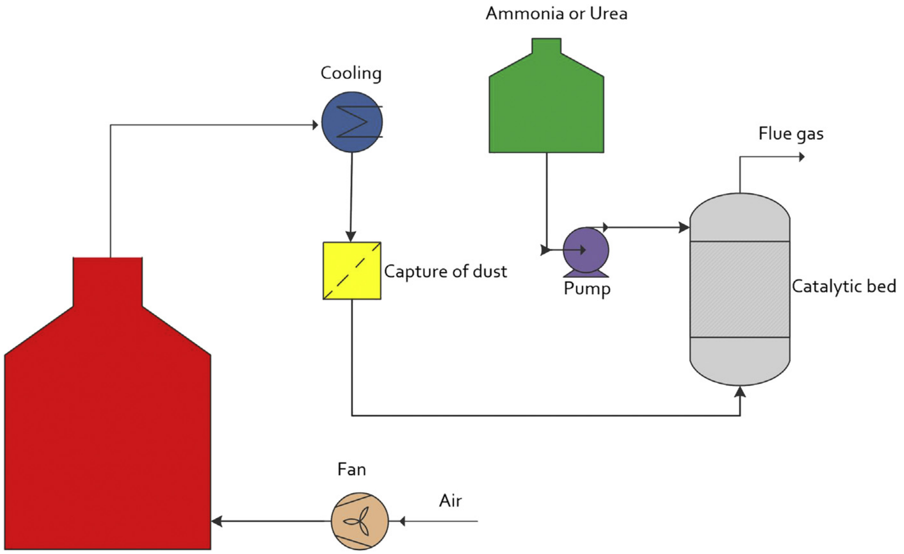

Figure 5.3 Schematic of a selective catalytic reduction (SCR) process.
Modified from Energie- en milieu-informatiesysteem (EMIS), VITO, 2015b. Selective Catalytic Reduction. VITO, Boeretang 200, B-2400 Mol, Belgium. [Online] Available from: http://emis.vito.be/techniekfiche/selective-catalytic-reduction?language=en.

(cold side). This configuration may require reheating of the flue gas, which dramatically increases the operational costs (U.S. EPA, 2003b).

In SCR, reactions occur within a lower and broader temperature range than SNCR, and 70–90% removal of the NO_x in the flue gas can be achieved, but it is significantly more expensive than SNCR systems (U.S. EPA, 2003b; Ramadan, 2004). Selective catalytic reduction can be used separately or in combination with other technologies such as low NO_x burners and natural gas reburn (NGR). It can also be applied to sources with low NO_x concentrations. Higher capital and operating costs than LNB and SNCR, difficult and costly retrofitting of SCR on industrial boilers, large number of reagent and catalyst requirements, probable downstream equipment cleaning requirement (U.S. EPA, 2003b), emissions of unreacted ammonia, and conversion of SO_2 to SO_3 by catalysts and the impact of that process on NO_x removal are some disadvantages of SCR (Ramadan, 2004).

5.1.4 Sulfur-Recovery Unit

The conversion of hydrogen sulfide (H_2S) to elemental sulfur is called sulfur recovery (U.S. EPA, 2015; Jafarinejad, 2016a). A sulfur-recovery unit (SRU) is an essential processing step to allow the overall facility to operate as the discharge of sulfur compounds to the atmosphere is severely restricted by environmental regulations (Street and Rameshni, 2011). H_2S-rich gas streams from amine-treating units and sour-water strippers (SWS) are treated in an SRU, which most often consists of a Claus process for bulk sulfur removal and subsequently a TGTU for the remaining H_2S removal. Other components entering the SRU may include NH_3, CO_2, and, to a minor extent, various hydrocarbons (European Commission and Joint Research Center, 2013; Jafarinejad, 2016a).

5.1.4.1 Claus Process

The basic Claus unit consists of a thermal stage and two or three catalytic stages (Street and Rameshni, 2011). Fig. 5.4 shows a typical Claus process. It consists of a reaction furnace followed by a series of catalytic stages where each catalytic stage comprises a gas reheater, a catalyst chamber, and a condenser (European Commission and Joint Research Center, 2013; U.S. EPA, 2015). The process includes multistage catalytic oxidation of H_2S according to the following overall reaction (U.S. EPA, 2015):

$$2H_2S + O_2 \leftrightarrow 2S + 2H_2O \tag{5.1}$$

The furnace usually operates at higher temperatures ranging from 980−1540°C (US EPA, 2015) or 1000−1400°C (Speight, 2005) with pressures rarely higher than 70 kilopascals (kPa). One-third of the H_2S is burned with air in it to form sulfur dioxide according to the following reaction:

$$2H_2S + 3O_2 \leftrightarrow 2SO_2 + 2H_2O + \text{heat} \tag{5.2}$$

Before entering a sulfur condenser, hot gas from the combustion chamber is quenched in a waste-heat boiler that generates high-to-medium pressure steam. About 80% of the heat released can be recovered as useful energy (U.S. EPA, 2015).

The catalytic reactors operate at lower temperatures, ranging from 200−315°C (U.S. EPA, 2015) or 200−350°C (Speight, 2005) and the remaining uncombusted two-thirds of the H_2S reacts with SO_2 to form elemental sulfur as follows:

$$2H_2S + SO_2 \leftrightarrow 3S + 2H_2O + \text{heat} \tag{5.3}$$

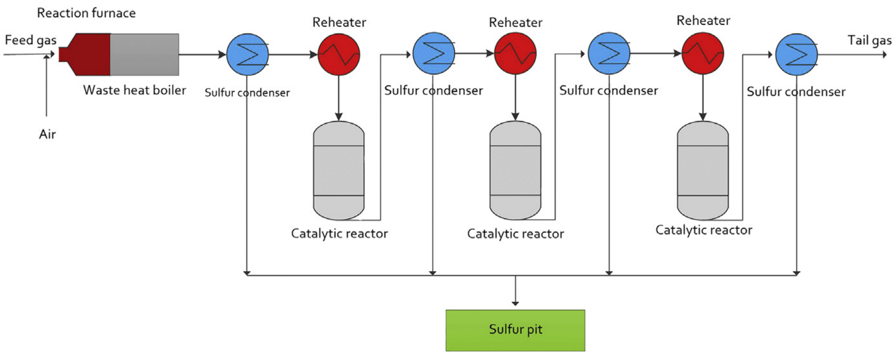

Figure 5.4 Typical Claus process (Jafarinejad, 2016a).

Liquid elementary sulfur is collected from the various condensers in a covered pit. Alumina or bauxite can be used as a catalyst (U.S. EPA, 2015). Feed/air ratio control, temperature control of the furnace, reactors and condensers, and good demisting of liquid sulfur, especially from the final condenser exit gas stream, are important parameters in achieving maximum sulfur recovery (European Commission and Joint Research Center, 2013). Typical sulfur-recovery efficiencies are in the range 95–97% (U.S. EPA, 2015) or 94–98% (European Commission and Joint Research Center, 2013) or 95–98% (Street and Rameshni, 2011), depending on the feed-gas composition, number of catalytic reaction stages, the type of reheating method used (auxiliary burners or heat exchangers, with steam reheat for a natural-gas processing plant and 3536–4223 kPa steam for a crude-oil refinery), and general plant configuration (Street and Rameshni, 2011; U.S. EPA, 2015). The tail gas containing H_2S, SO_2, sulfur vapor, traces of other sulfur compounds formed in the combustion section, and the inert gases from the condenser of the final catalytic stage is frequently entered a TGTU to recover additional sulfur and subsequently achieve higher recovery (U.S. EPA, 2015). Addition to TGTU, the SNO_x (a combined NO_x and SO_x abatement technique) or scrubber techniques may be used for this purpose (European Commission and Joint Research Center, 2013).

Many other side reactions also occur that produce COS and CS_2, which have caused problems in many Claus plant operations because they cannot be easily converted to elemental sulfur and carbon dioxide (European Commission and Joint Research Center, 2013). Some these possible side reactions include (U.S. EPA, 2015):

$$H_2S + CO_2 \rightarrow COS + H_2O \tag{5.4}$$

$$COS + H_2S \rightarrow CS_2 + 2H_2O \tag{5.5}$$

$$2COS \rightarrow CO_2 + CS_2 \tag{5.6}$$

The use of oxygen-enrichment technologies (e.g., OxyClaus process) can increase the overall capacity of the Claus plants; however, it does not increase the sulfur-recovery efficiency of these plants. An improved unique burner system and enhanced combustion conditions to reach a minimum temperature of 1350°C, high-performance catalyst process (e.g., Selectox), and automated control of the air feed are techniques that can be used and retrofitted to existing SRUs to increase the Claus process efficiency (European Commission and Joint Research Center, 2013; Jafarinejad, 2016a).

5.1.4.2 Tail-Gas Treatment Unit

Tail-gas treatment units (TGTUs) are a family of techniques that can be added to an SRU in order to increase removal and recovery of sulfur compounds. As noted in Chapter 3, according to the principles applied, the most frequently operated TGTU processes can be broadly divided into the following four categories:

- Direct oxidation to sulfur (PRO-Claus stands for Parson RedOx Claus with expected sulfur-recovery efficiency of 99.5% and the SUPERCLAUS process with expected sulfur-recovery efficiency of 98–99.3%);

- Continuation of the Claus reaction (cold-bed absorption (CBA) process with expected sulfur-recovery efficiency of 99.3–99.4%, the Clauspol process with expected sulfur-recovery efficiency of 99.5–99.9%, and the Sulfreen process (Hydrosulfreen with expected sulfur-recovery efficiency of 99.5–99.7%, Doxosulfreen with expected sulfur-recovery efficiency of 99.8–99.9%, and Maxisulf with expected sulfur-recovery efficiency of 98.5% (note that expected sulfur-recovery efficiency for third-stage Claus + Maxisulf process is 99–99.5%)));
- Reduction to H_2S and recovering sulfur from this H_2S (the Flexsorb process with expected sulfur-recovery efficiency of 99.9%, high Claus ratio (HCR) process, reduction, absorption, recycle (RAR) process with expected sulfur-recovery efficiency of 99.9%, the Shell Claus Offgas Treating (SCOT) process (H_2S scrubbing) with expected sulfur-recovery efficiency of 99.5–99.95% for amine-based process, and the Beavon sulfur-removal (BSR) process with expected sulfur-recovery efficiency of 99.5–99.9%) (European Commission and Joint Research Center, 2013); and
- Oxidation to SO_2 and recovering sulfur from SO_2 (the Wellman–Lord process with expected sulfur-recovery efficiency of 99.9%, the Clintox process, and the Labsorb process) (European Commission and Joint Research Center, 2013; U.S. EPA, 2015; Jafarinejad, 2016a).

Among these processes, the SCOT process, BSR process, and Wellman–Lord process are commonly often used to recover additional sulfur, and are described in this section.

5.1.4.2.1 Shell Claus Offgas Treating Process

The SCOT process is widely applied to recover sulfur from the Claus tail gas (Speight, 2005; European Commission and Joint Research Center, 2013; U.S. EPA,

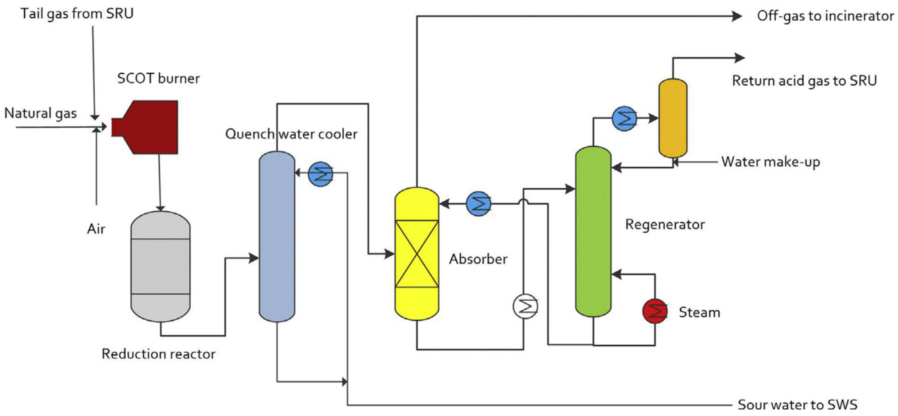

Figure 5.5 Simplified process flow diagram of Shell Claus Offgas Treating (SCOT) process. Modified from European Commission, Joint Research Center, 2013. Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas. Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control), Joint Research Center, Institute for Prospective Technological Studies Sustainable Production and Consumption Unit European IPPC Bureau; Jafarinejad, Sh., 2016a. Control and treatment of sulfur compounds specially sulfur oxides (SO_x) emissions from the petroleum industry: a review. Chemistry International 2 (4), 242–253.

2015; Jafarinejad, 2016a). Fig. 5.5 shows a simplified process flow diagram (PFD) of the SCOT process. In this type of scrubbing process, sulfur in the tail gas is converted to H_2S using hydrogenation and hydrolysis of all sulfur compounds by passing it through a cobalt-molybdenum catalyst at 300°C with the addition of a reducing gas. The gas is then cooled and sent to an absorber, where H_2S is absorbed by an amine solution (generic amine or specialty amine). The sulfide-rich amine solution is sent to a regenerator, where H_2S is removed and recycled to the upfront Claus reaction furnace. The amine solution is regenerated and returned to the absorber (European Commission and Joint Research Center, 2013).

5.1.4.2.2 Beavon Sulfur-Removal Process

The Beavon sulfur-removal (BSR) process is used to recover sulfur from the Claus tail gas (Street and Rameshni, 2011; U.S. EPA, 2015; Jafarinejad, 2016a). This process represents the best-available control technology (BACT), potentially achieving 99.99+% overall sulfur recovery with emissions of <10 ppmv H_2S and 30 ppmv total sulfur (Rameshni). It can also be effective at removing small amounts of SO_2, COS, and CS_2 not affected by the Claus process (Speight, 2005; Street and Rameshni, 2011). Fig. 5.6 shows a typical simplified BSR amine system scheme. This process has two steps. In the first step, all sulfur compounds are catalytically (cobalt-molybdate based) converted into H_2S through an hydrogenation/hydrolysis reaction at high temperature (300–400°C) (European Commission and Joint Research Center, 2013). The Claus tail gas is heated approximately to 290–340°C by inline substoichiometric combustion of natural gas in a reducing gas generator (RGG) (in the RGG, some reducing gas H_2 and CO are produced) for subsequent

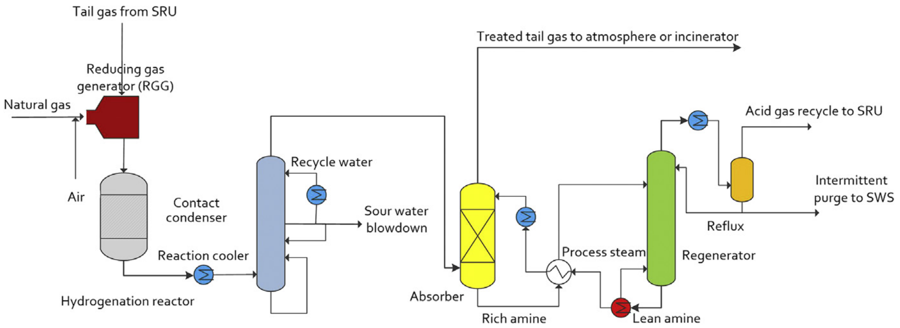

Figure 5.6 Typical simplified BSR amine system scheme.
Modified from Street, R., Rameshni, M., 2011. Sulfur Recovery Unit, Expansion Case Studies. Worley Parsons, 125 West Huntington Drive, Arcadia, CA 91007, USA. [Online] Available from: http://www.worleyparsons.com/CSG/Hydrocarbons/SpecialtyCapabilities/Documents/Sulfur_Recovery_Unit_Expansion_Case_Studies.pdf; Jafarinejad, Sh., 2016a. Control and treatment of sulfur compounds specially sulfur oxides (SO_x) emissions from the petroleum industry: a review. Chemistry International 2 (4), 242–253.

catalytic reduction of virtually all non-H_2S sulfur components to H_2S. Elemental sulfur (S_x) and SO_2 are converted by hydrogenation in the reactor according to the following reactions:

$$S_x + xH_2 \rightarrow xH_2S \tag{5.7}$$

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O \tag{5.8}$$

COS and CS_2 are converted by hydrolysis in the reactor according to the following reactions:

$$COS + H_2O \rightarrow H_2S + CO_2 \tag{5.9}$$

$$CS_2 + 2H_2O \rightarrow 2H_2S + CO_2 \tag{5.10}$$

The reactions are exothermic and heat is removed from the gas in the reaction cooler, which produces steam. The gas is cooled further in a direct-contact condenser (or quench tower) by a circulating water stream down to a suitable temperature for the second step and sourwater is condensed from the stream (Street and Rameshni, 2011; Rameshni).

In the second step, H_2S is generally removed by a chemical solution (e.g., amine process) or another tail-gas process (e.g., the Stretford redox process) (European Commission and Joint Research Center, 2013; Rameshni). In an amine-treatment process, gas is contacted with lean amine solution in the absorber, which the H_2S and some of the CO_2 are absorbed by the amine. The treated gas is sent to the thermal oxidizer where residual H_2S is converted to SO_2 before discharge to atmosphere. The rich amine is sent to the regenerator after being heated in the lean/rich exchanger by the hot lean amine from the bottom of the regenerator. In the regenerator, the acid gases are released from solution by heating the solution in the reboiler. The overhead from the regenerator is cooled and the condensate returned to the column. The cooled, water-saturated, acid gas is recycled to the Claus unit. The hot, lean amine is cooled first by heating the rich solution and then in the lean amine cooler before entering the absorber (Street and Rameshni, 2011; Jafarinejad, 2016a).

5.1.4.2.3 Wellman—Lord Process

The Wellman—Lord process uses a wet generative process to reduce flue-gas SO_2 concentration to less than 250 ppmv and can achieve approximately 99.9% sulfur recovery (U.S. EPA, 2015). This process is the most widely used regenerative process (European Commission and Joint Research Center, 2013) that incorporates the flue-gas pretreatment, sulfur-dioxide absorption, absorbent regeneration, and sulfate-removal processes. After absorbent regeneration, the obtained SO_2 can be liquefied or used for successive production of sulfuric acid or sulfur, e.g., the so-called Wellman—Lord and allied chemical process (Atanasova et al., 2013). Fig. 5.7 shows a schematic PFD of the Wellman—Lord and allied chemical processes. Sulfur-recovery unit tail gas is incinerated and all sulfur species are oxidized to form SO_2 in this process (U.S. EPA, 2015).

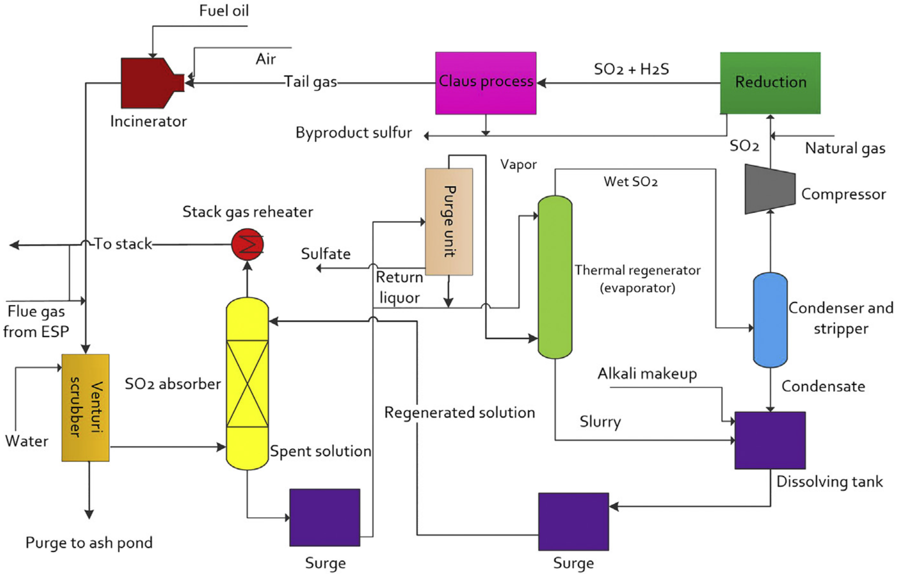

Figure 5.7 Schematic PFD of Wellman–Lord and allied chemical processes. Modified from Tri-State Synfuels Company, 1982. Tri-State Synfuels Project Review. In: Commercial Status of Licensed Process Units, June 1982, vol. 8. Prepared for U.S. DOE under cooperative agreement NO. DE -FC05–810R20807, 10.0 Flue gas desulfurization, Tri-State Synfuels Company, Indirect coal Iiquefaction Plant, Western Kentucky, Fluor engineers and Constructors, Inc., Contract 835604. [Online] Available from: http://www.fischer-tropsch.org/DOE/DOE_reports/20807-t1/doe_or_20807-t1-vol_3/doe_or_20807-t1-vol_3-J.pdf; Jafarinejad, Sh., 2016a. Control and treatment of sulfur compounds specially sulfur oxides (SO_x) emissions from the petroleum industry: a review. Chemistry International 2 (4), 242–253.

Gases are then entered in a preliminary absorber (venturi prescrubber) and cooled and quenched to remove excess water and to reduce gas temperature to absorber conditions, and most of the solid impurities, chlorides, part of the SO_2, etc., are captured (Tri-State Synfuels Company, 1982; Atanasova et al., 2013). The rich SO_2 gas is then reacted with a solution of sodium sulfite (Na_2SO_3) to form the bisulfite (Tri-State Synfuels Company, 1982; Atanasova et al., 2013; U.S. EPA, 2015):

$$SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3 \tag{5.11}$$

The off-gas is reheated and vented to stack. The resulting bisulfite solution is boiled in an evaporator crystallizer, where it decomposes to SO_2 and water (H_2O) vapor and sodium sulfite is precipitated:

$$2NaHSO_3 \rightarrow Na_2SO_3 \downarrow + H_2O + SO_2 \uparrow \tag{5.12}$$

Sulfite crystals are separated and redissolved for reuse as lean solution in the absorber (U.S. EPA, 2015). Sodium-sulfite slurry produced from the evaporators is dissolved in stripped condensate, which is derived from the evaporator overhead vapors. Sodium-carbonate makeup is added to the dissolving tank to replace the sodium lost in the purge streams. The sodium carbonate reacts with sodium bisulfite in the dissolving tank to form additional sodium sulfite (Tri-State Synfuels Company, 1982):

$$Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + H_2O + CO_2 \tag{5.13}$$

The wet SO_2 gas is directed to a partial condenser where most of the water is condensed and reused to dissolve sulfite crystals. The enriched SO_2 stream is then recycled back and used for conversion to elemental sulfur or production of sulfuric acid (Atanasova et al., 2013; U.S. EPA, 2015; Jafarinejad, 2016a).

Production of pure SO_2 with no residuals and high capital investments for the plant construction are the advantage and substantial disadvantage of the Wellman–Lord process, respectively. The large amount of steam needed for regeneration of the solution is another drawback (Atanasova et al., 2013). According to Kolev (2000) and Atanasova et al. (2013), three solutions have been proposed for substantial reduction of the steam consumption of the method on the basis of a significant increase of the SO_2 concentration in the saturated absorbent and consequently enhancement of the Wellman–Lord method:

- Additional saturation of the absorption solution with Na_2SO_3, after partial transformation of the initial Na_2SO_3 into $NaHSO_3$;
- Preliminary cooling of the flue gases in the packing beds of a contact economizer system and utilization of the waste heat of the gases for district heating water and for heating and humidifying of the air fed into the boiler combustor; and
- Development of new types of packings and liquid distributors.

5.1.5 Flue-Gas Desulfurization

Flue-gas desulfurization (FGD) is a scrubbing technique that uses an alkaline reagent (typically a sodium- or calcium-based alkaline regent) to remove SO_2 from flue gas (Tri-State Synfuels Company, 1982; Tilly, 1983; Srivastava and Jozewicz, 2001; U.S. EPA, 2003c; Ramadan, 2004; Dehghani and Bridjanian, 2010; European Commission and Joint Research Center, 2013; Jafarinejad, 2016a). The reagent is injected into the flue gas in a spray tower and directly into the duct and absorbed to neutralize and/or oxidize the SO_2. Thus solid sulfur compounds such as calcium sulfate (gypsum), sodium sulfate, etc., depending on alkaline reagent, are made and are removed from the waste-gas stream using downstream equipment (U.S. EPA, 2003c; Jafarinejad, 2016a).

Flue-gas desulfurization processes can be classified as once-through or regenerable, depending on how the sorbent is treated after it has sorbed SO_2 or how the generated solids by the process are handled (Srivastava and Jozewicz, 2001; U.S. EPA, 2003c; Jafarinejad, 2016a). In once-through technologies, the spent sorbent is disposed of as a waste or utilized as a byproduct. In regenerable technologies, SO_2 is released from the sorbent during the sorbent's regeneration, and the SO_2 may be further processed to yield H_2SO_4, elemental sulfur, or liquid SO_2. No waste is produced in regenerable technology applications (Srivastava and Jozewicz, 2001). Regenerable processes generally have higher costs than once-through technologies; however, regenerable processes might be selected if space or disposal options are restricted and markets for byproducts are available (U.S. EPA, 2003c; Jafarinejad, 2016a).

Both once-through and regenerable technologies can be further classified as wet, semidry, or dry (U.S. EPA, 2003c). Limestone-forced oxidation (LSFO), limestone-inhibited oxidation (LSIO), jet bubbling reactor (JBR), lime process, magnesium-enhanced lime (MEL), dual alkali, and seawater process are examples of wet once-through technologies, whereas lime-spray drying (LSD), furnace-sorbent injection (FSI), limestone injection into the furnace and activation of unreacted calcium (LIFAC) process, economizer sorbent injection (ESI), duct-sorbent injection (DSI), duct-spray drying (DSD), circulating fluidized bed (CFB), and Hypas sorbent injection (HSI) are examples of semidry or dry once-through technologies. In addition, the sodium-sulfite process, magnesium-oxide process, sodium-carbonate process, and amine process are examples of wet regenerable technologies, whereas activated carbon is an example of dry regenerable technologies (Srivastava and Jozewicz, 2001; Jafarinejad, 2016a).

High SO_2-removal efficiencies from 50% up to 98%, probable reusable of reaction products, relatively simple retrofitting, and relatively lower price and availability of reagents are some of the advantages of FGD technologies, whereas high operation and maintenance (O&M) and capital costs, scaling and depositing of wet solids on absorber and downstream equipment, visible plume of wet systems, nonusability for waste gas SO_2 concentrations greater than 2000 ppm, and increase of O&M costs due to disposal of waste products are some of the disadvantages of FGD technologies (U.S. EPA, 2003c; Jafarinejad, 2016a).

5.1.5.1 Wet FGD systems

In wet processes, flue gas is ducted to a spray tower where an aqueous slurry of sorbent is injected from the nozzles into the flue gas. A portion of the water in the slurry is evaporated and the waste-gas stream becomes saturated with water vapor. In the absorber, SO_2 dissolves in the slurry and initiates the reaction with dissolved alkaline particles. The slurry is collected at the bottom of the absorber and treated flue gas is passed through a mist eliminator to remove any entrained slurry droplets before exiting the absorber. The absorber bottom effluent is sent to a reaction tank to complete the SO_2—alkaline reaction and to form a neutral salt. In a once-through system, the spent slurry is dewatered to disposal or used as a byproduct (Fig. 5.8), but in a regenerable system, the spent slurry is recycled back to the absorber (U.S. EPA, 2003c; Jafarinejad, 2016a).

Lime is easier to manage on-site and has control efficiencies up to 95% but is significantly more costly, whereas limestone is very inexpensive but control efficiencies for limestone systems are limited to approximately 90%. There are special sorbents with reactivity-enhancing additives, which provide control efficiencies greater than 95% but are very costly. The volume ratio of reagent slurry to waste gas (L/G) determines the amount of reagent available for reaction with SO_2. A higher L/G can increase the control efficiency and decrease the formation of scale in the absorber due to oxidation of

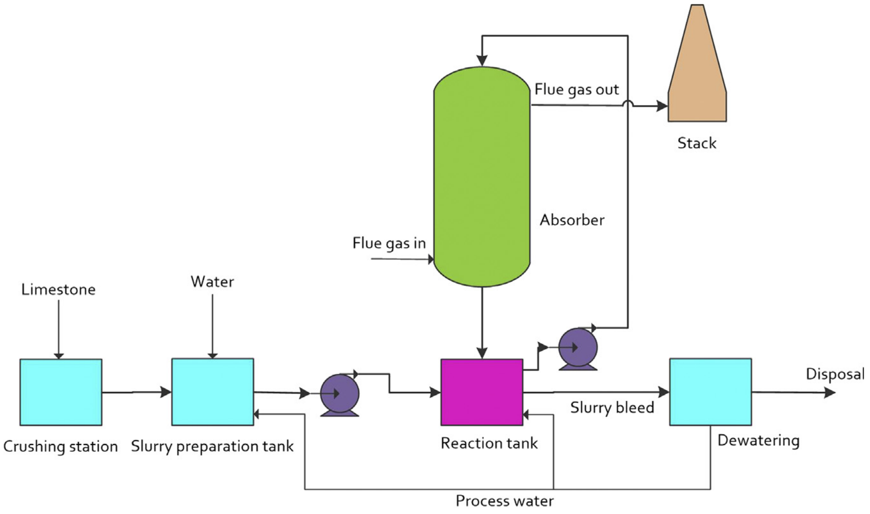

Figure 5.8 Schematic PFD of a limestone-based wet FGD process.
Modified from Srivastava, R.K., Jozewicz, W., 2001. Technical paper: flue gas desulfurization: the state of the art. Journal of Air & Waste Management Association 51, 1676–1688; Jafarinejad, Sh., 2016a. Control and treatment of sulfur compounds specially sulfur oxides (SO_x) emissions from the petroleum industry: a review. Chemistry International 2 (4), 242–253.

SO_2. This parameter is approximately 1:1 for wet scrubbers and is expressed as gallons of slurry/1000 ft^3 of flue gas (U.S. EPA, 2003c; Jafarinejad, 2016a).

5.1.5.2 Semidry FGD Systems

In semidry systems or spray dryers, an aqueous sorbent slurry similar to wet systems is injected, but the slurry has a higher sorbent concentration. The hot flue gas is mixed with the slurry solution, which causes water evaporation from the slurry. The remaining water on the solid sorbent enhances the reaction with SO_2. A dry waste product is generated, which is collected with a standard PM collection device such as a baghouse or ESP. This product can be disposed, sold as a byproduct, or recycled to the slurry (U.S. EPA, 2003c; Jafarinejad, 2016a).

Various calcium- and sodium-based reagents can be used as sorbent but lime is typically injected into spray dry scrubbers. A schematic of an LSD is shown in Fig. 5.9. Rotary atomizers or two-fluid nozzles are utilized to finely disperse lime slurry into the flue gas. A close approach to adiabatic saturation (from 10 to 15°C for flue gas) is required to achieve high SO_2 removal. High SO_2 capture in the spray dryer occurs when the sorbent is still moist (U.S. EPA, 2003c; Srivastava and Jozewicz, 2001; Jafarinejad, 2016a). Lower L/G ratios (approximately 1:3) should be used and flue gas with high SO_2 concentrations or temperatures can reduce the performance of the scrubber. SO_2 control efficiencies for spray dry scrubbers are generally between

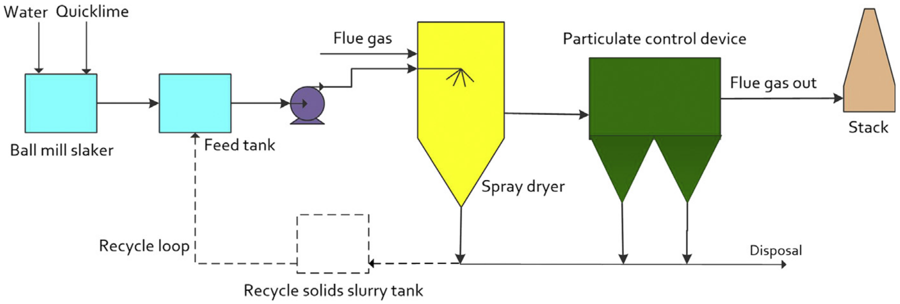

Figure 5.9 Schematic of LSD process.
Modified from Srivastava, R.K., Jozewicz, W., 2001. Technical paper: flue gas desulfurization: the state of the art. Journal of Air & Waste Management Association 51, 1676–1688; Jafarinejad, Sh., 2016a. Control and treatment of sulfur compounds specially sulfur oxides (SO_x) emissions from the petroleum industry: a review. Chemistry International 2 (4), 242–253.

80% and 90%. Large units may require multiple absorber systems. Carbon steel can be used to construct the absorber, and the capital and operating costs for spray dry scrubbers are lower than for wet scrubbers (U.S. EPA, 2003c; Jafarinejad, 2016a).

5.1.5.3 Dry FGD Systems

In dry systems, powdered sorbent is directly injected pneumatically into the furnace (temperature approximately between 950 and 1000°C), the economizer (temperature approximately between 500 and 570°C), or downstream ductwork (temperature approximately between 150 and 180°C) by dry sorbent-injection systems. Injection temperature and residence time are critical parameters for SO_2 removal. Injection needs suitable temperature conditions in order to decompose sorbent into porous solids with high surface area. A dry-waste product is collected with a standard PM collection device such as a baghouse or ESP. The flue gas is generally cooled

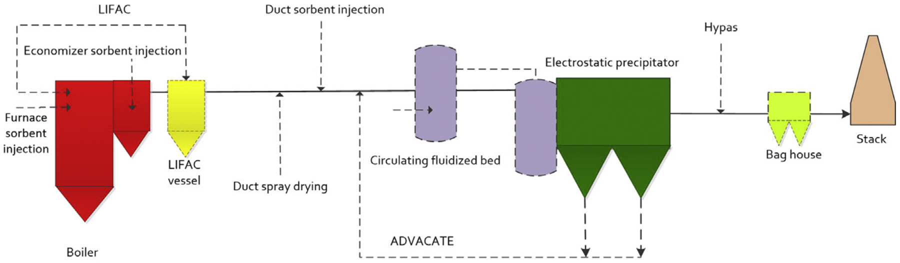

Figure 5.10 Schematic of once-through dry FGD processes involving dry-powder injection and duct-spray drying.
Modified from Srivastava, R.K., Jozewicz, W., 2001. Technical paper: flue gas desulfurization: the state of the art. Journal of Air & Waste Management Association 51, 1676–1688; Jafarinejad, Sh., 2016a. Control and treatment of sulfur compounds specially sulfur oxides (SO_x) emissions from the petroleum industry: a review. Chemistry International 2 (4), 242–253.

prior to the entering PM control device. To enhance SO_2 removal, water can be injected upstream of the absorber (U.S. EPA, 2003c; Srivastava and Jozewicz, 2001; Jafarinejad, 2016a). A schematic of once-through dry FGD processes involving dry-powder injection and duct-spray drying are shown in Fig. 5.10. The flue-gas flow for a plant without FGD is shown by the solid line. Sorbent-injection locations for alternative dry FGD processes with dry-powder injection or duct-spray drying are shown by the broken lines (Srivastava and Jozewicz, 2001; Jafarinejad, 2016a).

Various calcium- and sodium-based reagents and a number of proprietary reagents can be used as sorbent. SO_2 removal by the sorbent can be enhanced by injection of water downstream of the sorbent injection (U.S. EPA, 2003c; Jafarinejad, 2016a).

The capital and annual costs for dry scrubbers are significantly lower than for wet scrubbers. Dry systems are installed easily and are good candidates for retrofit applications. SO_2-removal efficiencies are between 50% and 60% for calcium-based sorbents and up to 80% for sodium-based sorbents injection into the duct (U.S. EPA, 2003c; Srivastava and Jozewicz, 2001; Jafarinejad, 2016a). Dry systems are good SO_2-control technologies for medium-to-small industrial boiler applications, and newer designs of these systems for small industrial boilers have achieved greater than 90% SO_2-removal efficiencies (U.S. EPA, 2003c; Jafarinejad, 2016a).

5.1.6 Vapor Recovery Unit

As noted in Chapter 2, VOCs can be emitted during loading and unloading operations of most volatile products, especially crude oil and lighter products (U.S. EPA, 2006b; European Commission and Joint Research Center, 2013; Barben Analytical, AMETEK, 2015). Vapor recovery units (VRUs) are used when crude oil is pumped into or out of a storage tank and/or lighter products are pumped into or out of a storage tank, tank car, tank truck, or ship. Vapor recovery can be done by various techniques such as:

Absorption: A suitable absorption liquid (e.g., glycols or mineral-oil fractions such as kerosene or reformate) absorbs the vapor molecules. Reheating in a further step is used to desorb the loaded scrubbing solution. The desorbed gases must either be condensed, further processed, incinerated, or reabsorbed in an appropriate stream (e.g., of the product being recovered).

Adsorption: Activate sites on the surface of adsorbent solid materials such as activated carbon (AC) or zeolite can retain the vapor molecules. The adsorbent is periodically regenerated. The resulting desorbate is then absorbed in a circulating stream of the product being recovered in a downstream wash column. Residual gas from the wash column is sent for further treatment.

Membrane gas separation: Selective membranes can be used to separate the vapor/air mixture into a hydrocarbon-enriched phase (permeate), which is subsequently condensed or absorbed, and a hydrocarbon-depleted phase (retentate).

Two-stage refrigeration/condensation: Vapor molecules are condensed and separated as a liquid by passing the vapor/gas mixture through very cold temperatures. As the humidity leads to the icing up of the heat exchanger, a two-stage condensation process providing alternate operation is required.

Hybrid systems: Available VRU techniques can be combined and used for recovery of vapor (European Commission and Joint Research Center, 2013).

Vapor recovery units can provide significant environmental and economic benefits in the petroleum industry. The gases flashed from crude oil or condensate and captured by VRUs can be sold at a profit or used in facility operations. Vapor recovery units also capture hazardous air pollutants and can reduce operator emissions below actionable levels specified in Title V of the Clean Air Act. By capturing methane, VRUs also reduce the emissions of a potent greenhouse gas (U.S. EPA, 2006b).

A VRU installed on crude-oil storage tanks is shown in Fig. 5.11. Hydrocarbon vapors are drawn out of the storage tanks under low-pressure, approximately between 4 ounces and 2 psi, and are first piped to a separator (suction scrubber) to collect any liquids that condense out. Condensed liquid is pumped off the bottom of the scrubber back into the storage tanks. Gas vapor is routed from the top of the scrubber to the compressor, which provides the low-pressure suction for the VRU system. Compressor control is critical in VRU design. To prevent the creation of a vacuum in the top of a tank when oil is withdrawn and the oil level drops, VRUs are equipped with a control pilot to shut down the compressor and permit the back flow of vapors into the tank. The vapors are then metered and removed from the VRU system for pipeline sale or on-site fuel supply (U.S. EPA, 2006b; Barben Analytical, AMETEK, 2015).

5.1.7 Vapor-Destruction Unit

When recovery is not easily feasible, VOC destruction can be done through, e.g., thermal oxidation (incineration) or catalytic oxidation. Safety measures (such as

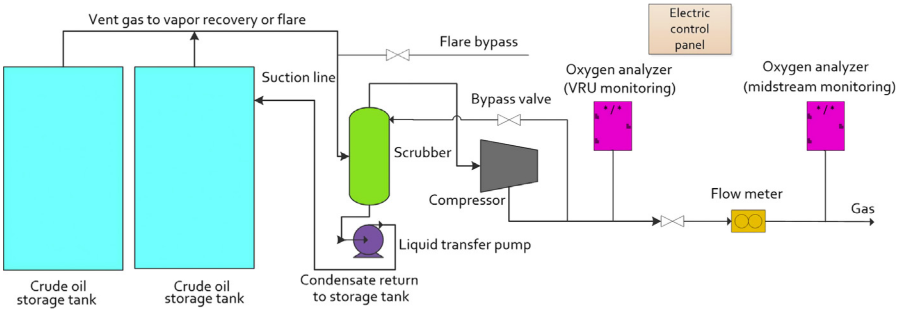

Figure 5.11 Schematic of VRU installed on crude-oil storage tanks.
Modified from United States Environmental Protection Agency (U.S. EPA), 2006b. Installing Vapor Recovery Units on Storage Tanks, Lessons Learned From Natural Gas STAR Partners. United States Environmental Protection Agency Air and Radiation (6202J) 1200 Pennsylvania Ave., NW Washington, DC 20460, October 2006. [Online] Available from: http://www3.epa.gov/gasstar/documents/ll_final_vap.pdf; Barben Analytical, AMETEK, 2015. Application Note, Vapor Recovery Units, Oil & Gas: Upstream. Barben Analytical 5200 Convair Drive, Carson City, NV 89706, USA, AMETEK, Inc., August, 2015. [Online] Available from: http://www.bat4ph.com/files/VRU_AN_RevA.pdf.

flame arrestors) are required to prevent explosion (European Commission and Joint Research Center, 2013).

5.1.7.1 Thermal Oxidation

Oxidizing combustible materials by enhancing the temperature of the material above its auto-ignition point in the presence of oxygen and maintaining it at high temperature for sufficient time to complete combustion to carbon dioxide and water is called thermal oxidation. The rate and efficiency of the combustion process can be affected by time, temperature, turbulence (for mixing), and the availability of oxygen (U.S. EPA, 2003d). This process typically occurs in single-chamber, refractory-lined oxidizers equipped with gas burner and a stack (European Commission and Joint Research Center, 2013). Note that the reaction is exothermic, so the resulting heat could be used to preheat the incoming exhaust (Rusu and Dumitriu, 2003). If gasoline is present, heat-exchanger efficiency is limited and preheat temperatures are maintained below 180°C to reduce ignition risk. Operating temperatures range from 760 to 870°C and residence times are typically 1 s (European Commission and Joint Research Center, 2013).

Thermal oxidation is one of the most positive and proven techniques for destroying VOCs with efficiencies up to 99.9999% possible. Based on actual field-test data, commercial incinerators should generally be run at 870°C with a nominal residence time of 0.75 s to ensure 98% destruction of nonhalogenated organics (U.S. EPA, 2003d). When a specific incinerator is not available for VOC destruction, an existing furnace may be applied to provide the required temperature and residence times (European Commission and Joint Research Center, 2013). Thermal incinerators are often the best choice when high efficiencies are required and the waste gas is above 20% of the lower explosive limit (LEL). The operating costs of this process are relatively high due to supplemental fuel costs, and it is not well suited to streams with highly variable flow and controlling gases containing halogen- or sulfur-containing compounds (U.S. EPA, 2003d).

5.1.7.2 Catalytic Oxidation

Catalytic oxidation typically occurs using a catalyst to enhance the rate of oxidation (the activation-energy barrier is lower using catalyst) by adsorbing the oxygen and the VOCs on its surface. A schematic of a catalytic oxidizer is shown in Fig. 5.12. Using catalyst, the oxidation reaction occurs at lower temperature than required by thermal oxidation, typically ranging from 320 to 540°C (European Commission and Joint Research Center, 2013). In addition, smaller incinerator size, lower fuel requirement, little or no insulation requirement, reduced fire hazards, and reduced flashback problems are some of the advantages of catalytic incinerators over other types of incinerators, but high initial cost, possible catalyst poisoning, particulate removal requirement before entering the incinerator, and probable requirement to dispose spent catalyst are some of the disadvantages of these incinerators (U.S. EPA, 2003e).

In a catalytic incinerator, a first preheating step (electrically or with postcombustion gas in a recuperative heat exchanger) is done to reach a temperature necessary to

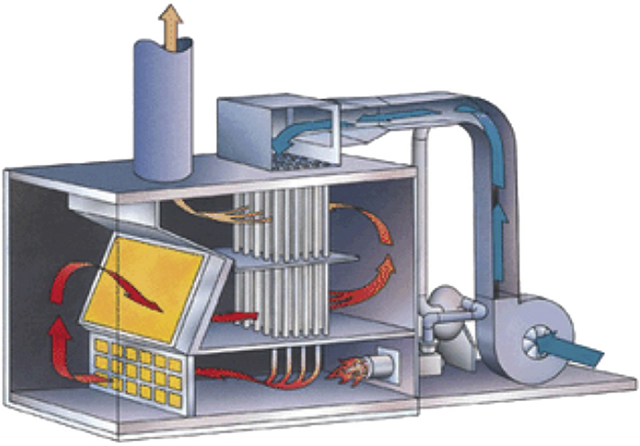

Figure 5.12 Schematic of a catalytic oxidizer made by Anguil Environmental Systems, Inc. (Rusu and Dumitriu, 2003).

initiate the VOC catalytic oxidation. An oxidation step takes place when the gas is passed through a bed of solid catalysts (European Commission and Joint Research Center, 2013; U.S. EPA, 2003e). Oxygen and VOC diffuse and are adsorbed onto the catalyst active sites on the surface of the catalyst where oxidation occurs, and the products are desorbed from these sites by the gas and transported by diffusion back into the gas stream. Note that PM can coat the catalyst so that the catalyst active sites are prevented from aiding in the oxidation of pollutants, which is called blinding (U.S. EPA, 2003e).

Volatile organic compound composition and concentration, operating temperature, oxygen concentration, catalyst characteristics, and space velocity (the volumetric flow of gas divided by the volume of the catalyst bed) can affect VOC destruction efficiency. With increasing space velocity, VOC destruction efficiency decreases, whereas temperature enhancing can increase it. Using large catalyst volumes and/or higher temperatures, higher destruction efficiencies in the range of 98−99% can be achieved (U.S. EPA, 2003e).

Noble metals and oxides of transition metals are two types of catalysts used in VOC oxidation. Catalysts such as the noble metals platinum (Pt) and palladium (Pd) are the most commonly used catalysts for oxidative removal of VOCs from gaseous stream (Papaefthimiou et al., 1997; Rusu and Dumitriu, 2003). Pt and Pd are frequently alloyed with other metals such as ruthenium (Ru), rhodium (Rh), osmium (Os), and iridium (Ir) and supported on oxides such as Al_2O_3 and SiO_2. VOC destruction using transition metals supported on different materials were reviewed by Rusu and Dumitriu (2003). Metal oxides are an alternative to noble metals as catalysts for VOCs oxidation, although they can have the same catalytic activity but at higher temperature. The most active oxides have a p-semiconductor nature and the most frequently used ones are the oxides of silver (Ag), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), and cobalt (Co) (Rusu and Dumitriu, 2003). Catalysts such as chromia/alumina, cobalt oxide, and copper oxide/manganese oxide have been applied for oxidation of gases containing chlorinated compounds, whereas platinum-based catalysts have been used for oxidation of sulfur-containing VOCs, although they are rapidly deactivated by the presence of chlorine (U.S. EPA, 2003e).

Both fixed-bed and fluidized-bed catalytic incinerators can be used for VOC destruction. Fixed-bed catalytic incinerators may use a monolith catalyst (widespread use) or a packed-bed catalyst. Very high mass transfer rates and high bedside heat transfer are the advantages of fluidized-bed catalytic incinerators. These incinerators are more tolerant of PM in the gas stream than either fixed-bed or monolithic catalysts due to the constant abrasion of the fluidized catalyst pellets. Gradual loss of catalyst by attrition is a disadvantage of fluidized bed systems, but attrition-resistant catalysts have been developed to overcome this problem (U.S. EPA, 2003e).

5.1.8 Scrubbing Systems

Scrubbing systems are a diverse group of air-pollution control devices that can be applied to remove particles and/or gases from industrial waste streams. Scrubbers are referred to as pollution-control devices that use liquid to scrub unwanted pollutants from a gas stream and/or inject a dry reagent or slurry into a dirty exhaust stream to scrub out acid gases (Joseph and Beachler, 1998). Scrubbing systems can be divided into dry or semidry scrubbing systems and wet scrubbing systems (Joseph and Beachler, 1998; Boamah et al., 2012; European Commission and Joint Research Center, 2013).

5.1.8.1 Dry or Semidry Scrubbing Systems

Dry or semidry scrubbing systems are used to remove acid gases such as SO_2 and HCL from waste-gas streams. These systems apply a powder sorbent material, either calcium- or sodium-based alkaline regent, to react with the acid gases in the flue gas and produce a solid salt that can be removed in a particulate control device such as a bag filter or ESP. These scrubbers do not require a stack steam plume or wastewater handling/disposal. In dry scrubbing systems or dry sorbent injection systems, the dry-powder sorbent material is injected directly into the ductwork or reaction chamber, whereas in semidry scrubbing systems or spray dryer absorbers (SDAs), the sorbent material is first mixed with water and then injected into a spray-drying vessel where all the liquid is totally evaporated by cooling the gas stream while the sorbent reacts with the acid gases to form solid salts that are removed by the particulate control device (Joseph and Beachler, 1998). The removal efficiency of the scrubbing system can generally be improved by the use of a reaction tower (European Commission and Joint Research Center, 2013). These systems have been discussed in detail in Sections 5.1.5.2 and 5.1.5.3.

5.1.8.2 Wet Scrubbing Systems

Wet scrubbing systems are devices that utilize a suitable liquid (water or alkaline solution) to remove particulate and/or gaseous pollutants (such as SO_2) from a process waste-gas stream (Joseph and Beachler, 1998; Weaver, 2006; Air & Waste Management Association (A&WMA), 2007; Faustine, 2008; European Commission and Joint

Research Center, 2013). A wet scrubbing system may consist of ductwork and a fan system, saturation chamber, scrubbing vessel, mist eliminator, pumping and possible recycle system, spent scrubbing liquid treatment and/or reuse system, and exhaust stack. Wet scrubbers generate wastewater stream that must be treated or reused in the plant. Since the gas stream is saturated with liquid and a steam plume is created, a mist eliminator or entrainment separator is also often an integral part of any wet scrubbing system to remove and/or recycle the scrubbing liquid in addition to providing additional pollutant removal (Joseph and Beachler, 1998).

As noted, wet scrubbing systems can be classified as once-through or regenerable, depending on how the sorbent is treated after it has sorbed pollutant (Srivastava and Jozewicz, 2001; U.S. EPA, 2003c). These systems were discussed in Section 5.1.5.

Based on the contact method, there are several configurations of wet scrubbers (European Commission and Joint Research Center, 2013). All designs attempt to prepare good liquid-to-pollutant contact in order to obtain high removal efficiencies up to 95% (Joseph and Beachler, 1998). Spray tower or spray chamber, cyclonic spray tower, dynamic scrubber, tray tower, venturi scrubber, orifice scrubber, packed-bed

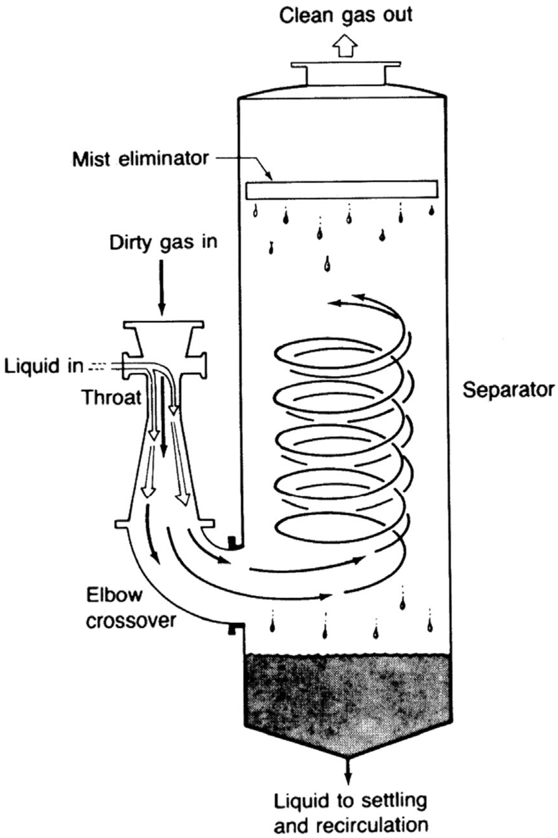

Figure 5.13 Venturi scrubber with cyclone separator and mist eliminator (A&WMA, 2007).

or packed tower, condensation scrubber, and charged scrubber are the types of wet scrubbers (Mussatti and Hemmer, 2002). A venturi scrubber with cyclone separator and mist eliminator is shown in Fig. 5.13.

Wet scrubbing systems have SO_x-removal efficiencies in the range 85–98% (European Commission and Joint Research Center, 2013). Collection efficiencies for wet scrubbers vary with the particle-size distribution of the waste-gas stream and generally decrease as the PM size decreases. Collection efficiencies also vary with scrubber type. Collection efficiencies range from greater than 99% for venturi scrubbers to 40–60% (or lower) for simple spray towers (Mussatti and Hemmer, 2002). The actual performance of a given scrubber generally depends on the specific dust characteristics, distribution and loading, gas velocity and pressure drop, the amount of scrubbing liquid or liquid-to-gas (L/G) ratio, waste-gas flow rate, temperature and humidity, droplet size, and residence time (Mussatti and Hemmer, 2002; MikroPol, 2015).

Removal efficiencies for a spray tower can be 90% for particles larger than 5 μm, from 60% to 80% for particles from 3 to 5 μm in diameter, and less than 50% for particles below 3 μm. Collection efficiencies for cyclonic spray towers are as high as 95% for particles greater than 5 μm and from 60% to 75% for submicron particles. Collection efficiencies for dynamic scrubbers are similar to those for cyclonic spray towers. Tray towers do not effectively remove submicron particles, but these towers can remove particles larger than 5 μm with efficiencies of 97%. Venturi scrubbers are more expensive than spray-tower, cyclonic, or tray-tower scrubbers, but can remove fine PM with higher efficiencies. These scrubbers are the most efficient of the wet scrubbers, and high gas velocities and turbulence in the venturi throat result in high collection efficiencies, ranging from 70% to 99% for particles larger than 1 μm in diameter and greater than 50% for submicron particles. Removal efficiencies for orifice scrubbers range from 80% to 99% for PM over 2 μm in diameter (Mussatti and Hemmer, 2002). Packed towers are most often used for gaseous pollutant absorption rather than PM removal, because when they are used with heavy, particulate-laden gas, they can be plugged by PM (Mussatti and Hemmer, 2002; A&WMA, 2007). Condensation scrubbers can effectively remove fine PM, and the collection efficiencies of these scrubbers are greater than 99% (Mussatti and Hemmer, 2002).

A wide range of design variations including several hybrids of technologies can be found in commercially available wet scrubbers. Venturi scrubbers with multiple throats, a combination of wet scrubber with other types of particulate removal such as a baghouse or ESP (Mussatti and Hemmer, 2002), various two-stage wet scrubber designs such as a venturi scrubber with a packed-bed section (Fig. 5.14), multiventuri inlet with a dynamic scrubber, etc., are examples of these developments (MikroPul, 2015).

5.1.9 Electrostatic Precipitator

Electrostatic precipitator (ESP) is a technique to remove particles in a gas stream using an electrostatic force (Turner et al., 1999; Mizuno, 2000; Boamah et al., 2012). It has been widely used in utility boilers, cement kilns, engines, in cleaning of indoor air in

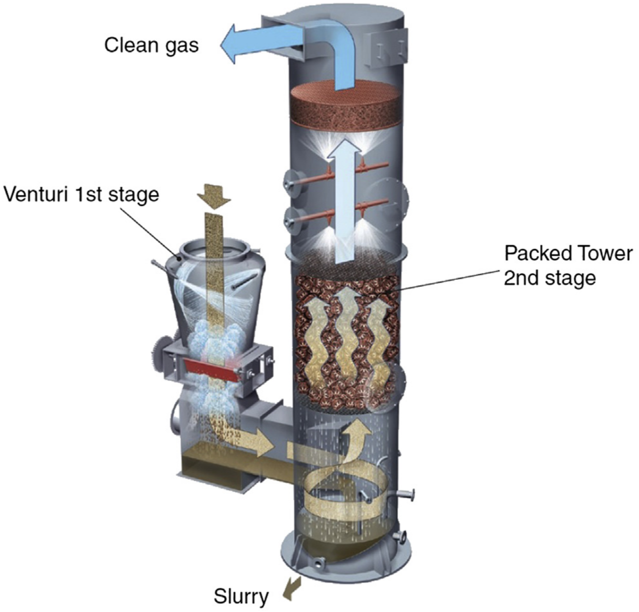

Figure 5.14 Two-stage wet scrubber design including a venturi scrubber with a packed-bed section (MikroPul, 2015).

houses, offices, hospitals, and factories for food processing, etc. (Mizuno, 2000). In the petroleum industry, ESPs can be applied in FCC units, FGD processes, power plants, and incinerators. It may not be applicable for some PM with high electric resistance. They can usually be installed in new and existing plants (European Commission and Joint Research Center, 2013).

A schematic of an ESP is shown in Fig. 5.15. An ESP may consist of baffles for distributing gas flow, discharge and collection electrodes (typically a group of large metal plates suspended vertically and parallel to each other), a particle clean-out system and collection hoppers, etc. The discharge electrodes are given a negative electric charge, whereas the plates are grounded and thus become positively charged. A high DC voltage system is applied to the discharge electrodes to charge the particles, which are then attracted to oppositely charged collection electrodes on which they become trapped (Boamah et al., 2012). The power supplies (consist of a step-up transformer, high-voltage rectifiers, and sometimes filter capacitors) for the ESP convert the industrial AC voltage (220–480 V) to pulsating DV voltage in the range of 20,000–100,000 V as needed. The particles are given an electrical charge by forcing them to pass through a corona, a region in which gaseous ions flow (Turner et al., 1999). These charged particles are moved toward the collecting electrode by a Coulomb force, and are collected on that electrode (Mizuno, 2000). The precipitated particles can be removed from the electrodes mechanically, usually by rapping (the impulse or vibrating type) in dry ESP, or by water wash in wet ESP (Boamah et al., 2012; European Commission and Joint Research Center, 2013).

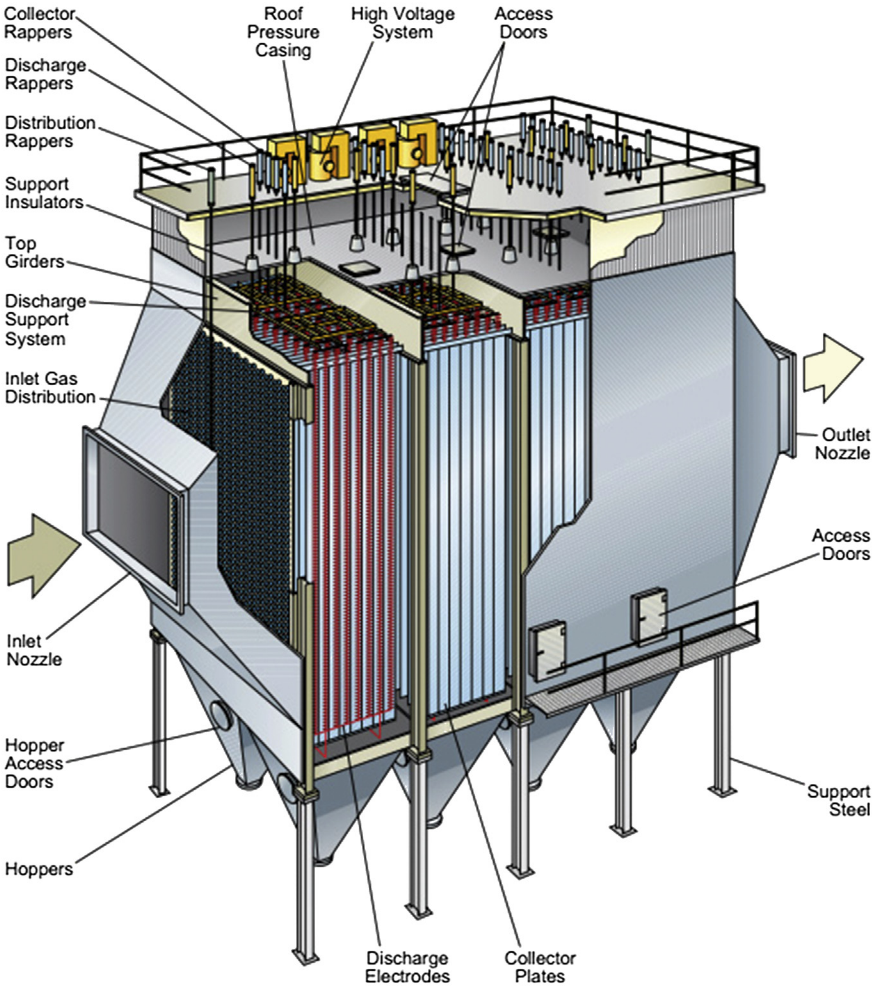

Figure 5.15 Schematic of an electrostatic precipitator (Courtesy of The Babcock & Wilcox Company).

There are various types of industrial ESP according to their applications. Electrostatic precipitators can be classified as cylindrical type or plate type based on the shape of the collecting electrodes; vertical gas flow and horizontal gas-flow based on the direction of gas flow; one stage and two stage based on electrodes geometry; and dry and wet-type based on whether water is used (Mizuno, 2000). Plate-wire ESPs can be used in a wide variety of industrial applications such as coal-fired boilers, petroleum refining catalytic cracking units, etc. (Turner et al., 1999). The wet type ESP can be applied for dust with extremely low or high resistivity, or to fulfill a requirement of very low emission (i.e., <1 mg/m^3), and can remove soluble pollutants such as NO_2, SO_2, HCl, and NH_3. A wet-type ESP can also be applied after a dry-type ESP to decrease particle emission (Mizuno, 2000).

Electrostatic precipitators can be operated with high collection efficiency usually greater than 99% and a low-pressure drop. Submicron particles with diameter <1 μm can also be collected effectively. The pressure drop is normally less than 1000 Pa, and this advantage of ESP results in low operation cost. The collection efficiency, η, of ESP is given by Deutsch as follows:

$$\eta = 1 - \exp(-w_e f) = 1 - \exp\left(\frac{-w_e A}{Q}\right) \tag{5.14}$$

where $f = A/Q$ is the specific collection area (s/m), A denotes the area of the collecting electrode (m^2), Q is the gas-flow rate (m^3/s), and w_e denotes the migration velocity (m/s). The particles are migrated toward the collecting electrode with a velocity w_e as follows:

$$w_e = \frac{qEC_m}{3\pi\mu d_p} \tag{5.15}$$

where q is the particle charge (C), E denotes the electric field (V/m), μ is the viscosity (Pa.s), d_p denotes the diameter of particle (m), and C_m is the Cunningham correction factor, which can be obtained from the following formula:

$$C_m = 1 + 2.54\left(\frac{\lambda}{d_p}\right) + 0.8\left(\frac{\lambda}{d_p}\right)\exp\left(\frac{-0.55 d_p}{\lambda}\right) \tag{5.16}$$

where λ is the mean-free path of gas molecules (m), which can be calculated as follows:

$$\lambda = 6.61 \times 10^{-8}\left(\frac{T}{293}\right)\left(\frac{101,300}{P}\right) \tag{5.17}$$

where T denotes the temperature (K) and P is the pressure (Pa). For air at atmospheric pressure and room temperature (300 K), λ is approximately 0.07 μm. For particles ≤1 μm, the correction factor C_m is necessary to account for viscosity.

For the collection efficiency, the following relationship based on the voltage (V) and the current (I) is often found in many industrial ESPs, with the value $n \approx 2$:

$$\eta = V^n I \tag{5.18}$$

Higher collection efficiency can usually be obtained when the ESP is operated with the maximum available voltage (Mizuno, 2000). The collection efficiency is affected by many factors, such as the geometry of the electrodes, the characteristics of dust particles, the number of fields, residence time (size), upstream particles removal devices, etc. (Mizuno, 2000; European Commission and Joint Research Center, 2013), and there are many reports of modifying the theoretical collection efficiency (Mizuno, 2000).

In the petroleum industry, three-field ESPs and four-field ESPs are commonly used at FCC units. Electrostatic precipitators can be applied on dry mode or with ammonia injection to improve the particle collection. For the calcining of green coke, the ESP collection efficiency may be decreased, which is attributed to the difficulty of coke particles to be electrically charged (European Commission and Joint Research Center, 2013).

Example 5.1

In an ESP, assume that the gas-flow rate, the particle diameter, the electric field, the particle charge, the viscosity, the temperature, and the pressure are 35 m^3/s, 0.5 μm, 60,000 V/m, 1.6×10^{-18} C, 1.81×10^{-5} kg/ms, 293 K, and 10,1300 Pa, respectively. Also suppose that each plate has the dimensions 5 m by 3 m and the collection efficiency of the ESP must be 99%. What is the required number of plates?

Solution: The mean-free path of the gas molecules can be calculated using Eq. (5.17):

$$\lambda = 6.61 \times 10^{-8}\left(\frac{293}{293}\right)\left(\frac{101,300}{101,300}\right) = 6.61 \times 10^{-8}\ (\mathrm{m})$$

The Cunningham correction factor can be obtained from Eq. (5.16):

$$\begin{aligned} C_m &= 1 + 2.54\left(\frac{6.61 \times 10^{-8}}{5 \times 10^{-7}}\right) + 0.8\left(\frac{6.61 \times 10^{-8}}{5 \times 10^{-7}}\right)\exp\left(\frac{-0.55 \times 5 \times 10^{-7}}{6.61 \times 10^{-8}}\right) \\ &= 1.333 \end{aligned}$$

The migration velocity is calculated using Eq. (5.15):

$$w_e = \frac{1.6 \times 10^{-18} \times 60,000 \times 1.333}{3\pi \times 1.81 \times 10^{-5} \times 5 \times 10^{-7}} = 1.5 \times 10^{-3}\ (\mathrm{m/s})$$

According to Eq. (5.14), for an efficiency of 99%, the area of the collecting electrodes is 107,453.97 m^2, which was obtained as follows:

$$0.99 = 1 - \exp\left(\frac{-0.0015A}{35}\right)$$

Since a single plate gives a collecting area of $2 \times 5 \times 3 = 30\ m^2$ (counting both sides) and based on this fact each of the two terminal plates offers only a single collecting side, it is necessary to add 1 to the number of plates; thus the required number of plates can be obtained as follows:

$$n = \frac{107,453.97}{30} + 1 = 3581.79 + 1 = 3583$$

5.1.10 Multistage Cyclone Separators

Cyclones, which are also referred to as cyclone separators, cyclone collectors, centrifugal separators, and inertial separators (U.S. EPA, 2003f), have been utilized since the late 1800s to remove dust from industrial gas streams (Dirgo and Leith, 1985). They are typically used for the removal of PM greater than 10 μm, but special cyclones with a high collection efficiency can be effective at removing PM less than or equal to 10 μm and less than or equal to 2.5 μm. In some applications, many small cyclones can operate in parallel, which is called a multicyclone or multitube cyclone system (U.S. EPA, 2003f).

Cyclones are important precleaner devices for more expensive final control devices such as fabric filters or ESPs. In addition for pollution-control purposes, cyclones are applied in many process applications such as recovering and recycling of food products, facilitation of catalyst recycling and PM removal from the fluid-cracking process, etc. (U.S. EPA, 2003f).

Many different types of cyclones have been built, and depending on how the gas stream is introduced into the device and how the collected dust is discharged, they can generally be classified into four types: tangential inlet, axial discharge; axial inlet, axial discharge; tangential inlet, peripheral discharge; and axial inlet, peripheral discharge (U.S. EPA, 2003f). The tangential inlet, axial discharge is most often used for industrial gas cleaning (Dirgo and Leith, 1985; U.S. EPA, 2003f).

A typical tangential inlet cyclone with the various symbols indicated is shown in Fig. 5.16. The Stairmand-type high efficiency cyclone is one example of a standard

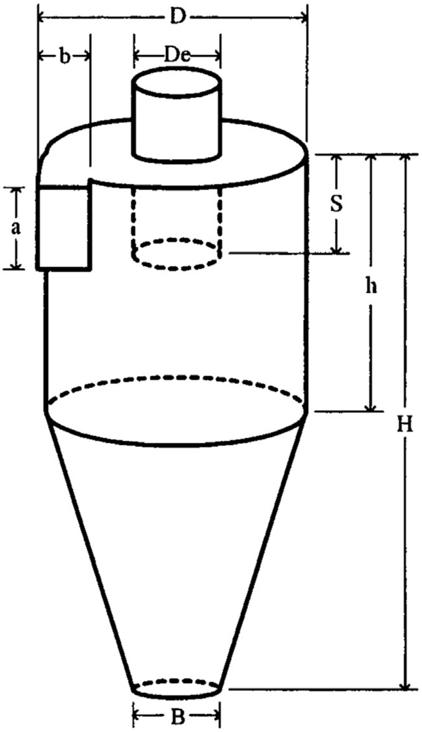

Figure 5.16 Typical tangential inlet cyclone (Kuo and Tsai, 2001).

cyclone design that is commonly used (Dirgo and Leith, 1985; Kuo and Tsai, 2001). The relative dimensions of a Stairmand-type high efficiency cyclone are $a = S = D_e = 0.5D$, $b = 0.2D$, $h = 1.5D$, $H = 4D$, and $B = 0.375D$, where D is cyclone diameter; a denotes the height of the cyclone inlet; b is the width of cyclone inlet; D_e denotes the diameter of the cyclone exit tube; S is the length of the vortex finder or outlet duct length; h denotes the height of the cyclone cylinder; H is the total height of the cyclone; and B denotes the diameter of the bottom of the cyclone or dust outlet diameter (Kuo and Tsai, 2001).

In a cyclone, the swirling motion creates centrifugal forces that cause the particles to be thrown against the walls of the cylinder and slowed by friction with the wall surface and then dropped into a conical dust hopper below. The gas left in the middle of the cylinder after the dust particles have been removed moves upward and exits the cylinder. The accumulated particles are periodically removed from the hopper for disposal (A&WMA, 2007; Boamah et al., 2012).

Cyclone-collection efficiency, η, is defined as the fraction of particles of a given size that is retained by the cyclone (Dirgo and Leith, 1985), and the particle diameter corresponding to 50% collection efficiency is called the cutoff diameter of the cyclone, $d_{p_{50}}$ (Kuo and Tsai, 2001). The theories developed to predict efficiency differ greatly in complexity. The operating parameters of the system; particle diameter and density, and gas velocity and viscosity; and cyclone dimensions and geometry have been considered in all, most, and few theories to predict cyclone performance, respectively. Some theories use all eight cyclone dimensions, while others include as few as three (Dirgo and Leith, 1985). Some of the available equations for theoretical collection efficiency and cutoff diameter of the cyclone are given in Table 5.2.

The control-efficiency range for conventional cyclones is estimated to be 70–90% for PM greater than 10 μm, 30–90% for PM less than or equal to 10 μm, and 0–40% for PM less than or equal to 2.5 μm. The collection efficiency of multicyclones is reported to be 80–95% for PM equal to 5 μm (U.S. EPA, 2003f).

In refineries, multicyclones and ESPs are employed in FCC units and in heavy oil and residue cracker units. Third-stage separator (TSS) is a cyclonic collection device or system installed following the two stages of cyclones which common configuration of it consists of a single vessel containing many conventional cyclones or improved swirl-tube technology. The particle concentration and size distribution of the catalyst fines downstream of the regenerator internal cyclones mainly affect the performance (European Commission and Joint Research Center, 2013).

5.1.11 Prevention or Reduction of Emissions From Flaring

Flaring refers to the burning of combustible gases, while venting refers to the release of combustible gases into the atmosphere. Flares are most commonly situated around a gasoline plant, refinery, or production well (Indriani, 2005) and are used for safety and environmental control of discharges of undesired or excess combustibles and for surges of gases in emergency situations, upsets, unplanned events, or unanticipated equipment failure. Low-pressure flare, high-pressure flare, steam-assisted flare, air-assisted flare, gas-assisted flare, and high-pressure water injection flare are the types

Table 5.2 Some of the Available Equations for Theoretical Collection Efficiency and Cutoff Diameter of the Cyclone (Dirgo and Leith, 1985; Kuo and Tsai, 2001)

Theory	Equation for the Theoretical Collection Efficiency	Equation for the Cutoff Diameter	Parameters
Lapple	$d_{p_{50}} = \sqrt{\dfrac{9\mu b}{2\pi\rho_p v_i C N_t}}$		$d_{p_{50}}$, The cutoff diameter (m); d_p, particle diameter (m); μ, gas viscosity (Pa s); b, cyclone inlet width (m); ρ_p, particle density (kg/m^3); v_i, gas inlet velocity (m/s); C, slip-correction factor of the particle corresponding to $d_{p_{50}}$; $N_t = tv_i/\pi$; D, number of turns; and t, residence time that equals to the volume of the cyclone divided by the volumetric flow rate (Q).
Theodore and DePaola	$\eta = \dfrac{1}{1 + \left(d_{p_{50}}/d_p\right)^2}$	$d_{p_{50}} = \sqrt{\dfrac{9\mu b}{2\pi\rho_p v_i C N_t}}$	
Stairmand		$d_{p_{50}} = \sqrt{\dfrac{9\mu Q}{\pi\rho_p v_{t\max} C(H - S)}}$	$v_{t\max}$, maximum tangential velocity; H, total height of cyclone; and S, length of vortex finder or outlet duct length.
Barth	$\eta = \dfrac{1}{1+\left(\dfrac{\pi h^* v_t^2 \rho_p d_p^2}{9\mu Q}\right)^{-3.2}}$	$d_{p_{50}} = \sqrt{\dfrac{9\mu Q}{\pi\rho_p v_{t\max} C(H - S)}}$	v_t, tangential gas velocity at the edge of the central core; and h^*, height of the central core.
Leith and Licht	$\eta = 1 - \exp\left[- 2(C_g\psi)^{\frac{1}{2n+2}}\right]$		C_g, dimension factor of a cyclone; $\psi = C\rho_p d_p^2 v_i \big/ 18\mu D$, impaction parameter; and n, vortex exponent.
Dietz	$\eta = 1 - \left[K_0 - \sqrt{\left(K_1^2 + K_2\right)}\right] \times \exp\left[\dfrac{-\pi\rho_p d_p^2 v_i(2S - a)}{18\mu ab}\right]$		The subscripted K terms are functions of particle and gas properties as well as cyclone dimensions.
Li and Wang	$\eta = 1 - \exp\left[\dfrac{-2\pi\lambda(S + L)}{a}\right]$		λ, a characteristic value; and $L = 2.3D_e\sqrt[3]{\frac{D^2}{ab}}$, The natural length of cyclone.
Iozia and Leith	$\eta = \dfrac{1}{1 + \left(d_{p_{50}}/d_p\right)^{\beta}}$	$d_{p_{50}} = \sqrt{\dfrac{9\mu Q}{\pi\rho_p v_{t\max}\chi_c}}$	$v_{t\max} = 6.1v_i\left(\frac{ab}{D^2}\right)^{0.61}\left(\frac{D_e}{D}\right)^{-0.74}\left(\frac{H}{D}\right)^{-0.33}$, The maximum tangential velocity; χ_c, length of the central core; and β can be calculated from $\ln\beta = 0.62 - 0.87\ln\left(d_{p_{50}}\right) + 521 \times \ln\left(\frac{ab}{D^2}\right) + 1.05\left[\ln\left(\frac{ab}{D^2}\right)\right]^2$.

of flare systems (European Commission and Joint Research Center, 2013). Flaring generates air emissions and presents potential fire hazards and impacts to visibility (U.S. Forest Service, 2011) and also leads to burning of potential valuable products. Therefore its use must be restricted and the amount of flared gas decreased as much as possible due to environmental and energy efficiency issues (European Commission and Joint Research Center, 2013).

According to Indriani (2005) and the European Commission and Joint Research Center (2013), emissions from flaring can be prevented and reduced by the following methods:

- Correct designing of plants, which can include sufficient flare-gas recovery-system capacity, application of high-integrity relief valves, and other measures to use flaring only as a safety system for other than normal operations (startup, shutdown, emergency);
- Plant management such as organizational and control measures to reduce the case of flaring by, e.g., balancing RFG system, or using advanced process control;
- Working on designing parameters of flares, which include height, pressure, assistance by steam, air or gas, type of flare tips, etc., to enable smokeless and reliable operations and to ensure efficient combustion of excess gases during flaring from nonroutine operations;
- Monitoring and reporting, which includes continuous monitoring (measurements of gas flow and estimations of other parameters) of gas sent to flaring and associated parameters of combustion (e.g., mixture flow gas and heat content, ratio of assistance, velocity, purge gas flow rate, pollutant emissions) (European Commission and Joint Research Center, 2013);
- The use of gas reinjection, which includes the reinjection of natural gas into an underground reservoir in order to increase the pressure within the reservoir and thus induce the flow of crude oil;
- The use of natural-gas liquid (NGLs) recovery;
- The use of gas to pipeline, which includes capturing and transporting of gas by pipeline to end users;
- The use of gas-to-liquids (GTL) systems, which includes production of liquid fuels from a gas that can be carried out by both direct conversion of gas (methane) and indirect conversion of synthesis gas (syngas) using Fischer-Tropsch (F-T) synthesis or methanol; and
- Fuel switch such as utilization of gas as an alternative fuel in power-generation facilities (Indriani, 2005).

5.2 Control of Odor

As noted in Chapter 2 Section 2.3.4, odors in a petroleum refinery are mainly created by sulfur compounds (e.g., hydrogen sulfide, mercaptans, sulfides, disulfides), nitrogen compounds (e.g., ammonia, amines), and hydrocarbons (e.g., aromatics) (European Commission and Joint Research Center, 2013; Jafarinejad, 2015b, 2016b). The techniques that can be used to reduce or control the odor generation include:

- The use of nitrate-based products in septic water areas (e.g., storage tanks, sewage systems, oil/water separators) in order to replace bacteria feedstock and to favor the development of denitrificative bacteria, which will both reduce added nitrates in nitrogen and existing hydrogen sulfide in sulfates;
- Reduction of VOCs and odor generation by covering some units of the wastewater treatment plant (WWTP) (e.g., CPI and API separators) with closed sealed covers;

- Reduction of odors from water-buffer tanks by maintaining the smallest possible surface area of oil and water in contact with air by using a fixed-roof tank or a floating-roof tank (European Commission and Joint Research Center, 2013; Jafarinejad, 2016b);
- Reduction and control of fugitive emissions;
- Control of flares and prevention or reduction of emissions from them;
- Control of fuel quality;
- Use of scrubbing systems for odorous gases; and
- Use of incineration systems for odorous gases (Orszulik, 2008; Jafarinejad, 2016b).

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Treatment of Oily Wastewater

6

6.1 Overview of Wastewaters and Management of Them in the Petroleum Industry

Large quantities of effluents containing oil, water, and sludge can be produced from the activities and processes in the petroleum industry. Draining of these effluents not only pollutes the environment but also reduces the yield of oil and water (Zhong et al., 2003; Jafarinejad, 2014a,b, 2015a,b,c,d). As discussed in Chapter 2, the major sources of aqueous waste from E&P activities are produced water, drilling fluids, cuttings, well-treatment chemicals, cooling water, process, wash and drainage water, spills and leakage, and sewerage, sanitary, and domestic wastewater (E&P Forum/UNEP, 1997). In refineries, due to use of relatively large volumes of water, four types of wastewater—cooling water, process water, stormwater (i.e., surface water runoff), and sanitary wastewater—can be produced (U.S. EPA, 1995; IPIECA, 2010). Most cooling water is recycled over and over and typically does not come into direct contact with process oil streams and therefore contains fewer contaminants than process wastewater, but cooling water also may contain some oil contamination due to leaks in the process equipment. Water used in processing operations also accounts for a significant portion of the total wastewater. Process wastewater arises from desalting crude oil, steam-stripping operations, pump-gland cooling, product fractionator reflux drum drains, and boiler blowdown. Because process water often comes into direct contact with oil, it is usually highly contaminated. Surface water runoff is intermittent and contains constituents from spills, leaks in equipment, and any materials that may have collected in drains. It also consists of water coming from crude and product storage-tank roof drains (U.S. EPA, 1995). Wastewater generation in petrochemical plants is from process operations (e.g., vapor condensation, process water and spent caustic in crackers, and aromatic plants), cooling tower blow down, pump and compressor cooling, paved utility area drains, cooling water, and stormwater runoff (IL & FS Ecosmart Limited Hyderabad, 2010; MIGA, 2004). Liquid-tank bottoms (European Commission and Joint Research Center, 2013), leaking liquids from tanks and pipelines, and ballast water from transporting vessels and specially tankers (Cholakov, 2009) can be the sources of wastewater from the storage, transportation, distribution, and marketing sectors.

Water management in the petroleum industry can be done by finding an appropriate beneficial use for the water or by selecting appropriate water disposal options. However, beneficial uses and waste options are highly dependent on water quality and may need water treatment prior to use or disposal. Treatment of wastewater may be required in order to meet beneficial use specifications or to meet predisposal regulatory limits (Arthur et al., 2005). Improved and optimized water management

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in the petroleum industry can potentially result in reductions in the volume and cost of raw water used in its operations; probable reductions in wastewater flow or contaminant load or both, which may result in lower wastewater-treatment operating and maintenance costs; and reduction in the mass of contaminants in the treated effluent, thus improving the quality of a wastewater discharge and ultimately the environmental impact of the petroleum industry's discharge (IPIECA, 2010).

As discussed in Chapter 3, use of produced water or process water as wash water, use of tank bottoms, emulsions, heavy hydrocarbons, and hydrocarbon-bearing soil for road oil, road mix, or asphalt (that have density and metals content consistent with road oil or mixes), recycling drilling muds, recovering oil from produced water and drilling muds (E&P Forum, 1993), recycling lubrication and cooling water used by pumps, avoid unwanted materials such as rig wash, stormwater runoff, etc., entering fluid system during drilling (Reis, 1996), recovery of oil from tank bottoms via centrifuging and filtering (E&P Forum, 1993; European Commission and Joint Research Center, 2013), reuse of rinse waters, using of recycled water for desalter, separate keeping of the relatively clean rainwater runoff from wastewater in the process streams, minimizing the number of storage tanks that my lead to reduce tank bottom solids and decanted wastewater (Speight, 2005), reuse of wastewater generated by the overhead reflux drum as a desalter wash water, reuse of spent caustic within the refinery, recycling cooling waters, recycling, in multistage desalters, part of the brine effluent water of second stage desalters to the first stage, minimizing the wash water quantity, recycling of monoethanolamine-solutions, solvent recovery, use of stripped sourwater and sourwater as desalter wash water (stripped sourwater only) or as wash water in overhead FCC main column to reduce the process water flow to the effluent-treatment plant (European Commission and Joint Research Center, 2013), etc., are examples of practices to manage wastewaters prior to treatment in the petroleum industry.

6.2 Wastewater Characterization

Crude oil contains various organic and inorganic compounds including salts, suspended solids, and water-soluble metals (Ishak et al., 2012). Oily wastewater generated in the petroleum industry is complex in composition (Uan, 2013; Jafarinejad, 2015d). Composition of wastewater depends on the complexity of the petroleum industry process, but in general, compounds in wastewater can include free, dispersed, emulsified, and dissolved oil and dissolved formation minerals (Ishak et al., 2012). The main contaminants in wastewaters from petroleum industry sectors such as refineries are oils and greases, which can exist in four forms: free (droplets with diameters larger than 150 μm), dispersed (droplets in the range of 20—150 μm), emulsified (droplets smaller than 20 μm), and dissolved oil (not in the form of droplets) (Pombo et al., 2011; European Commission and Joint Research Center, 2013). Oil is a mixture of hydrocarbons [benzene, toluene, ethylbenzene, and xylene (BTEX), polyaromatic hydrocarbons (PAHs), and phenol], while dissolved formation minerals are inorganic compounds, which include anions and cations including heavy metals (Ishak et al., 2012).

The typical characteristics of an oily wastewater can include oil and grease (O&G), chemical oxygen demand (COD), soluble chemical oxygen demand (SCOD), biochemical oxygen demand (BOD), soluble biochemical oxygen demand (SBOD), TSS, TDS, BTEX, phenols, ammonium nitrogen (NH_4-N), total Kjeldahl nitrogen (TKN), total phosphorus (P_{total}), S^{2-}, hardness, turbidity, alkalinity, pH, conductivity, SO_4^{2-}, F^-, Cl^-, heavy metals, etc. (Nacheva, 2011; Ishak et al., 2012). The characteristics of oil in wastewater and oily wastewater from the petroleum industry can vary significantly depending on the characteristics of the crude oil and the process units in the petroleum industry (Schultz, 2007).

6.3 Selection of Oil/Water Separation and Treatment Technologies

Oil in the petroleum industry wastewater stream may exist in one or more of three forms:

1. Free oil: This is floating oil and refers to oil in the form of separate oil globules of sufficient size (droplets with diameters larger than 150 μm) that can occur as a result of buoyancy force to the top of the water (Mohr et al., 1998). This type of oil can be removed by either skimming the surface in the skim tank or by gravity separation, e.g., in the American Petroleum Institute (API) separator (Yokogawa Corporation of America, 2008).
2. Emulsified oil: This refers to oil in the form of much smaller droplets or globules, with a diameter of 20 μm or less, which form stable suspension in the water. For design purposes, emulsified oil may also be referred to as emulsions in which the droplets are so small that they will not rise at a rate that allows a practical size separation device. According to the API, gravity cannot separate a true emulsion regardless of how long a true oil–water emulsion stands under quiescent conditions. According to Mohr et al. (1998), it is possible to design enhanced gravity separators to treat waters containing this type of oil for small flow rates (Mohr et al., 1998). This type of oil can be separated from the wastewater by chemical addition to lower the pH followed by addition of dissolved oxygen or nitrogen to remove the emulsified oils as they break free from the wastewater (Yokogawa Corporation of America, 2008).
3. Dissolved oil: This is not in the form of droplets and is a true molecular solution within the water, which may not be removed by gravity separation. It can be removed by biological treatment, adsorption by activated carbon or other adsorbents, or absorbents (Mohr et al., 1998; Yokogawa Corporation of America, 2008).

The oil-droplet size distribution in petroleum industry wastewater is crucial for determining the proper oil–water separation system and its efficiency. According to Benyahia et al. (2006), API separator, corrugated plate interceptor (CPI) separator, upflow sand filters, induced gas flotation (IGF), dissolved air flotation (DAF), and filters are effective at removing oil-droplet sizes approximately larger than 150, 40–270, 2–270, 10–100, 5–100, and 5–30 μm, respectively. According to Arthur et al. (2005), the minimum size of particles (droplets) can also be removed by API separator, CPI separator, IGF (no flocculants), IGF (with flocculants), hydrocyclone, mesh coalescer, media filter, centrifuge, and membrane filter are 150, 40, 25, 3–5, 10–15, 5, 5, 2, and 0.01 μm, respectively.

In addition, understanding the sources of oil in wastewater, the characteristics of the oil, the concentration of the oil and suspended solids in the raw wastewater, the presence of oil-wetted solids, the design limitations of the various types of oil–water separation equipment, temperature that impacts the type and size of selected oil–water separator, temperature and pH that impact material selection for oil–water separation equipment, the impact of oil on downstream-treatment equipment, and the treatment objectives can be critical to the proper selection and design of oil–water separation systems. The ultimate wastewater-treatment discharge requirements for oil concentration and other parameters such as BOD, COD, TSS, TKN, ammonia, etc., are important in selecting an oil–water-separation system. For example, if the effluent permit needs BOD or COD removal and installation of a biological-treatment system is planned, this may impact the selection of the oil–water separator (to ensure excessive oil does not enter the biological-treatment step), which is typically used as a primary treatment step prior to biological treatment (Schultz, 2007).

Treatment of petroleum industry wastewater such as refinery wastewater for discharge into water bodies is different from treatment of it for reuse in other petroleum industry (refinery) units. Wastewater treatment for reuse requires more advanced treatment systems, because the quality requirements are higher (Pombo et al., 2011).

6.4 Wastewater Treatment

Oily wastewater treatment is necessary before discharging it into the environment; otherwise, its high mineral and organic content may severely pollute coastal waters, estuaries, rivers, groundwater, the seashore, and soil (Uan, 2013). Oily wastewater pollution can affect drinking water and groundwater resources and crop production, endanger aquatic resources and human health, pollute the atmosphere, and destruct the natural landscape; even oil-burner safety issues can arise due to coalescence (Yu et al., 2013). According to the World Bank Group (1998), some of the emissions levels that should be achieved are presented in Table 6.1. Effluent requirements are for direct discharge to surface waters. Discharge to an offsite wastewater-treatment plant (WWTP) should meet applicable pretreatment requirements.

Oily wastewater treatment can typically be classified as:

- Process wastewater pretreatment
- Primary treatment
- Secondary treatment
- Tertiary treatment or polishing (U.S. EPA, 1995; Benyahia et al., 2006; IPIECA, 2010; European Commission and Joint Research Center, 2013; Goldblatt et al., 2014; Jafarinejad, 2015d).

After primary treatment, the wastewater can be discharged to a publicly owned treatment works (POTWs) or undergo secondary treatment before being discharged directly to surface waters under a national pollution discharge elimination system

Table 6.1 **Maximum Effluent Level From the Petroleum Industry (World Bank Group, 1998)**

Parameter	Maximum Value
BOD (mg/L)	30
COD (mg/L)	150
TSS (mg/L)	30
Oil and grease (mg/L)	10
pH	6–9
Chromium	
Hexavalent (mg/L)	0.1
Total (mg/L)	0.5
Lead (mg/L)	0.1
Phenol (mg/L)	0.5
Benzene (mg/L)	0.05
Benzo(a)pyrene (mg/L)	0.05
Sulfide (mg/L)	1
Nitrogen (total) (mg/L)	10 (this parameter may be up to 40 mg/L in processes that include hydrogenation).
Temperature increase	≤3°C (the effluent should result in a temperature increase of no more than 3°C at the edge of the zone where initial mixing and dilution take place; where the zone is not defined, use 100 m from the point of discharge, provided there are no sensitive ecosystems within this range).

(NPDES) permit (U.S. EPA, 1995). Most petroleum refineries in the world have facilities for primary and secondary treatment, but some have tertiary treatment facilities (Goldblatt et al., 2014).

Wastewater-treatment plants can be a significant source of air emissions. Air releases arise from fugitive emissions from the numerous tanks, ponds, and sewer system drains (US EPA, 1995) (e.g., API, CPI, DAF units, water buffer tanks, and biotreaters). The generation of volatile organic compounds (VOCs) and odors can be further decreased by covering some of these units with closed and sealed covers. Cover vents can be collected and treated with an appropriate off-gas treatment system (e.g., biofilter, activated carbon absorber, incinerator, and thermal oxidizer) or can be reinjected into the aeration basin. Covering the CPI and API can reduce VOC emissions from oil separators to 3 g/m^3. In a water-buffer tank, by using a fixed-roof tank or a floating-roof tank, the emission of VOC and other odorous compounds can be reduced by 80–90% compared to an open system. When vented emissions from the fixed-roof tank are collected and routed to an appropriate off-gas treatment system, this ratio reaches 99.9% or more (European Commission and Joint Research Center, 2013). In WWTPs, solid wastes are also generated in the form of sludges from a number of treatment units such as API separators or other gravitational separation techniques, etc. (U.S. EPA, 1995).

6.4.1 Process Wastewater Pretreatment

In some cases the wastewater generated from some of the units of the petroleum industry can be pretreated prior to discharge to wastewater treatment (IPIECA, 2010). Some of the practices that are used in the petroleum industry as pretreatment include:

- Neutralization of wastewater to adjust the pH of the wastewater to within the desired range for discharge or to establish proper conditions before an oxidation-reduction chemical reaction, for precipitation of heavy metals as hydroxides, for proper clarification, and for better adsorption;
- Emulsion breaking of certain oil–water mixtures using chemicals such as coagulants, flocculants, and wetting agents in a tank with agitator(s) and skimmers (Orszulik, 2008);
- Desalter oil–water separation using a separation tank (e.g., a floating-roof tank in order to control VOC emissions, which typically have a residence time of a day or so to provide equalization, upset buffering, etc.) and sending skimmed oil to refinery slopes, water to WWTP, and solids to the sludge treatment plant or the coker unit (IPIECA, 2010);
- Reduction and recovery of hydrocarbons from wastewater at source such as nitrogen or air stripping for benzene recovery from wastewater, liquid–liquid extraction from wastewaters for phenol extraction from wastewater using a countercurrent extraction column, high-pressure wet air oxidation (>20 barg) to convert sulfur-containing substances to sulfates, and amines and nitriles to molecular nitrogen, low-pressure oxidation (<20 barg) (European Commission and Joint Research Center, 2013); and
- Sourwater stripping (IPIECA, 2010; European Commission and Joint Research Center, 2013).

The crude unit, vacuum unit, catalytic cracker unit, delayed coker unit, visbreaker unit, hydrotreater units, hydrocracker unit, and sulfur plant are process units that produce sourwater. Sourwater from these units can be stripped in a sourwater stripper (SWS) (IPIECA, 2010). Most SWSs are single stage, but the two-stage SWS can be used to reach much lower H_2S and NH_3 concentrations in the stripped water. Fig. 6.1 shows a simplified process flow diagram (PFD) of a two-stage SWS. In a single-stage SWS, the collection vessel provides both hold-up for feed and acts as a settler, where oil separation occurs. From this vessel, sourwater is pumped via a feed/effluent exchanger, to the top of the stripper column. The sourwater is counter currently stripped in the column by steam, either injected live or generated in a reboiler. This column is usually refluxed to decrease the water content in the sour gas. The operating pressure in the column varies from 0.5 to 1.2 barg depending on the destination of the off-gas (SRU, or an incinerator, or the sour flare). When necessary pH control is used to maximize either H_2S or NH_3 removal. The two-stage SWS differs from the single-stage SWS. The first column operates at a lower pH (6) and,

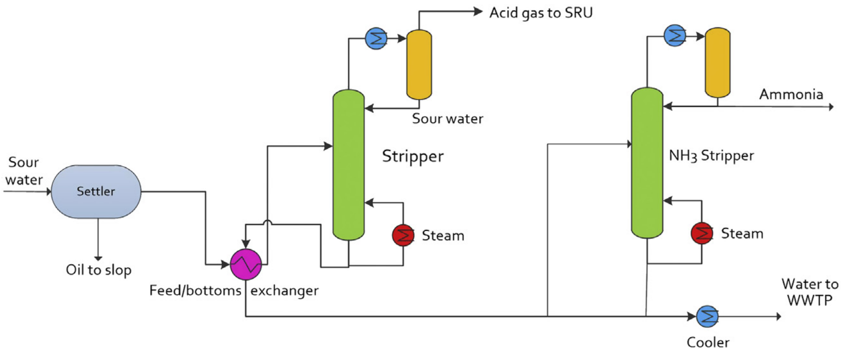

Figure 6.1 Simplified process flow diagram of a two-stage sourwater stripper (SWS). Modified from European Commission, Joint Research Center, 2013. Best Available Techniques (BAT) Reference Document for the Refining of Mineral Oil and Gas, Industrial Emissions Directive 2010/75/EU (Integrated Pollution Prevention and Control). Joint Research Center, Institute for Prospective Technological Studies Sustainable Production and Consumption Unit European IPPC Bureau.

eventually, at a higher pressure (9 barg) to remove H_2S over the top and NH_3/water via the bottom, and the second stage operates at a higher pH (10), to remove the NH_3 over the top, and a stripped water stream at the bottom (European Commission and Joint Research Center, 2013). The design and operation of the SWS can highly affect the composition of the stripped sourwater. Table 6.2 lists the expected level of contaminants in stripped sourwater by a single-stage SWS (IPIECA, 2010). In the two-stage SWS, the overall H_2S and NH_3 recovery will be 98% and 95%, respectively, which is associated with residual concentrations in the stripped waters in the respective range 0.1−1.0 and 1−10 mg/L (European Commission and Joint Research Center, 2013).

Table 6.2 **Expected Level of Contaminants in Stripped Sourwater by a Single-Stage SWS (IPIECA, 2010)**

Contaminant	Expected Concentration (mg/L)
COD	600−1200
Free hydrocarbons	<10
Suspended solids	<10
Phenol	Up to 200
Benzene	0
Sulfides	<10
Ammonia	<100

6.4.2 Primary Treatment

Primary wastewater treatment includes separation of oil, water, and solids in two stages. During the first stage, API separators, or CPI separators, or parallel plate interceptor (PPI) separators, or tilted plate interceptor (TPI) separators, or hydrocyclone separators, or buffer and/or equalization tanks can be used (U.S. EPA, 1995; Schultz, 2007; European Commission and Joint Research Center, 2013). Wastewater moves very slowly through the separator allowing free oil to float to the surface and be skimmed off and solids to settle to the bottom and be scraped off to a sludge-collecting hopper. Physical or chemical methods are used in the second stage to separate emulsified oils from the wastewater (U.S. EPA, 1995). Physical methods may include the use of a series of settling ponds with long retention time, or the use of DAF, or dissolved gas flotation (DGF), or induced air flotation (IAF), or IGF, or sand filtration (U.S. EPA, 1995; Benyahia et al., 2006; Schultz, 2007; European Commission and Joint Research Center, 2013). Chemicals, such as ferric hydroxide or aluminum hydroxide, can be applied to coagulate impurities into a froth or sludge that can be more easily skimmed off the top (U.S. EPA, 1995). The effluent from primary treatment facilities should contain less than 20 mg/L of (insoluble) O&G. Most of the soluble organic matter usually remains with the effluent (Goldblatt et al., 2014). API separator sludge, primary treatment sludge, sludges from other gravitational separation techniques, float from DAF units, and wastes from settling ponds are some of the wastes associated with the primary treatment of wastewater in the petroleum industry that may be considered hazardous (U.S. EPA, 1995).

6.4.2.1 First Stage of Primary Treatment

The first-stage oil—water separators are designed to remove large quantities of free oil and heavy suspended solids from wastewater and are usually used when oil concentrations in the raw wastewater exceed approximately 500 mg/L. All of these separators work based on Stokes' law, where wastewater components of different density (specific gravity) tend to separate from each other (Schultz, 2007). The droplet rise velocity can be calculated from Stokes' law:

$$V_r = \frac{gd^2(\rho_d - \rho_c)}{18\mu} \tag{6.1}$$

where V_r is the droplet rise velocity (cm/s), g denotes the gravitational constant (980 cm/s^2), μ is the absolute viscosity of continuous fluid (water) (poise), d denotes the diameter of droplet (cm), ρ_d is the density of particle (droplet) (gr/cm^3), and ρ_c is the density of continuous fluid (gr/cm^3). If droplets are spherical, flow is laminar, both horizontally and vertically, and droplets are the same size, the droplet rise velocity calculation using Stokes' law will be valid. As Stokes' law implies the viscosity of the continuous liquid, the density difference between the continuous liquid and the droplet and the droplet size are the most important variables in the calculation of the rise velocity and therefore the size of the separator required. Stokes' equation was originally developed to describe the motion of solid particles falling in a liquid, so droplet rise velocity is a negative number (Mohr et al., 1998).

Decantation and coalescence are two mechanisms of oil—water separation by gravity (Pombo et al., 2011). The API separator is a long and narrow tank designed for gravity separation of oil and TSS from wastewater. A typical API separator is shown in Fig. 6.2. This separator has the ability to remove large concentrations of suspended solids (influent TSS up to 20,000 mg/L) (Schultz, 2007). Retention time, tank design, oil properties, operating conditions, and the added flocculants or coagulants can affect the performance of API gravity separators (Arthur et al., 2005). The effluent oil concentration can be in the range of 100—300 mg/L. The API separator is by far the most common type of oil—water separator found in the petroleum industry, especially in refineries and petrochemical plants, due to its ability to handle wide variations in flow and load, as well as high concentrations of suspended solids, but this separator typically requires the largest plot area and is the most expensive oil—water gravity separators. The API separator can also be covered to control odor and VOC emissions (Schultz, 2007), but it cannot usually remove emulsified or dissolved oil. High pH at the API separators can stabilize emulsions and for pH reduction at these separators, spent caustic streams should be either neutralized or routed directly to equalization (IPIECA, 2010).

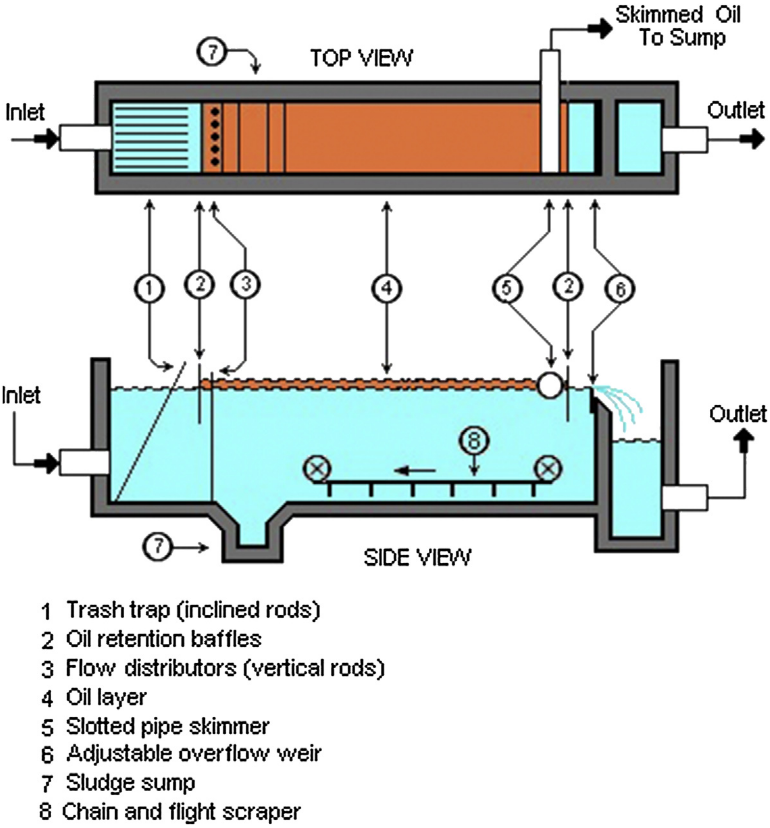

Figure 6.2 Typical API separator (Robinson, 2013).

The internal plates used in CPIs, PPIs, and TPIs reduce the residence time required to achieve the targeted oil—water separation and consequently reduces the required separation system and plot space compared to APIs (European Commission and Joint Research Center, 2013). These separators are very effective in oil—water (two-phase) separation, but they are less effective when solids (a third phase) are present in wastewater (IPIECA, 2010). For example, in CPIs, influent oil and TSS concentration are 500—10,000 mg/L and less than 100 mg/L, respectively, and effluent oil concentration can be in the range of 100—300 mg/L. While CPIs are smaller and less expensive than the more common API separator, operating problems (fouling and plugging) associated with high TSS in the influent has restricted their use in the petroleum refining industry. In the petrochemical industry, where influent TSS may be substantially lower, they can be applied with great success (Schultz, 2007).

The hydrocyclone separator also works on the concept of Stokes' law for removal of oil from wastewater, but it requires a pressurized feed of at least 35 psi to create a high-energy cyclonic spinning action in the hydrocyclone tube bundle in the unit. The specific gravity differences between water and oil are accentuated by the centrifugal forces created by the spinning action of the wastewater to allow oil removal in a very small footprint. These separators are usually applied in oil fields due to available pressurized feed from crude production separators. Because pumping oily wastewater to the required hydrocyclone feed pressure can break up oil particles into fine particles and can cause severe oil emulsions the hydrocyclone will not remove, these separators are not commonly used in petroleum refineries and petrochemical plants (Schultz, 2007).

6.4.2.2 Second Stage of Primary Treatment

The second stage of primary treatment is designed to remove small oil droplets and suspended solids, oil emulsions, and oil wetted solids that have not been separated in the first stage of primary treatment. The most common technique is gas flotation. Air or nitrogen is usually used as the flotation gas, but nitrogen can be preferred for safety reasons when the units are covered for VOC and/or odor control (Schultz, 2007). Dissolved gas flotation and IGF are the same techniques as DAF and IAF, but they use gases instead of air to reduce risks (European Commission and Joint Research Center, 2013). Air—gas flotation systems use air—gas bubbles attached to the oil droplets and suspended solids to aid flotation of the oil and suspended solids. The air—gas bubbles reduce the net specific gravity of the oil air—gas composite droplets, thereby increasing the rise velocity of the droplets (Mohr et al., 1998). To assure maximum effectiveness in these systems, the addition of a coagulant (e.g., $FeSO_4$ or $FeCl_3$) to break oil emulsions and the addition of a flocculent (e.g., a polyelectrolyte) to build small oil and suspended solids particles into larger particles, which are easier to float from the wastewater, is usually required (Schultz, 2007). In these systems, both oil and suspended solids are skimmed off the top (U.S. EPA, 1995).

A typical DAF unit is shown in Fig. 6.3. Dissolved gas flotation or DGF units can usually process higher levels of influent oil, up to 500 mg/L or higher, with much higher oil-removal efficiencies, up to and in excess of 95% removal (effluent oil concentration is 10—30 mg/L). In these systems, influent TSS can be less than

Figure 6.3 Typical dissolved air flotation (DAF) unit.
Pan America Environmental, Inc., 2013. Dissolved Air Flotation systems, The DAF Series Dissolved Air Flotation Systems are Designed to Remove Petroleum Products, FOG, TSS, BOD, COD and Other Contaminants in a Wide Variety of Industries & Applications, DAF-8 through DAF-600. Pan America Environmental, Inc., Wauconda, IL, USA. [Online] Available from: http://panamenv.com/wp-content/uploads/DAF-DISSOLVED-AIR-FLOTATION-2013.pdf.

500 mg/L and they are very effective at removing suspended solids from wastewater, achieving removal efficiencies of up to, and in excess of, 95% (effluent TSS is less than 25 mg/L). Sludge and float volume can be 0.1% to 0.5% of forward flow. These systems are very responsive to flow and load changes and can be fitted with an integral flash mix and flocculation tank, which improves the removal efficiency of these wastewater components (Schultz, 2007).

A typical IAF unit is shown in Fig. 6.4. Induced air flotation or IGF units are the least expensive flotation systems available. In these systems, influent oil concentration and

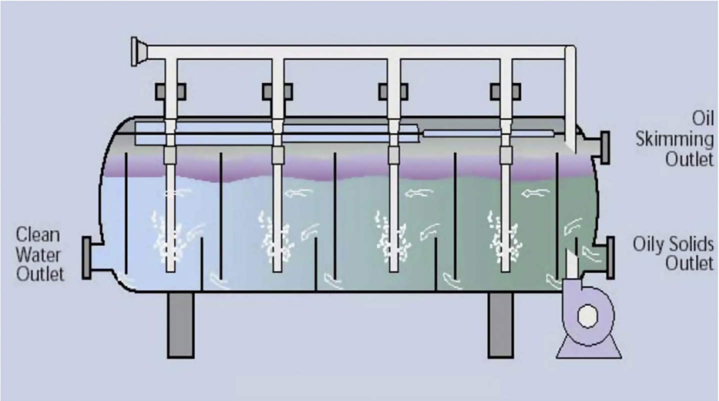

Figure 6.4 Typical induced air flotation (IAF) unit (Arthur et al., 2005).

effluent oil concentration are less than 300 and 20−75 mg/L, respectively. Float volume is also 1−10% of the forward flow. If oil and TSS levels are low and there is little variability in wastewater flow and load, these units can provide acceptable performance. Induced air flotation or IGF units are not designed for TSS removal. These units are used in some petroleum refineries, but DAF or DGF are very common in petroleum refineries and petrochemical plants due to their robust design and ability to provide high-quality effluent even under highly variable flows and loads (Schultz, 2007).

Clarifiers and sand filtration (or dual media) can be alternative processes to flotation (European Commission and Joint Research Center, 2013). Sand and anthracite media can be used in media filters. Dual-media filters consist of a layer of anthracite over sand. Anthracite traps the larger particles and sand traps the finer solids (IPIECA, 2010). Media filters can typically remove oil particles down to the 2 to 5 μm range and influent oil, influent TSS, and effluent oil concentrations can be less than 50 mg/L, less than 50−100 mg/L, and less than 20 mg/L, respectively. Oil can plug and foul the media (Schultz, 2007) and the filter is periodically backwashed to remove the trapped particles (IPIECA, 2010). An air scour can be used during the backwash cycle to remove some of the accumulated oil, but its use is not preferred in petrochemical plants because it can be a significant source of VOCs and may require a VOC control deice. Crushed walnut shells can also be used as the filtering media in walnut shell filters, which have a very high affinity for attracting and capturing oil particles (Schultz, 2007).

6.4.3 Secondary Treatment

In secondary treatment, dissolved oil and other organic pollutants are sometimes consumed by microorganisms (U.S. EPA, 1995). Microorganisms (naturally occurring, commercial, specific groups, and acclimatized sewage sludge) oxidize organic matter into simple products (CO_2, H_2O, and CH_4) under aerobic, anaerobic, or semi-aerobic conditions. A C:N:P ratio (100:5:1) is adequate for microorganisms to grow (Ishak et al., 2012). Biological-treatment processes can generally be classified into two categories:

- Suspended growth processes such as activated sludge (AS) process, sequencing batch reactors (SBRs), continuous stirred tank bioreactor (CSTB), membrane bioreactors (MBRs), and aerated lagoons; and
- Attached growth processes such as trickling filters (TFs), fluidized bed bioreactor (FBB), and rotating biological contactor (RBC) (EPA, 1997; IPIECA, 2010; Ishak et al., 2012).

Biological treatment may require the addition of oxygen through a number of different techniques, including AS process, trickling filters, RBCs, etc. Biomass waste can be generated in secondary treatment, which is typically treated anaerobically and then dewatered (U.S. EPA, 1995).

In recent years, hybrid systems have also been developed to overcome a lack of conventional systems, increase oil-removal efficiencies, and improve effluent quality. These systems are a combination of suspended and attached growth processes in the same reactor such as the combination of AS process and submerged biofilters (fixed-bed biofilters) (Ishak et al., 2012).

In some cases when deep nitrogen removal is required and a petroleum industry site (e.g., a refinery site) is required to meet tight ammonia or nitrogen limits, application of either a nitrification (by the use of nitrifying bacteria) or a combined nitrification/denitrification step are options (IPIECA, 2010; European Commission and Joint Research Center, 2013).

6.4.3.1 Suspended Growth Processes

In suspended growth processes, microorganisms are thoroughly mixed with the organics in the liquid and maintained in suspension mode within the liquid. Organic constituents are used as food by microorganisms for their growth and the active biomass can be formed (IPIECA, 2010; Ishak et al., 2012). The AS process is one of the most commonly used suspended growth processes in oily wastewater-treatment plants (IPIECA, 2010; Pombo et al., 2011; Ishak et al., 2012; European Commission and Joint Research Center, 2013). Conventional (plug flow), complete mix, and SBR are typical AS processes used in wastewater treatment (Ishak et al., 2012).

6.4.3.1.1 Activated Sludge Process

As Fig. 6.5 shows, the activated sludge (AS) process is carried out in two main compartments: the aeration tank and the secondary settling tank or clarifier (Pombo et al., 2011). Wastewater is introduced into an aerated tank of microorganisms, which are collectively referred to as activated sludge or mixed liquor. Submerged diffused or surface mechanical aeration system or combinations thereof can be used for aeration, which maintain the activated sludge in suspension (EPA, 1997). The organic material in wastewater is used

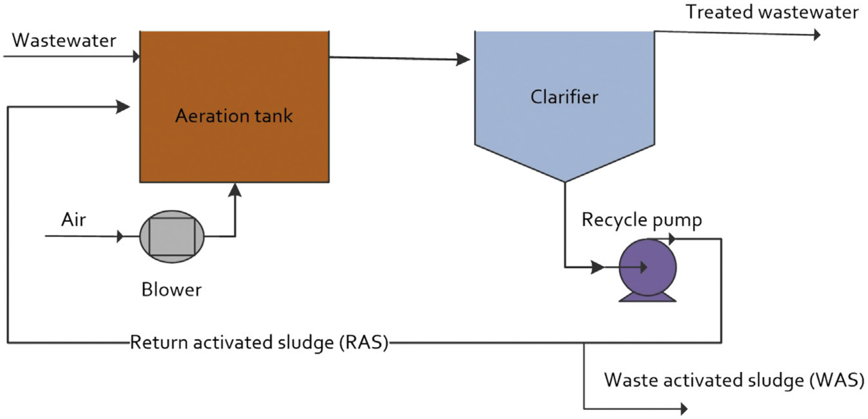

Figure 6.5 Schematic of an activated sludge (AS) process.
Modified from Environmental Protection Agency (EPA), 1997. Waste Water Treatment Manuals, Primary, Secondary and Tertiary Treatment. Environmental Protection Agency, Ardcavan, Wexford, Ireland.

as a carbon source and energy by microorganisms for the microbial growth, which is converted into cell tissue, water, and oxidized products such as CO_2 (IPIECA, 2010). Following a period of contact between the wastewater and the activated sludge, the outflow is separated from the sludge in a clarifier. To maintain the desired microbiological mass in the aeration tank, sludge is returned to the aeration tank (return-activated sludge (RAS)), while excess due to biological growth is periodically or continuously wasted (waste-activated sludge (WAS)) to increase sedimentation efficiency in the clarifier (EPA, 1997). Biomass in the mixed liquor is referred to as mixed-liquor suspended solid (MLSS), whereas the organic portion of the biomass is called the mixed-liquor volatile suspended solids (MLVSS) (IPIECA, 2010). The efficiency of treatment can be affected by the concentration at which the mixed liquor is maintained in the aeration (EPA, 1997).

6.4.3.1.2 Activated Sludge Treatment With Powdered Activated Carbon

Activated carbon (both powdered activated carbon (PAC) and granular activated carbon (GAC)) has been applied for a long time in water and wastewater treatment due to its large surface area for adsorption (Tri, 2002; Jafarinejad, 2015e). Powdered activated carbon has a diameter of less than 200 mesh (Tri, 2002). Activated sludge treatment with PAC is similar to the conventional AS process, but in this process, PAC is added into the aeration tank or mixed liquor. The removal of contaminants is achieved and enhanced by a combination of biodegradation and adsorption (Tri, 2002; IPIECA, 2010). A schematic of a typical powdered activated carbon treatment (PACT) process is shown in Fig. 6.6. Most of the PAC is recycled with the activated sludge, but the system requires a continuous makeup of fresh carbon.

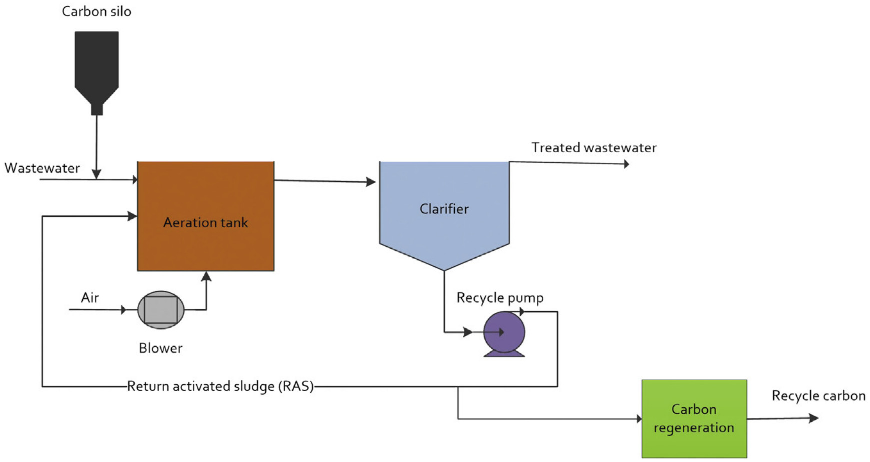

Figure 6.6 Schematic of a typical powdered activated carbon treatment (PACT) process. Modified from IPIECA, 2010. Petroleum Refining Water/Wastewater Use and Management. IPIECA Operations Best Practice Series, London, United Kingdom.

The PACT process is generally used for petroleum industry wastewater in those cases where stringent standards must be met for certain contaminants (IPIECA, 2010). According to Tri (2002), the PACT process could generally remove organic compounds more efficiently than what would be expected from either biodegradation or adsorption alone. The dosage of PAC and the mixed-liquor-PAC-suspended-solids concentration are related to the sludge age as follows:

$$X_p = \frac{X_i \theta_c}{\theta} \tag{6.2}$$

where X_p is the equilibrium PAC MLSS content (mg/L), X_i denotes the PAC dosage (mg/L), θ_c is the solid retention time (d), and θ denotes the hydraulic retention time (HRT) (d). Carbon dosage typically ranges from 20 to 200 mg/L. The organic removal per unit of carbon is increased with higher sludge ages, which improves process efficiency (Tri, 2002).

6.4.3.1.3 Sequencing Batch Reactors

The sequencing batch reactors (SBR) is a fill-and-draw AS system for both municipal and industrial wastewater treatment that aeration, sedimentation, and clarification can all be achieved using a single-batch reactor. It operates without a clarifier and in this system, wastewater is added to a single-batch reactor, treated to remove undesirable components, and then discharged. To optimize the performance of the system, two or more batch reactors are used in a predetermined sequence of operations. A typical sequencing batch reactor (SBR) system is shown in Fig. 6.7. The operation of an SBR is based on a fill-and-draw principle, which consists of five steps: fill, react, settle, draw, and idle. These steps can be altered for different operational applications. Sequencing batch reactors are typically used at flow rates of 219 L/s (5 MGD) or less. The more sophisticated operations needed at larger SBR plants tend to discourage the use of these plants for large flow rates. The SBR technology is particularly attractive for treating smaller wastewater flows. The majority of plants were designed at wastewater flow rates of less than 22 L/s (0.5 MGD) (Metcalf and Eddy, 1991; U.S. EPA, 1999; Gurtekin, 2014).

The SBR system is used in some refineries, but it has limited application in petroleum industry wastewater treatment (IPIECA, 2010). Leong et al. (2011) studied the sludge characteristics and treatment performances of the SBR in the removal of varying influent phenol concentrations. The results showed that almost complete phenol removal can be achieved with a sufficiently long react step, and a change of sludge morphology does not affect the phenol-removal efficiency in the SBR with increase phenol loading. However, with increasing influent phenol concentration to 400 mg/L, microfloc prevailed, resulting in poor sludge settleability, and deteriorated quality of effluent with discharged suspended solids. Ishak et al. (2012) concluded that activity and biological performance in treatment plants may be affected by toxic compounds such as phenol that leads to constant drop in bacterial count during the acclimatization period.

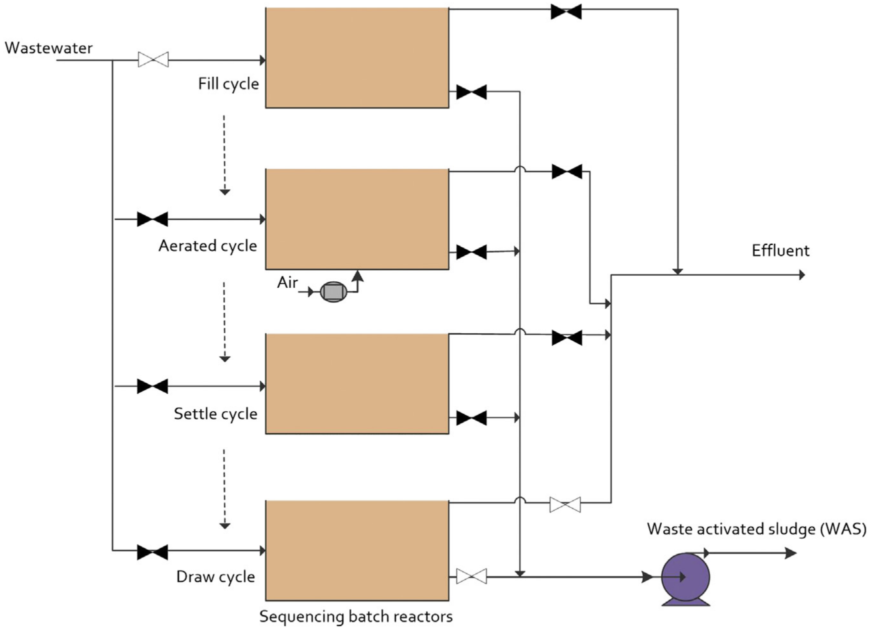

Figure 6.7 Schematic of a typical sequencing batch reactor (SBR) system.
Modified from IPIECA, 2010. Petroleum Refining Water/Wastewater Use and Management. IPIECA Operations Best Practice Series, London, United Kingdom; Environmental Protection Agency (EPA), 1997. Waste Water Treatment Manuals, Primary, Secondary and Tertiary Treatment. Environmental Protection Agency, Ardcavan, Wexford, Ireland.

6.4.3.1.4 Continuous Stirred Tank Bioreactor

The continuous stirred tank bioreactor (CSTB) is the other suspended growth process (Ishak et al., 2012) and is based on a conventional mixed-flow reactor (MFR) or continuous stirred tank reactor (CSTR). It requires air supply and the stirrer can be either at the top or bottom of the reactor. Gargouri et al. (2011) used a CSTB to optimize a feasible and reliable bioprocess system in order to treat hydrocarbon-rich industrial wastewaters. They developed a successful bioremediation by an efficient acclimatized microbial consortium (*Aeromonas punctata* (*Aeromonas caviae*), *Bacillus cereus*, *Ochrobactrum intermedium*, *Stenotrophomonas maltophilia*, and *Rhodococcus* sp.). The performance of the bioaugmented reactor has been demonstrated by the reduction of COD rates up to 95% and reduction of residual total petroleum hydrocarbon (TPH) from 320 to 8 mg TPH/L. In addition, the treated wastewater could be considered as nontoxic according to the phytotoxicity test since the germination index of *Lepidium sativum* ranged between 57% and 95%. While treatment by this process may provide satisfactory results and present a feasible technology for the treatment of hydrocarbon-rich wastewater from petrochemical industries and petroleum refineries its use is not common in petroleum industry wastewater treatment.

6.4.3.1.5 Membrane Bioreactors

The membrane bioreactor (MBR) process is a modification of the conventional AS process in which the membrane filtration unit (e.g., microfiltration (MF) or ultrafiltration (UF)) instead of a secondary sedimentation tank is used to separate the effluent from the activated sludge (solid/liquid separation) (Tri, 2002; Rahman and Al-Malack, 2006; Pombo et al., 2011; Ishak et al., 2012; Uan, 2013). The membrane configurations applied are mainly tubular, hollow fiber, and flat sheet (plate) and its materials can be polymeric, metallic, and inorganic (ceramic). Backwashing, high resistivity to corrosion, and fouling control are some of the major characteristics of ceramic membranes. However, they are more expensive than polymeric membranes, such as polyvinylidene fluoride (PVDF), polyethersulfone (PES), polyethylene (PE), and polysulfone (PSF) membranes, which appear to be most widely used in current applications. The pore size of membranes is typically 0.01−0.45 μm (Uan, 2013).

Membrane bioreactor systems generally come in two different configurations:

- A submerged membrane bioreactor (SMBR) in which the membrane module is submerged inside the bioreactor and the permeate is suctioned directly by dead-end filtration (Tri, 2002). Note that membranes might be either submerged in the aeration tank or in the membrane tank. In submerged configurations, the air is supplied for biological processes and membrane scouring (Uan, 2013). A SMBR is more often used to treat municipal wastewater, and can apply both hollow-fiber membranes (horizontal or vertical) and flat-plate membranes (vertical) (Pombo et al., 2011).
- A cross-flow membrane bioreactor (CFMBR) in which the membrane module is installed outside the aeration tank. The mixed-liquor (liquid-solids mixture) is pumped to the membrane module where it is filtrated by cross-flow filtration through the membrane. The permeate is discharged and the retentate (excess flow) is circulated to the aeration tank (Tri, 2002). In this configuration, tubular membranes are often used (horizontal or vertical) (Pombo et al., 2011).

The high quality of treated water, small footprint size of the treatment plant, and reduced sludge production and better process reliability or flexibility of operation are some of the advantages of the MBR process compared to conventional AS processes (Tri, 2002; Zhidong et al., 2009; Uan, 2013). Despite the advantages of this process, membrane fouling can increase the cost of treatment by MBR compared to conventional treatment. In addition, effects of membrane fouling on the decline of permeate flux can be described using the resistance-in-series model as follows (Tri, 2002):

$$J = \frac{\Delta P}{\mu R_t} \tag{6.3}$$

where J is the permeate flux (m^3/m^2 s), ΔP denotes the transmembrane pressure (Pa), μ is the viscosity of the permeate ($Pa \cdot s$), and R_t denotes the total resistance for filtration (1/m), which can be calculated from the following equation:

$$R_t = R_m + R_c + R_f \tag{6.4}$$

where R_m is the intrinsic membrane resistance, R_c denotes the cake-layer resistance, and R_f is the fouling resistance due to irreversible and pore plugging (Tri, 2002).

Feed characteristics, biomass characteristics (e.g., the presence of compounds with high molecular weight), membrane characteristics and the unit configuration, and operational conditions (e.g., the hydrodynamic conditions) are generally the parameters that affect membrane fouling (Pombo et al., 2011; Uan, 2013). Optimization of reactor and module design and aeration (fine bubbles for aeration and larger coarse bubbles for fouling control) can also be beneficial to membrane-fouling control (Uan, 2013).

A schematic of a typical MBR system is shown in Fig. 6.8. Typical aerobic HRTs for MBRs used for oily wastewater treatment can be in the range of 0.5–3 days, whereas the proper sludge retention time (SRT) for them should be controlled at 20–50 days; however, SRT highly depends on HRT and the feed characteristics (Uan, 2013). According to the IPIECA (2010), the MBR system usually operates at higher MLSS concentrations (15,000–20,000 mg/L) than conventional AS systems. The cost of MBR systems is higher than conventional AS processes due to the introduction of membranes, and they are not used in the petroleum industry. However, for AS systems that need tertiary filtration, MBR is more cost competitive because it has membrane. For the petroleum industry applications where further tertiary treatment such as reverse osmosis will be applied, MBR can be attractive compared to the alternative option of using media filtration and microfiltration after biological treatment (IPIECA, 2010). In the future, the rapidly decreasing membrane cost may be an important driving force for the widespread utilization of MBRs (Uan, 2013).

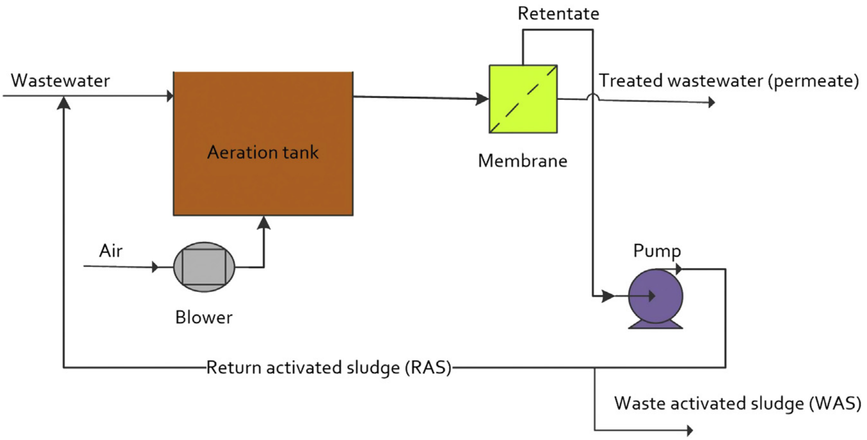

Figure 6.8 Schematic of a typical membrane bioreactor (MBR) system.
Modified from IPIECA, 2010. Petroleum Refining Water/Wastewater Use and Management. IPIECA Operations Best Practice Series, London, United Kingdom; Uan, D.K., 2013. Potential application of membrane bioreactor (MBR) technology for treatment of oily and petrochemical wastewater in Vietnam – an overview. Petroleum Safety & Environment, Petrovietnam – Journal 6, 64–71.

The feasibility of using a MBR process to treat oily wastewater has been explored by researchers. Yaopo et al. (1997) studied the treatment of petrochemical wastewater with a MBR and reported removal efficiency of COD (78–98%), BOD_5 (96–99%), SS (74–99%), and turbidity (99–100%). Scholz and Fuchs (2000) investigated the application of the MBR process with external membrane module configuration to treat synthetic oily wastewater containing either fuel oil or lubricant oil and a surfactant. Influent concentration was in the range of 500–1000 mg/L in terms of hydrocarbon and biomass concentration in the system was maintained up to 48 g/L. At the HRT of 13.3 h, the removal efficiency for fuel oil as well as lubricant oil was 99.9%. Total organic carbon (TOC) and COD removal efficiencies were also reported at 94–96% for fuel oil and 97–98% for lubricant oil and the removal efficiency of surfactant was in the range of 92.9–99.3%. They concluded that the treated wastewater (effluent) can be reused in industrial processes (Scholz and Fuchs, 2000; Tri, 2002; Pombo et al., 2011). Rahman and Al-Malack (2006) used a CFMBR (with tubular ceramic membranes) to treat petroleum refinery wastewater and evaluated the performance of this process at MLSS concentrations of 5000 and 3000 mg/L. The results of this investigation showed that COD removal efficiency was more than 93% at both MLSS values and HRT did not have a significant effect on the system's performance. Wiszniowski et al. (2011) investigated removal of petroleum pollutants and monitoring of bacterial community structure in a plug-flow MBR and observed removal of COD (93%), BOD (99%), TOC (96%), and nearly complete removal of petroleum-originated nonpolar micropollutants. The study also showed that the bacterial community was affected at high petroleum pollutant concentration (1000 μL/L). At this dosage, bacterial population began to diverge.

6.4.3.1.6 Aerated Lagoons

Lagoons or waste stabilization ponds are in-ground earthen basins used for the treatment of municipal and industrial wastewaters by a natural process involving the use of algae and bacteria. A complex combination of physical, chemical, and biological processes can occur in lagoons for wastewater treatment, and weather conditions, lagoon type and configuration, and system design can affect their performance. They can be classified as anaerobic, facultative, aerobic, and aerated. Anaerobic lagoons are usually 2.5–5 m deep in which all biological activities are anaerobic. These lagoons can be a good choice for treatment of industrial wastewater or mixed domestic and industrial wastewaters with a high BOD_5 concentration. They can usually be applied for pretreatment followed by a facultative or aerobic lagoon to remove the soluble BOD_5 produced by the anaerobic activity. Aerobic-anaerobic or facultative lagoons are usually 1.2–1.5 m deep with an aerobic water layer overlying an anaerobic layer, which includes the settled sludge and anaerobic degradation of SS. Aerobic lagoons are usually very shallow (between 0.30 and 0.45 m) so that sunlight can penetrate the entire depth and dissolved oxygen can present throughout the water column. These lagoons can usually be employed in sunny, warm climates where there is no risk of ice cover (National Guide to Sustainable Municipal Infrastructure, 2004).

In aerated lagoons, the natural aeration process is enhanced by mechanical or diffused aeration units that promote biological treatment (U.S. EPA, 2002; National Guide to Sustainable Municipal Infrastructure, 2004). These lagoons can usually be classified as completely mixed aerated lagoons and partially mixed aerated lagoons based on the amount of mixing provided or the required aeration energy to hold the liquid mass in total or partial suspension, respectively (U.S. EPA, 2002; Pombo et al., 2011). In the first case, biomass can be settled as sludge in a secondary pond, whereas in the second case, the formation and separation of biological flakes and settling of solids can take place in the lagoon itself (Pombo et al., 2011). Aerated lagoons are usually 2—6 m deep and are generally followed by a facultative lagoon in which the suspended solids that do not settle in the mixed or partially mixed aerated lagoon will settle and anaerobically decompose (National Guide to Sustainable Municipal Infrastructure, 2004).

In aerated lagoons, removal efficiencies are generally between 80% and 90% for TSS, 65% and 80% for COD, and 50% and 95% for BOD, depending on the type of system (Pombo et al., 2011), and both the BOD and TSS of effluent can reliably be less than 30 mg/L if provisions for settling are included at the end of the system (U.S. EPA, 2002). These lagoons are usually employed where land area is not expensive or when discharge standards are not overly restrictive (U.S. EPA, 2002; IPIECA, 2010). Because aerated lagoons cannot achieve comparable effluent quality to AS systems, they are used less frequently for wastewater treatment in the petroleum industry due to the current stringent effluent standards for this industry (IPIECA, 2010).

6.4.3.2 Attached Growth Processes

Attached growth processes, which are also called biofilm or fixed-film processes, are treatment processes in which microorganisms are attached to an inert material (e.g., rocks, gravel, slag, plastic, and various synthetic materials) to generate biofilm containing extracellular substances (EPA, 1997; Ishak et al., 2012). The resulting film or slime contains the microorganisms comes in contact with the applied wastewater to treat it. These processes can be classified as packed media (e.g., TFs) and moving or buoyant media (e.g., RBC) (EPA, 1997). Trickling filters, FBB, and RBC are discussed in this section.

6.4.3.2.1 Trickling Filters

A trickling filter (TF) is an aerobic biological process in which the biomass is attached to the bed medium, which may be rock, slag, or plastic (U.S. EPA, 1996). A schematic of a typical TF system without recirculation is shown in Fig. 6.9. This system typically consists of a filter bed, a wastewater distributor, an underdrain system for transferring the treated wastewater, and a clarifier. The organic materials are degraded by the biological film (microorganisms) on the surface of the packed media (EPA, 1997; Arthur et al., 2005; IPIECA, 2010). When the biomass reaches a certain thickness, part of it sloughs off. When this system is applied as the major treatment process, a clarifier is used to separate the sloughed biomass (U.S. EPA, 1996).

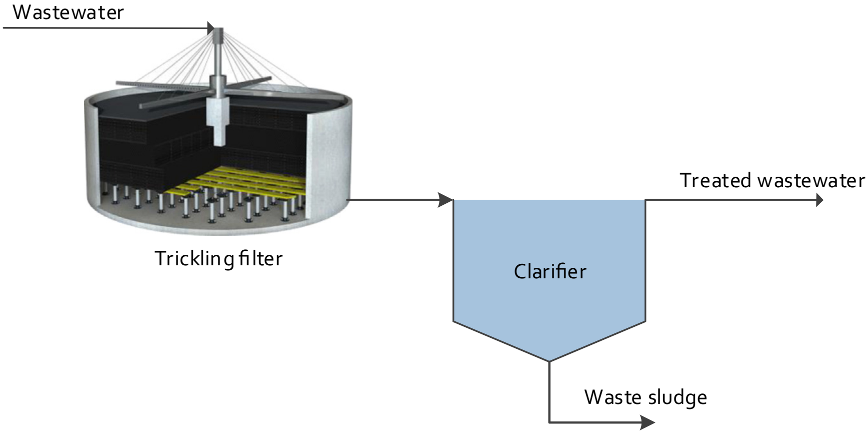

Figure 6.9 Schematic of a typical trickling filter system.
Modified from Environmental Protection Agency (EPA), 1997. Waste Water Treatment Manuals, Primary, Secondary and Tertiary Treatment. Environmental Protection Agency, Ardcavan, Wexford, Ireland.

When a high-quality discharge is not required, a TF may be applied as a secondary treatment system by itself in the petroleum industry, e.g., in refineries. This system may also be used upstream of an AS unit to reduce the loading or to attenuate the organic loading on the unit. According to Bush (1980), removal efficiencies can be in range of 60–85% for BOD, 30–70% for COD, 60–85% for SS, and 50–80% for oil, depending on the filter type, its loadings, medium type, etc. (Bush, 1980). There are four basic categories of TF design based on their organic loadings:

- Low-rate filters that are commonly used for loadings of less than 40 kg BOD_5/100 m^3-day;
- Intermediate rate filters that can be loaded up to 64 kg BOD_5/100 m^3-day;
- High-rate filters that are generally loaded at the maximum organic loading capabilities of the filter and receive total BOD_5 loading ranging from 64 to 160 kg BOD_5/100 m^3-day; and
- Roughing filters designed to allow a significant amount of soluble BOD to bleed through the TF. These filters generally have a design load ranging from 160 to 480 kg BOD_5/100 m^3-day.

The BOD_5 removal rates for low-rate, intermediate rate, high-rate, and roughing filters are 80–90%, 50–70%, 65–85%, and 40–65%, respectively (U.S. EPA, 2000). According to Bush (1980), TF can be applied as a roughing device rather than as a complete treating unit because high removal efficiencies can only be obtained at very low loadings, and at such loadings, the cost of the TF is higher than other comparative processes.

6.4.3.2.2 Fluidized Bed Bioreactor

The fluidized bed bioreactor (FBB) generally includes immobilized cells or enzymes (as biocatalyst) in or onto solid supports, which move with the fluid. These small solid supports or particles can create a large surface area for cells to stick to and enable a high rate of oxygen and nutrients transfer to the cells (Godia and Sola, 1995). A FRB can typically be classified as aerobic or anaerobic (Godia and Sola, 1995; Wan et al., 2010; Haribabu and Sivasubramanian, 2014). In FBB systems, where three phases (solid-liquid-gas) exist, the hydrodynamic characterization may be difficult (Godia and Sola, 1995). In FBB, the resulting biomass onto solid supports comes in contact with the applied wastewater to treat it.

Some researchers have explored the feasibility of using FBB to treat the petroleum industry's wastewaters. For instance, Sokol (2003) investigated the aerobic treatment of refinery wastewater in a three-phase FBB with a low-density (matrix particle density smaller than that of water) biomass support [KMT (Kaldnes Miljotechnologi AS) particles made of polypropylene]. The largest COD removal, approximately 90%, was achieved when a bioreactor was operated at the ratio of bed (settled) volume to bioreactor volume (V_b/V_R) = 0.55 and the air velocity $U = 0.029$ m/s. The pH was controlled in the range of 6.5−7.0 and the temperature was maintained at 28−30°C. The steady-state biomass loading occurred in the bioreactor after culturing for about 2 weeks. It was concluded that the excess biomass can be sloughed off through the particle−particle and particle−wall collisions, and the intensive motion of the particles can eliminate clogging and channeling of the bed. Lohi et al. (2008) also studied aerobic biodegradation of diesel fuel (DF)-contaminated wastewater in a three-phase FBB with the solid-phase lava rock particles as support for the biomass under unsteady and steady state conditions in which the particles were fluidized by the upward flows of influent wastewater and air. The results of this study showed that the reactor under unsteady state operation achieved 100% DF removal from synthetic wastewater loaded with 0.43−1.03 kg/m^3 day of DF. An average of over 97% of the influent COD was also removed from the wastewater with COD concentrations in the range, 547−4025 mg/L. For influent COD concentrations up to 1345 mg/L, the removal was greater than 90%. Under steady-state operation, the reactor was able to remove 100% of the DF and an average of 96% of the COD from the wastewater. It had approximately 200 mg/L of DF and 1237 mg/L of COD at a low hydraulic residence time of 4 h. In addition, Kuyukina et al. (2009) investigated the biotreatment of petroleum-contaminated water in a continuous FBB with recycle; and tested different type biocatalysts including Rhodococcus bacteria immobilized in hydrophobized carriers such as sawdust, poly(vinyl alcohol) cryogel (cryoPVA), and poly(acrylamide) cryogel (cryoPAAG). The hydrophobized sawdust-supported biocatalyst demonstrated substantially higher metabolic activity than C_{12}-cryoPAAG-based biocatalyst due to a larger number of immobilized Rhodococcus cells and therefore had benefits for application in FBBs. They reported that designed FBB process was successful, providing 70−100% removal of *n*-alkanes (C_{10}−C_{19}) and 66−70% removal of 2−3-ring PAHs from contaminated water after 2−3 weeks.

6.4.3.2.3 Rotating Biological Contactors

Rotating biological contactor (RBC) systems allow the microorganisms to adhere and form a layer of biological mass on large diameter discs or structured modules in which a central horizontal shaft rotates the discs or modules, thereby exposing the biofilm sequentially to the wastewater and to the atmosphere (where oxygen is absorbed). Thus biological degradation of the wastewater pollutants occurs (EPA, 1997; Suzuki

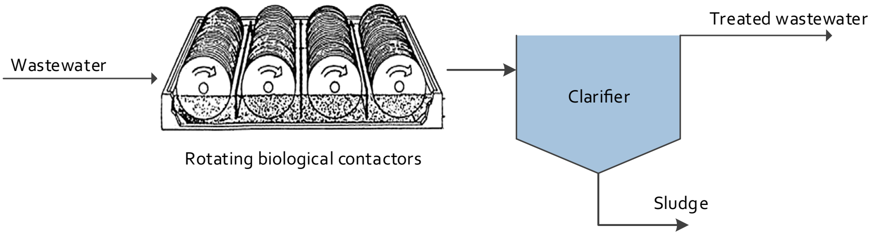

Figure 6.10 Schematic of a typical rotating biological contactor (RBC) system.

and Yamaya, 2005; Ishak et al., 2012). Either a geared motor connected directly to the shaft by a peripheral drive on the discs or air bubbles acting tangentially on vanes attached to the discs can rotate them. There is a large variety of support media on the market but the characteristic unit consists of a series of closely spaced (2—3 cm apart) plastic (e.g., polystyrene) discs 1—3 m in diameter (EPA, 1997). In a conventional RBC system, approximately 40—45% of the total disk surface area is submerged in the wastewater to be treated (Suzuki and Yamaya, 2005). A schematic of a typical RBC system is shown in Fig. 6.10.

Relatively low energy consumption, simple operation and maintenance, and successive treatment of the influent contaminants are some of advantages of RBC systems (Suzuki and Yamaya, 2005). Moreover, the need for additional aerators is eliminated due to oxygen-transfer facilitation in the system by the rotating discs (Chavan and Mukherji, 2008).

Tran and Chowdhury (1991) studied the feasibility of the coupling of RBC with a porous biomass support system (PBSS) using polyurethane foam as porous support media to biodegrade petroleum refinery wastewater on a laboratory scale. For all of the hydraulic loadings (0.01, 0.02, 0.03, and 0.04 $m^3/m^2/d$), the removal efficiency of total COD and oil were above 80%. Ammonia nitrogen and phenol removal were above 90% and 80%, respectively. The maximum biomass concentration within polyurethane foam was about 30 g/m^2 in the first stage for 0.03 $m^3/m^2/d$ hydraulic loading. They concluded that this system can be used effectively for practical purposes with moderate hydraulic loading rates. Suzuki and Yamaya (2005) designed a single-stage RBC with biodrum to remove hydrocarbons in wastewater from industrial discharges at 25°C and at pH 7.0 in a batch mode. The biodrum, a cylindrical mesh drum, filled with random packing of polyurethane foam cubes retaining petroleum-degrading achlorophyllous microalga Prototheca zopfii cells was approximately 40% submergence in the culture. The amount of algal cells, immobilized in the 1-cm-cube pieces, was greater than in pieces of smaller pore size under the experimental conditions studied. They concluded that the removal rate for n-alkanes (C_{14}, C_{15}, and C_{16}) in the RBC with biodrum system was significantly increased as compared to those in the RBC system with polycarbonate biodisk. Kubsad et al. (2005) assessed the efficiency of RBC to treat the synthetic wastewater from a petrochemical industry producing acrylonitrile in a laboratory scale. At hydraulic loading of 0.011 $m^3/m^2/d$, the removal efficiencies for cyanide, COD, BOD_5, and $NH_4^+ - N$ were greater than 99%, 95.2%, 99.1%, and 77%, respectively. They reported that the COD/nitrogen (N) ratio did not affect cyanide removal, whereas the substrate/cyanide ratio affected the performance of the process, with more than 99% cyanide removal achieved at a ratio of 20/1. Chavan and Mukherji (2008) investigated a consortium of phototrophic microorganisms and a bacterium developed on the discs of an RBC for treatment of wastewater containing diesel oil. The reactor was fed with oil-degrading bacterium, *Burkholderia cepacia*, and oil-tolerant phototrophic microorganisms. Residual diesel in the effluent was 0.003%. They noted that the advantages of this system include good TPH removal, no soluble-carbon source requirement, and good settleability of biosolids. The nitrogen/phosphorus (N/P) ratio affected the relative dominance of the phototrophic microorganisms and bacterial culture, which was a critical factor in determining the performance efficiency of the reactor. At 21 h HRT and organic loading of 27.33 g TPH/m^2 d, the N/P ratios 28.5/1 and 38/1 both yielded high and almost comparable TPH and COD removal efficiencies. These studies suggest that the RBC system may be a feasible technology for the treatment of oily wastewater from the petroleum industry.

6.4.3.3 Nitrification or Combined Nitrification/Denitrification

Nitrification is generally the biological oxidation of ammonia or ammonium to nitrite (e.g., with *Nitrosomonas* bacteria) followed by oxidation of the nitrite to nitrate (e.g., with *Nitrobacter*) as follows:

$$2NH_4{}^+ + 3O_2 \xrightarrow{\text{Nitrifying bacteria such as } \textit{Nitrosomonas}} 2NO_2{}^- + 2H_2O + 4H^+ \quad (6.5)$$

$$2NO_2{}^- + O_2 \xrightarrow{\text{Nitrifying bacteria such as } \textit{Nitrobacter}} 2NO_3{}^- \quad (6.6)$$

Denitrification is an anoxic process that occurs in the absence of dissolved oxygen in which nitrate $\left(NO_3{}^-\right)$ is sequentially reduced to nitrite $\left(NO_2{}^-\right)$, nitric oxide (NO), nitrous oxide (N_2O), and nitrogen (N_2) in the presence of a carbon source and heterotrophic bacteria (e.g., *Pseudomonads*). The nitrate produced during nitrification becomes the oxygen source for heterotrophic bacteria that use the available BOD, thus bacteria, oxidized nitrogen as the oxygen source, and a carbon source are required for denitrification (EPA, 1997; European Commission and Joint Research Center, 2013).

As noted, in some cases when deep nitrogen removal is required and a petroleum industry site needs to meet tight ammonia or nitrogen limits, application of either a nitrification or a combined nitrification/denitrification step is possible (IPIECA, 2010; European Commission and Joint Research Center, 2013).

The processes for biological nitrogen removal can be incorporated or retrofitted into both activated sludge and percolating or trickling filter plants (EPA, 1997). To upgrade a WWTP with a nitrification/denitrification process, an additional nonaerated reactor (anoxic tank) can often be added to the WWTP after (postdenitrification) or before (predenitrification) the aeration basin. Theses configurations are shown in Fig. 6.11 (Trevi nv, 2014). In the postdentrification system, a carbon source (e.g., methanol) is added to anoxic tank to aid the denitrification process. In the

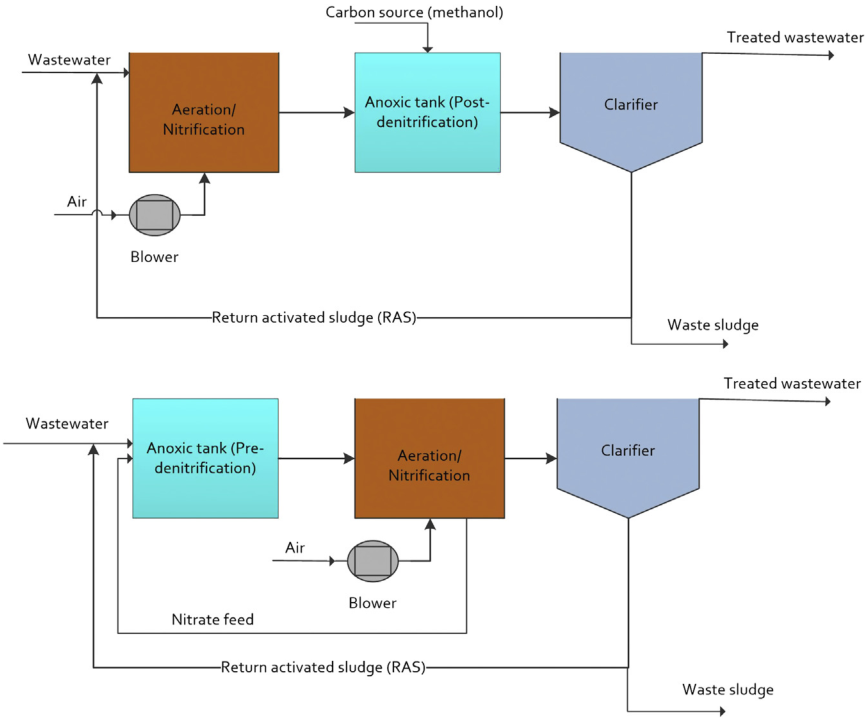

Figure 6.11 Chematic of nitrification/denitrification systems.
Modified from Trevi nv, 2014. Biological Nitrogen Removal. Trevi nv, Dulle-Grietlaan, Gentbrugge, Belgium. [Online] Available from: http://www.trevi-env.com/en/technique_biological_nitrogen_removal.php.

predenitrification system, the BOD in the incoming wastewater acts as the food source for the anoxic tank. A portion of the treated wastewater from the aeration basin is recycled so that the reduction of nitrates in the effluent can take place (IPIECA, 2010; Trevi nv, 2014). According to the European Commission and Joint Research Center (2013), natural nitrogen removal is usually about 10% in an activated sludge process, 70−80% in a nitrification/denitrification biotreater, and up to 90% in a tertiary (add-on) denitrification system.

6.4.4 Tertiary Treatment or Polishing

Tertiary treatment or polishing refers to any treatment that takes place downstream of the secondary treatment plant for obtaining a very high-quality effluent to meet discharge limits (U.S. EPA, 1995; Goldblatt et al., 2014). In other words, when the petroleum industry needs to meet stringent limits for different contaminants such as TSS, COD, dissolved and suspended metals, and trace organics such as PAHs, tertiary treatment should be considered (IPIECA, 2010). The polishing step may include processes such as sand filtration, activated carbon (Bush, 1980; U.S. EPA, 1995; Benyahia et al., 2006; IPIECA, 2010; Goldblatt et al., 2014), chemical oxidation (Bush, 1980; IPIECA, 2010; Goldblatt et al., 2014), membrane-separation technologies, e.g., ultrafiltration (Benyahia et al., 2006; European Commission and Joint Research Center, 2013), and reverse osmosis (European Commission and Joint Research Center, 2013; Goldblatt et al., 2014), or other treatments which will remove recalcitrant pollutants to make the effluent suitable for discharge or maybe for reuse (Goldblatt et al., 2014).

Note that most of the processes described below are not widely practiced in the petroleum industry and are not yet commonplace; however, these are options that should be considered based on regulatory and cost pressures in a local region (IPIECA, 2010).

6.4.4.1 Sand Filtration

According to the World Bank Group (1998), the maximum effluent level for TSS from the petroleum industry is 30 mg/L. Furthermore, according to the IPIECA (2010), refineries at many locations require to meet limits as low as 15 mg/L for SS on a consistent basis. The effluent from the biological-treatment system typically contains about 5—50 mg/L of organic matter in suspended or colloidal form (Bush, 1980) or about 25—80 mg/L of SS depending on the operating conditions in the clarifier that can be filtered using sand filtration. A typical sand filtration system is shown in Fig. 6.12. Anionic or cationic polymers can be added to the effluent from the clarifier to improve particle-removal efficiency. Contaminant particles greater than almost 5 μm in size can typically be removed by this type of treatment (IPIECA, 2010). A granular-media filter can reduce organic matter in suspended or colloidal form to around 3—20 mg/L. Anthracite and sand, activated carbon and sand, resin beds and sand, and resin beds and anthracite can be used in dual-media filters (Bush, 1980). Dual-media filters typically consist of a layer of anthracite over sand (Schultz, 2007). Anthracite traps the larger particles and sand traps the finer solids. The filter is periodically backwashed to remove the trapped particles (IPIECA, 2010). Bush (1980) has recommended that a pilot study be done for a particular system due to dependence of filter performance on the particular characteristics of the specific liquid feed (Bush, 1980).

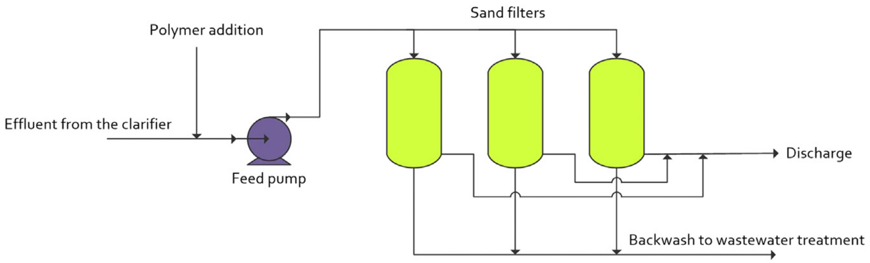

Figure 6.12 Typical sand filtration system.
Modified from IPIECA, 2010. Petroleum Refining Water/Wastewater Use and Management. IPIECA Operations Best Practice Series, London, United Kingdom.

6.4.4.2 Activated Carbon Adsorption

Activated carbon adsorption is normally a polishing step for the effluent that can remove dissolved and refractory organic compounds (Bush, 1980; Pombo et al., 2011; Okiel et al., 2011). This process is only used if a very high-quality effluent is required (Bush, 1980) and may allow the treated effluent to be reused as industrial water (Pombo et al., 2011).

An activated carbon adsorption system can consist of the adsorbers in which the wastewater stream contacts the activated carbon (e.g., GAC) bed (fixed beds in parallel, or a moving bed), a transport system for moving the carbon from the adsorbers to the regenerator and back, and a regeneration system (thermal (conventional system), chemical, solvent, or biological system). A typical activated carbon adsorption system is shown in Fig. 6.13. In these adsorption systems, flow rate, bed depth, and contact time can be 5–10 gpm/ft^2, 10 ft minimum, and 15–38 min, respectively (Bush, 1980).

According to Bush (1980), the BOD, oil content, and phenol of effluent from an AS system can be reduced by an adsorption system to 3–10 mg/L, less than 1 mg/L, and almost 0, respectively. Okiel et al. (2011) studied the removal of oil from oil–water emulsions by adsorption on bentonite, PAC, and deposited carbon (DC). Oil-removal efficiencies increased with increasing contact time and the weight of adsorbents and decreased with increasing the concentration of adsorbate (oil). For example, at 836 mg/L initial oil concentration, using 0.5 g PAC and stirring for 2.0 h, oil-removal efficiency was 82.78%, whereas using 1.0 g of PAC and stirring for 4.0 h, oil removal was 93.54%. They concluded that adsorptive capacities by DC and bentonite were higher than those of the PAC.

6.4.4.3 Chemical Oxidation

Chemical oxidation refers to the use of oxidation reagents such as hydrogen peroxide, chlorine dioxide, and ozone for reduction of residual COD, nonbiodegradable compounds, and trace organic compounds (Bush, 1980; IPIECA, 2010). A typical chemical oxidation system is shown in Fig. 6.14. Utilization of this system is not

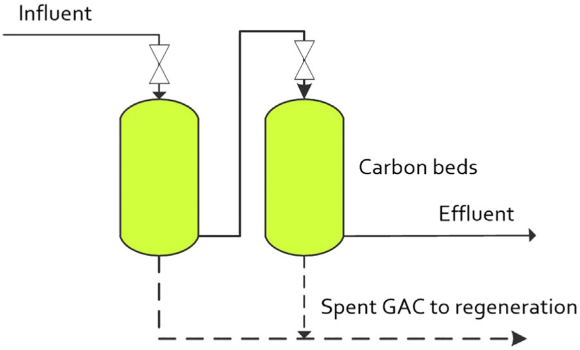

Figure 6.13 Typical activated carbon adsorption system.
Modified from IPIECA, 2010. Petroleum Refining Water/Wastewater Use and Management. IPIECA Operations Best Practice Series, London, United Kingdom.

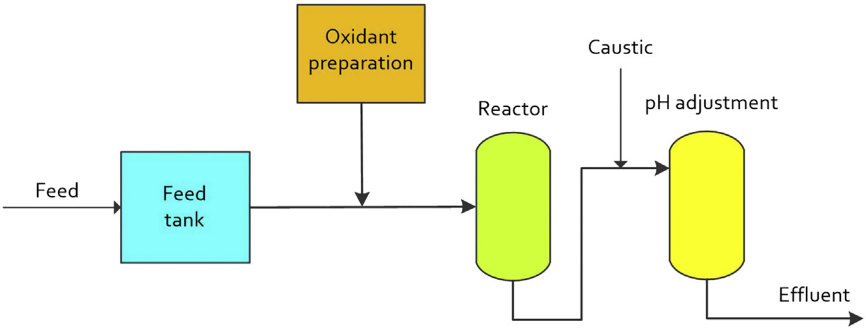

Figure 6.14 Typical chemical oxidation system.
Modified from IPIECA, 2010. Petroleum Refining Water/Wastewater Use and Management. IPIECA Operations Best Practice Series, London, United Kingdom.

common in the WWTPs in the petroleum industry (IPIECA, 2010), but it is applicable to small, concentrated streams, where conventional biological oxidation processes are not feasible (Bush, 1980). In other words, when the wastewater contains highly toxic recalcitrant compounds such as the aromatic fraction from the dissolved organic compounds and use of the biological process is not suitable, application of this system may be effective to degrade these compounds (Mota et al., 2008).

6.4.4.4 Pressure-Driven Membrane-Separation Technologies

Membrane-separation technology is the use of a membrane as a selective barrier to regulate or restrict the passage of pollutants such as organics, nutrients, turbidity, microorganisms, inorganic metal ions, etc., and allow relatively clear water to pass through (Shon et al., 2013). A membrane is an interphase between two adjacent phases acting as a semipermeable and selective barrier that separates particles based on molecular or physical size (Muro et al., 2012). The transport selectivity of the membrane is the main advantage of membrane technology as compared with other methods. Separations with membranes also do not need additives, and upscaling and downscaling of these processes as well as their integration into other separation or reaction processes are easy (Dach, 2008).

Membrane processes can typically be divided according to their driving forces as follows:

- Pressure-driven processes: conventional or particle filtration, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), pervaporation (PV), and gas permeation (GP) or gas separation;
- Concentration-driven processes: dialysis and osmosis;
- Temperature (heat)-driven processes: membrane distillation (MD); and
- Electrically driven processes: electrodialysis (ED) and membrane electrolysis (ME) (Dach, 2008; Shon et al., 2013).

The majority of commercial membranes are constructed from organic polymers (polysulfones and polyamides) and inorganic materials (ceramic membranes based on oxides of zirconium, titanium, silicium, and aluminum). Plate-and-frame, spiral wound, tubular, and hollow-fiber configurations are the four main types of membrane configurations applied in the industry (Muro et al., 2012).

Membranes are generally characterized by the pore flow or molecular weight of particle that is retained or separated by the membrane. However, structure, porosity, thickness, the electrostatic repulsion between the membrane surface and the contaminant, wettability surface, and operating conditions can also affect the rejection of solutes and consequently the performance of membranes. Membrane pore flow is differentiated by the size of particles diameter that membranes can separate (micrometers, μm) and nominal molecular weight cutoff (MWCO). MWCO is a performance-related parameter, which refers to the lower limit of a solute molecular weight for which the rejection is 95–98% (Muro et al., 2012). It is the ability of a membrane to reject the species of a certain molecular weight measured as Daltons (Da) (Arthur et al., 2005).

The principle of irreversible thermodynamics (IT) can be used to describe transport phenomena of solutes through a membrane, which leads to two basic equations for the solvent (water) flux (J_v) and solute flux (J_s) according to Spiegler and Kedem (1966) as follows:

$$J_v = L_p(\Delta P - \sigma \Delta \Pi) \tag{6.7}$$

$$J_s = P_s \Delta C_s + (1 - \sigma) J_v C_{\text{int}} \tag{6.8}$$

where ΔP and $\Delta \Pi$ define respectively the membrane transmembrane pressure and the osmotic differences between each side of the membrane, L_p is the hydraulic permeability to pure water, σ denotes the local reflection coefficient, P_s is the solute permeability, C_{int} denotes the solute concentration in the membrane, and $\Delta C_s = C_m - C_p$ with C_m and C_p the concentrations respectively at the surface of the membrane in the bulk side and in the permeate (Dach, 2008). The membrane's selective capacity can be expressed by the retention coefficient (R). It refers to the fraction of the solute retained by the membrane for a given feed concentration (Pombo et al., 2011). In constant fluxes and constant transport parameters (L_p and σ), by integrating the Eq (6.8) across membrane thickness, the following equation can be obtained for rejection or retention (Dach, 2008; Bolong et al., 2012; Jafarinejad, 2015f):

$$R = 1 - \frac{C_p}{C_m} = \frac{\sigma\left(1 - \exp\left(-\frac{1-\sigma}{P_s} J_v\right)\right)}{1 - \sigma \exp\left(-\frac{1-\sigma}{P_s} J_v\right)} \tag{6.9}$$

Note that the solute concentrations at the membrane surface in the bulk side and in the bulk solution are assumed to be the same (Bolong et al., 2012; Jafarinejad, 2015f).

Membrane fouling is one of the significant challenges in any membrane process that reduces the efficiency of membrane filters (Shon et al., 2013; Pombo et al., 2011). Clogging of the pores, adsorption of solute by the membrane, and formation of a gel on the membrane surface, etc., can cause membrane fouling (Pombo et al., 2011). It can be either reversible or irreversible. Reversible fouling can be removed by physical procedures, whereas irreversible fouling can be removed by chemical cleaning and other methods (Pombo et al., 2011; Muro et al., 2012). Membrane fouling can usually be controlled by operating the system within the critical flux range or adding chemicals (especially to prevent inorganic scaling and fouling), and/or by pretreatment (Shon et al., 2013).

Microfiltration, UF, NF, and RO apply high pressure across the membranes to accomplish filtration of contaminants from the wastewater (Arthur et al., 2005). The main differences between these membrane-filtration processes are listed in Table 6.3. It should be noted that a single membrane-separation technology is not usually a good solution to the problem of oily wastewater treatment. It may require combining with a different or a membrane-separation technology, e.g., combination of UF with RO (IPIECA, 2010; Yu et al., 2013), combination of MF with RO, combination of MF or UF with NF (IPIECA, 2010), combination of MF with UF, etc. (Yu et al., 2013).

6.4.4.4.1 Microfiltration

Microfiltration (MF) membranes can usually be used after conventional treatment methods, as pretreatment before RO to prolong the useful life of the RO membrane and reduce fouling and operational costs of this process, and as part of an MBR to retain biomass (Pombo et al., 2011). As Table 6.3 depicts, MF can remove particles greater than approximately 0.1 μm.

A schematic of a typical MF or UF system with GAC pretreatment that may be used for reuse purposes is shown in Fig. 6.15. In this system, GAC pretreatment is used to reduce the oil and grease content to less than 1 mg/L (Bush, 1980; IPIECA, 2010), and biocide (e.g., chlorine or chloramines) addition is for the prevention of membrane biofouling. Microfiltration and UF can both produce a very clear filtrate with less than 1 mg/L SS, but these processes will not be able to achieve any significant reduction in dissolved salts and metals present in the feed (IPIECA, 2010).

Song et al. (2006) studied low-cost coal-based MF carbon membrane with pore size of 1.0 μm at the operation conditions of 0.10 MPa transmembrane pressure and 0.1 m/s cross-flow velocity for the treatment of oily wastewater. They reported that the oil-rejection coefficients of oily wastewater were up to 97%, and the oil concentrations of the permeate were less than 10 mg/L. Hua et al. (2007) investigated cross-flow MF process for oily wastewater treatment using a ceramic (α-Al_2O_3) membrane with 50 nm pore size. They obtained TOC removal efficiencies higher than 92.4% under all experimental conditions. Cui et al. (2008) prepared NaA zeolite MF membrane on α-Al_2O_3 tube by an in situ hydrothermal synthesis method with average interparticle pore size of 1.2 μm and investigated for water separation and recovery from oily water. Better than 99% oil rejection was obtained and water containing less than 1 mg/L oil was produced at 85 L/h m^2 by it at a membrane pressure of 50 kPa. Madaeni et al. (2012) used γ-Al_2O_3-based ceramic MF membrane to remove coke particles from petrochemical wastewaters before introducing to the coalescers. Perfect elimination of coke particles from oily wastewaters was achieved. Kumar et al.

Table 6.3 **Main Differences Between Membrane-Filtration Processes (Dach, 2008; Muro et al., 2012, Shon et al., 2013)**

Membrane Process	MF	UF	NF	RO	
Membrane	Porous isotropic	Porous asymmetric	Finely porous asymmetric/composite	Nonporous asymmetric/ composite	Shon et al. (2013)
Transfer mechanism	Sieving and adsorptive mechanisms (the solutes migrate by convection)	Sieving and preferential adsorption	Sieving/electrostatic hydration/diffusive	Diffusive (solutes migrate by diffusion mechanism)	Shon et al. (2013)
Pressure range (bar)	0.1−2	1−5	3−20	5−120	Dach (2008)
MWCO (Da)	>100,000	1000−300,000	200−1000	<200	Dach (2008)
Hydrolic permeability range (L/h m^2 bar)	>1000	10−1000	1.5−30	0.05−1.5	Dach (2008)
Retained particle diameters (μm)	0.1−10	0.001−1	0.001−0.01	0.0001−0.001	Muro et al. (2012)
Retained solutes	Bacteria, fat, oil, grease, colloids, organics, microparticles	Proteins, pigments, oils, sugar, organics, microparticles	Pigments, sulfates, divalent cations, divalent anions, lactose, sucrose, sodium chloride	Salts, sodium chloride, inorganic ions	Muro et al. (2012)
Typical solution treatment	Solution with solid particles	Solution with colloids and/or macromolecules	Ions, small molecules	Ions, small molecules	Shon et al. (2013)

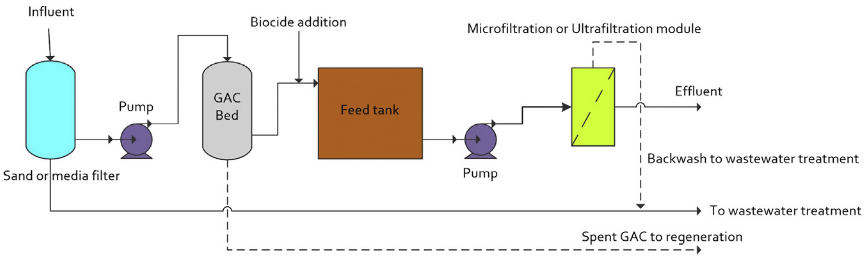

Figure 6.15 Microfiltration or ultrafiltration system with GAC pretreatment.
Modified from IPIECA, 2010. Petroleum Refining Water/Wastewater Use and Management. IPIECA Operations Best Practice Series, London, United Kingdom.

(2015) prepared a tubular ceramic MF membrane with an average pore size of 0.309 μm by an extrusion technique using inexpensive clay mixtures, namely, ball clay, kaolin, feldspar, quartz, pyrophyllite, and calcium carbonate, and used it for synthetic oily wastewater treatment. They reported that the applied pressure of 69 kPa offered the highest rejection of oily wastewater (99.98%) with permeate flux of 3.16×10^{-5} m/s.

6.4.4.4.2 Ultrafiltration

Ultrafiltration (UF) membranes can usually be used after conventional treatment methods, as pretreatment before RO, and as part of an MBR (Pombo et al., 2011). As Table 6.3 depicts, UF can typically operate at a pressure range of 1−5 bar.

Li et al. (2006) used a tubular UF module equipped with PVDF membranes modified by inorganic nanosized alumina particles to purify oily wastewater from an oilfield. They reported that retentions of COD and TOC were more than 90% and 98%, respectively, and the addition of nanosized alumina particles improved membrane antifouling performance. The results indicated that after UF treatment, oil content was below 1 mg/L, SS content was below 1 mg/L, and solid-particle median diameters were less than 2 μm. They concluded that the quality of the permeated water met the requirement by oil-field injection or drainage. Karhu et al. (2013) investigated the performance of a commercial industrial-scale UF-based process for treatment of highly concentrated oily wastewaters at two plants in 2008 and 2011. They reported that the removal performances of BOD_7, COD, TOC, and total surface charge (TSC) in 2008 and 2011 for both plants were very high. Salahi et al. (2015) prepared polyethersulfone UF hollow-fiber membranes via phase inversion induced by a dry-jet wet spinning process and investigated the treatment of the outlet wastewater of the API unit of Tehran refining as the feed. They reported that the prepared membranes exhibited COD, TOC, and O&G removals of about 83.1%, 96.3%, and 99.7%, and final flux and fouling of about 84.1 L/h m^2 and 63%, respectively. They concluded that quality of the finally treated outlet water was high and even better than the standard water that was introduced to cooling towers. Huang et al. (2015) studied oily wastewater treatment by polyvinylpyrrolidone (PVP) grafted PVDF UF membranes. The membranes were prepared stepwise using defluorination, double-bond hydration, and PVP grafting. The oily wastewater treatment performance of the PVDF—PVP membranes were significantly better than that of the PVDF membranes. In addition, external fouling was the major cause of flux decline. Moreover, flux recovery of the fouled PVDF—PVP membranes after cleaning using 3 wt% NaOH aqueous solution exceeded 90% and was much superior to that of the fouled PVDF membranes.

6.4.4.4.3 Nanofiltration

The properties of nanofiltration (NF) membranes lie between those of nonporous RO membranes and porous UF membranes. Commercial NF membranes possess a fixed charge developed by dissociation of surface groups such as sulfonated or carboxyl acids. The properties of NF membranes therefore allow ions to be separated by a combination of the size and electrical effects of UF and the ion-interaction mechanisms of RO. Nanofiltration has replaced RO in many applications due to lower energy consumption and higher flux rates (Shon et al., 2013).

A schematic flow diagram of a combination of a MF or UF with NF or RO system incorporating GAC pretreatment for oil removal, which can be used for reuse purposes, is shown in Fig. 6.16.

Rahimpour et al. (2011) investigated treatment of oily wastewater produced by washing of gasoline reserve tanks using self-made and commercial NF membranes. They pretreated wastewater by the MF membrane and then did various NF experiments under the permeated flux between 20 and 265 kg/h m^2, the applied pressures in the range of 5, 10, 15, and 20 bar, and temperatures in the range of 20, 30, and 40°C. They reported that the COD and electrical conductivity (EC) were considerably decreased, even more than 10 times lower than the initial value in raw and pretreated feeds. Jin et al. (2012) prepared a novel composite NF membrane incorporated SiO_2 nanoparticles for oily wastewater desalination. The permeation performance for polyamide (PA)-SiO_2 membrane increased nearly 50% without loss of salt rejection rate by adding 1.0% (wt) nano-SiO_2 nanoparticles. The order of rejection to inorganic salts was $Na_2SO_4 > MgSO_4 > MgCl_2 > NaCl$; revealed both PA and PA-SiO_2 membrane were negatively charged. The PA-SiO_2 membrane had a higher stable flux and could remove nearly 50% of salts when treated with oily wastewater in one-cycle filtration. They concluded that desalination of oily wastewater using the nacomposite PA-SiO_2 membrane was feasible. Muppalla et al. (2015) used fouling-resistant NF membranes for the separation of oil—water emulsion and micropollutants from water. The membranes showed rejections in the range of 22—37% for NaCl, 33—44% for $MgSO_4$, 20—36% for $MgCl_2$, and 45—61% for Na_2SO_4 when tested using 500—4000 ppm feed solution at 3.5—28 kg/cm^2 applied pressure. Rejection of organic micropollutants was also decreased according to the increase in their hydrophobicity as follows: benzoic acid > 2-chlorophenol > 2,4-dimethyl phenol > bisphenol-A. In addition, the composite membranes exhibited 95.5—99.5% oil rejection when tested using 500—1000 ppm engine oil in water emulsion as the feed at 3.5 kg/cm^2 applied pressure. Altalyan et al. (2016) examined the removal of VOCs from groundwater at Southlands—Botany Bay (Sydney region) by RO and NF. They reported that the

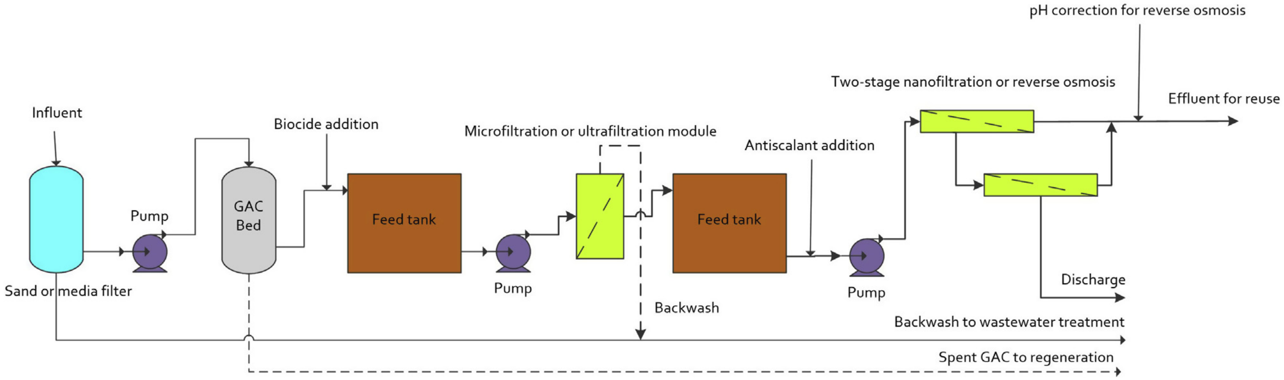

Figure 6.16 Schematic flow diagram for a combination of MF or UF with NF or RO system.
Modified from IPIECA, 2010. Petroleum Refining Water/Wastewater Use and Management. IPIECA Operations Best Practice Series, London, United Kingdom.

removal efficiency of RO was better than NF in rejecting the VOCs detected in groundwater. The performance of NF and RO membranes in rejecting hydrophilic VOCs was also higher than that for hydrophobic compounds and the highest rejection achieved by NF and RO membranes amounted to 98.4% and 100%, respectively. They expressed that hydrophilic compounds can be effectively rejected by NF/RO membranes using the size-exclusion mechanism (steric hindrance), whereas hydrophobic compounds can be adsorbed into NF/RO membranes and then diffused through the dense polymeric matrix, resulting in lower removal for these compounds compared to hydrophilic compounds.

6.4.4.4.4 Reverse Osmosis

Reverse osmosis (RO) is a process that uses semipermeable (usually spiral wound) membranes (Dach, 2008) to separate and remove dissolved solids, ions (dissolved salts), organic, pyrogens, submicron colloidal matter, color, nitrate, and bacteria from wastewater (Palit, 2012). Reverse osmosis occurs when the pressure differential (Δp) is greater than the osmotic pressure ($\Delta\Pi$) and the water flows from the concentrated to the diluted side (Pombo et al., 2011).

Reverse osmosis can be the most common membrane process used for desalination from oily wastewater (Pombo et al., 2011) and can produce water suitable for reuse in the petroleum industry. Salt rejection of RO membranes can be 99% or higher. The RO process requires effective oil and grease removal pretreatment due to fouling susceptibility of RO membranes by oil and hydrocarbons. Most membrane manufacturers recommend <0.1 mg/L O&G in the RO influent, and cases have been documented where as little as 0.001 mg/L of a hydrocarbon in the influent irreversibly fouled RO systems (IPIECA, 2010).

Al-Jeshi and Neville (2008) investigated to determine the feasibility of using RO membranes to treat water containing up to 50% (by volume) oil and evaluated the effect of varying the feed pressure, pH, and temperature on the separation performance of two thin-film composite polyamide RO membranes. They reported that in experiments involving contaminated water with up to 30% oil, high permeate quality was attained with more than 99% oil rejection being achieved. In some circumstances, oil contamination resulted in an increase in membrane flux and, as an example, at 50% oil contamination, an increase in membrane flux of 40% was observed. However, membrane permeate quality deteriorated at these high concentrations. The product water quality improved significantly with decreasing feedwater pH and temperature effects on permeate quality were found to be minimal. Increased feedwater pressure also led to significant improvement in permeate quality in terms of the TOC. Kim et al. (2011) used NF and RO membranes to remove salt ions from oil sands process-affected water (OSPW). Feedwater must be pretreated to manage fouling, because membrane treatments of OSPW are impeded by membrane fouling due to suspended solids. They investigated NF and RO pretreatment methods such as coagulation—flocculation—sedimentation (CFS), with and without coagulant and coagulant aids. They reported that membrane permeability was enhanced by the addition of coagulant and coagulant aids. Organic and oily constituents in OSPW increased the negative charge and hydrophobicity of the membrane, decreasing membrane performance. Efficient chemical cleaning was achieved with 1 mM acid, and flux recovery was achieved to 81% after cleaning. They concluded that the pretreatment improved desalination of OSPW for both NF and RO membranes. Silva et al. (2015) treated oil-in-water emulsions to obtain high-quality water for reuse. To this end, they used pretreatment with electro-coagulation to minimize fouling on the membrane and initially reduce the pollutant load, followed by RO. A residence time of 6 min was found to be enough to reach a constant level in terms of removal efficiencies, which were, regardless of the type of emulsion, over 99.5% in turbidity, 96% in color, and 92% in COD. The subsequent step of RO reached 100% removal of COD and absorbance, over 99.9% of turbidity, 98.9% of TDS, 99.1% electrolytic conductivity, and 99.6% of aluminum ions, achieving the limiting flux for permeate of 20 L/h m^2 at a net pressure drop through the membrane of 2.874 MPa. Over the 2 h of the experiment, there was a small permeate flux decrease.

6.4.4.5 Other Advanced Wastewater Treatment Methods

Ion exchange, electrodialysis (ED), electrodialysis reversal (EDR), and advanced oxidation processes (AOPs) such as hydrogen peroxide/ultraviolet (H_2O_2/UV), ozonation process, Fenton and photo-Fenton, heterogeneous photocatalysis, electrochemical oxidation, wet air oxidation (WAO), and supercritical water oxidation (SCWO) are other advanced wastewater treatment methods that will remove recalcitrant pollutants to make the effluent suitable for discharge or reuse.

6.4.4.5.1 Ion Exchange

Ion exchange is a reversible reaction in which charged ions present in the solution are replaced by similarly charged ions present within the insoluble exchange material (Arthur et al., 2005). This process is primarily used for water softening or hardness removal, where calcium, magnesium, and other cations are exchanged for sodium and for water demineralization. It can effectively be used to remove barium, cadmium, chromium (III), silver, radium, nitrites, selenium, arsenic (V), chromium (VI), and nitrate. Ion exchange is usually the best choice for small systems that need to remove radionuclides (National Drinking Water Clearinghouse, 1997). In the petroleum industry, it can be an option for the removal of dissolved inorganic compounds such as heavy metals, nitrates, etc., from the wastewater (Arthur et al., 2005; IPIECA, 2010).

Ion-exchange materials may be classified as: (1) naturally occurring ion exchangers (organic and inorganic); (2) synthetic ion exchangers (organic and inorganic); (3) composite ion exchangers; and (4) ion-exchange membranes (IEMs) (International Atomic Energy Agency, Vienna, 2002). Naturally occurring inorganic zeolites and synthetically produced organic resins may be applied in ion-exchange process (Arthur, Langhus, and Patel). Ion-exchange resins are classified as cation exchangers, which exchange positively charged ions and anion exchangers, which exchange negatively charged ions. The resins can further be divided into strong-acid cation resins, weak-acid cation resins, strong-base anion resins, and weak-base anion resins, which are summarized in Table 6.4.

Table 6.4 **Characteristics, Reactions, and Regeneration of Ion-Exchange Resins (Arthur et al., 2005)**

Type of Resin	Characteristics	Ion-Exchange Reaction	Regeneration
Strong-acid cation resins	The hydrogen or sodium forms of these resins are highly dissociated and H^+ or Na^+ ions are readily exchangeable over the entire pH range. The hydrogen form and sodium form can be used for complete deionization and water softening, respectively.	$2RSO_3Na + Ca^{2+} \leftrightarrow (RSO_3)_2Ca + 2Na^+$	These resins are regenerated to the hydrogen form by contact with a strong-acid solution, or to the sodium form with a sodium chloride solution.
Weak-acid cation resins	These resins have carboxylic acid (COOH) group and behave similarly to weak organic acids that are weakly dissociated. Capacity of these resins depends in part on solution pH and they have high affinity for divalent salts. These resins are used to treat industrial water with high hardness, exclusively for calcium bicarbonate and carbonate.	$2RCOONa + Ca^{2+} \leftrightarrow (RCOO)_2Ca + 2Na^+$	Regeneration of these resins to the hydrogen form is possible with significantly less acid than is required for strong-acid resins.
Strong-base anion resins	These resins are highly ionized and can be used over the entire pH range. These resins are used in the hydroxide (OH^-) form for water deionization.	$RR'_3NOH + Cl^- \leftrightarrow RR'_3NCl + OH^-$	Regeneration with concentrated sodium hydroxide (NaOH) converts the exhausted resin to the hydroxide form.
Weak-base anion resins	These resins have weak-base functional groups in which the degree of ionization is dependant on pH. These resins exhibit minimum exchange capacity above a pH of 7.	$RNH_3OH + Cl^- \leftrightarrow RNH_3Cl + OH^-$	

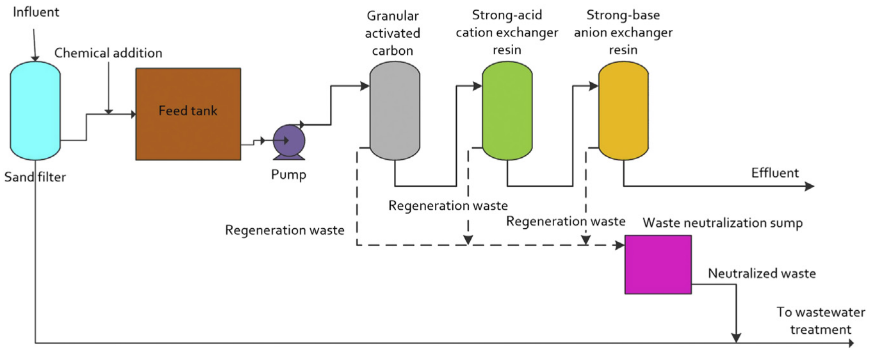

Figure 6.17 Schematic process flow diagram of an ion-exchange system.
Modified from IPIECA, 2010. Petroleum Refining Water/Wastewater Use and Management. IPIECA Operations Best Practice Series, London, United Kingdom.

Ion exchange is usually applicable when the dissolved solids concentration is less than 400 mg/L. This process can be applied to treat the petroleum industry effluent (e.g., refinery effluent) to a suitable standard for reuse. For example, it can be used to treat the effluent for supplementing the raw feedwater to the refinery or to boiler feedwater quality using weak acid and base resins or alternately stronger resins, respectively. A schematic PFD of an ion-exchange system, which can be used for reuse purposes, is shown in Fig. 6.17 (IPIECA, 2010).

Cechinel et al. (2016) investigated four brown macro-algae, *Ascophyllum nodosum*, *Fucus spiralis*, *Laminaria hyperborea*, and *Pelvetia canaliculata* as natural cation exchangers for the removal of transition metals from a petrochemical wastewater. They reported that *L. hyperborea* showed a higher uptake capacity than the other brown algae tested. The equilibrium affinity constants for the functional groups decreased in the following order: Cu > Zn > Ni ≈ Ca, except for *L. hyperborea*, which presented a lesser affinity for Ca. Ion-exchange breakthrough curves obtained from a fixed-bed column packed with raw *L. hyperborea* led to an operating capacity of 0.22, 0.10, and 0.05 mEq/g for Cu, Zn, and Ni, corresponding to 1558, 515, and 528 BV (7.2 BV/h), respectively. The treatment strategy consisted of the operation of two consecutive columns; the first one for copper-ions removal (operating capacity of 1558 BV—7.2 BV/h) and the second one for zinc and nickel removal (operating capacity of 163 BV—7.3 BV/h). The elution of Cu, Zn, and Ni from the natural resin was achieved with 10 and 6 BV of HCl (0.4 M, 1.2%) (150 and 90 g HCl/L of resin), using a flow rate of 3.6 BV/h, respectively, for the first and second columns.

6.4.4.5.2 Electrodialysis and Electrodialysis Reversal

Electrodialysis (ED) and electrodialysis reversal (EDR) processes may be used to remove ions (dissolved salts) from oily wastewater in the petroleum industry. Electrodialysis refers to transportation of salt ions from one solution through IEMs to another solution under the influence of an electrical field in an ED cell. Dissolved anions move toward the anode while cations are attracted by the cathode. The cell consists of a feed or dilute compartment and a concentrate compartment formed by an anion-

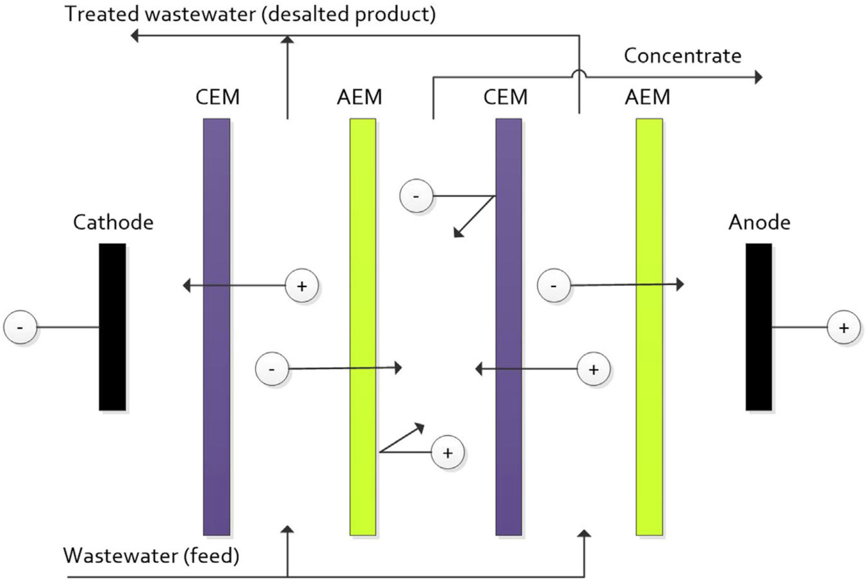

Figure 6.18 Principle of the electrodialysis method.

exchange membrane (AEM) and a cation-exchange membrane (CEM) placed between two electrodes. Anion-exchange membrane is permeable to anions but not to cations, and CEM works analogously but in the opposite way. The concentrate and desalted water (treated wastewater) are continuously removed from the system (Fig. 6.18). Almost all practical ED units consist of multiple ED cells with alternating AEMs and CEMs, which is called an ED stack (Arthur et al., 2005; Pombo et al., 2011).

An EDR unit operates on the same general principle as a standard ED system except that both the product (treated wastewater) and the concentrate channels are identical in construction (Arthur et al., 2005). The polarity of electrodes is periodically reversed, so that the direction of the ion movement is also reversed. Therefore the concentrate streams become the product water stream and vice versa (Arthur et al., 2005; Pombo et al., 2011). The periodic switching of polarity works as a self-cleaning mechanism, reducing the surface fouling of the IEM and consequently prolonging the membrane life (Pombo et al., 2011). Flushing allows these systems to operate with fewer pretreatment chemicals, minimizing membrane fouling (Arthur et al., 2005). These systems can operate under higher loads of organic matter, colloid particles, and microorganisms than can RO systems. These systems can also operate at relatively higher water recoveries (Pombo et al., 2011).

Tertiary oil-extraction technologies, especially polymer flooding, have been successfully applied to enhance oil recovery, but the enormous amount of produced oily wastewater is must be treated and reused. Electrodialysis is an important process in treating oily wastewater for reinjection (Guo et al., 2014). Jing et al. (2009) used an ED system to remove TDS from polymer flooding wastewater in crude oil. They studied the influence of flow rate and electrical potential on rate of TDS removal during ED operations. The removal rate of the main ions in polymer flooding wastewater was $Ca^{2+} > Cl^- > Na^+ > HCO_3^-$. They noted that from an economical viewpoint, energy consumption increased greatly and electrical potential increased for the same flow rate, but the influence of flow rate on energy consumption was not evident. Guo et al. (2014) revealed the fouling mechanism of an AEM caused by anion polyacrylamide (APAM) in ED. They carried out fouling experiments with different APAM concentrations at different current densities. The highest fouling phenomenon was observed with a higher APAM concentration at the current density close to the limiting value, which was indicated by evident increase of hydrophobicity and electrical resistance of the AEM. They reported gel-layer formation on the diluate side of the fouled AEM and the presence of APAM on this side. Zuo et al. (2014) focused on the characterization of SiO_2/PVDF AEM fouling in ED for the treatment of polymer flooding produced wastewater containing SS, APAM, and crude oil in the Daqing oilfield in China. Using morphological study, they reported only a small amount of cake layers located on the external surface of the SiO_2/PVDF AEMs fouled by SS and APAM, respectively. Meanwhile, there were more contaminants adsorbed on the membrane surface and in the membrane pores in the presence of crude oil. They also found that the SiO_2/PVDF membranes exhibited better antifouling capacity than the PVDF membranes indicated in the membrane-fouling behavior and desalination time. In addition, they revealed that the foulants on the membrane surfaces comprised not only organic substances but also inorganic elements. Guo et al. (2015) investigated chemical cleaning of ion-exchange membranes in plant-scale ED for treating oily wastewater. They reported that HCl was a more efficient cleaning agent for both CEM and AEM than NaOH and suggested that NaOH could effectively remove APAM fouling on CEMs, while HCl was better at removing APAM on AEMs, which can be reasonably explained by the deprotonation/protonation effects of NaOH/HCl on the electrostatic interactions between APAM molecules and ion-exchange membranes. They also expressed that NaOH was more effective at removing oil on IEMs, and inorganic precipitations could be eliminated by HCl cleaning through double decomposition and neutralization reactions. Moreover, they concluded that the inorganic fouling on the IEMs was mainly caused by the deposition of calcite, and the inorganic scales could mostly be removed by HCl cleaning.

6.4.4.5.3 Advanced Oxidation Processes

The advanced oxidation processes (AOPs) refer to clean technologies based on the generation of extremely reactive and nonselective hydroxyl radicals, with very high oxidative power ($E_0 = 2.8$ V) to degrade toxic organic compounds in a medium (Mota et al., 2008; Santos et al., 2011; Jafarinejad, 2015e). Due to their powerful capability to oxidize numerous organic compounds into CO_2, H_2O, etc., AOPs have been selected for various applications (Santos et al., 2011; Jafarinejad, 2014a,b, 2015a,b,e; Esplugas et al., 2002; Mota et al., 2008). These processes not only destruct pollutants but also inhibit consequent generation of toxic residues, whereas nondestructive physical separation processes only remove the pollutants, transferring them to other phases, thereby generating concentrated residues (Mota et al., 2008).

Nearly complete mineralization of organic compounds, including recalcitrant pollutants, no sludge production in some AOPs, and short time (i.e., minutes) needed for destruction depending on wastewater characteristics are some of the advantages of AOPs. In contrast, the addition of chemicals such as H_2O_2 and O_3 in some cases, use of electric energy when UV radiation is applied, and the effect of organic matrix of the solution on the reaction time are some of the disadvantages of these processes (Diya'uddeen et al., 2011; Dores et al., 2012).

According to Mota et al. (2008), the electrophylic addition of a hydroxyl radical to organic compounds (unsaturated or aromatic) that contain a π bond leading to the formation of organic radicals (Eq. 6.10), the hydrogen abstraction by reacting the hydroxyl radical with a saturated aliphatic compound (Eq. 6.11), and electron transfer with reduction of the hydroxyl radical into a hydroxyl anion by an organic substrate (Eq. 6.12) may be the possible reaction pathway in the AOPs. Note that a number of chemical species in water such as carbonate and bicarbonate ions can react with the hydroxyl radicals, hence competing with the organic substrates through the hydroxyl radicals (Mota et al., 2008).

$$\mathrm{HO^{\bullet} + Unsaturated\ or\ Aromatic \rightarrow Unsaturated - OH\ or\ Aromatic - OH} \tag{6.10}$$

$$\mathrm{HO^{\bullet} + R - H \rightarrow R^{\bullet} + H_2O} \tag{6.11}$$

$$\mathrm{HO^{\bullet} + R - X \rightarrow [R - X]^{+\bullet} + HO^{-}} \tag{6.12}$$

There are several AOPs for the generation of hydroxyl radicals, which can be classified as homogeneous and heterogeneous (Huang et al., 1993). These processes can also be classified based on light usage in them. Using to these classifications, Mota et al. (2008) presented the types of AOPs, which are shown in Table 6.5. Some of the processes applied for oily wastewater treatment by different researchers are discussed in this section.

In application of AOPs for treatment purposes, the following items should be considered:

- Due to use of the high-cost reagents such as H_2O_2 and O_3 and electric energy when UV radiation is applied, AOPs can be expensive processes.
- The AOPs can be considered an alternative treatment of wastewater that cannot be biologically treated.
- Use of AOPs as preliminary treatment operations to reduce toxicity followed by biological treatment can decrease the costs of these processes (Mota et al., 2008; Jafarinejad, 2015d).
- Wastewaters with higher COD would require very high consumption of reagents, precluding the treatment, thus the AOPs can be effective for wastewaters with COD below 5 g/L (Andreozzi et al., 1999; Mota et al., 2008).
- For wastewaters with high organic load, pretreatment operations such as dilution, coagulation, and flocculation are needed to decrease the initial load (Rivas et al., 2004; Mota et al., 2008).
- The AOPs can generally be applied in pre- or posttreatment in a biological process, contributing to the destruction of toxic or refractory pollutants (Pombo et al., 2011).

Table 6.5 Advanced Oxidation Processes (Mota et al., 2008)

Nonphotochemical	Photochemical
Homogeneous Processes	
Ozonation in alkaline media (O_3/HO^-)	Photolysis of water in vacuum ultraviolet (VUV)
Ozonation with hydrogen peroxide (O_3/H_2O_2)	UV/H_2O_2
Fenton (Fe^{2+} or Fe^{3+}/H_2O_2)	UV/O_3
Electro-oxidation	$UV/O_3/H_2O_2$
Electrohydraulic discharge (ultrasound)	Photo-Fenton (Fe^{2+} or $Fe^{3+}/H_2O_2/UV$)
Wet air oxidation (WAO)	
Supercritical water oxidation (SCWO)	
Heterogeneous Processes	
Catalytic wet-air oxidation (CWAO)	Heterogeneous photocatalysis: ZnO/UV, SnO_2/UV, TiO_2/UV, TiO_2/H_2O_2/UV

6.4.4.5.3.1 Hydrogen Peroxide/Ultraviolet Hydrogen peroxide (H_2O_2) is an oxidant with standard reduction potentials of 1.77 V, which can be used in water and wastewater purifications. The individual use of H_2O_2 is not efficient in oxidizing more complex and recalcitrant pollutants with a low reaction rate; however, its use in combination with other reagents or energy sources enhances the generation of hydroxyl radicals that will act as oxidizing agents (Mota et al., 2008). Hydroxyl radicals can be generated by photolysis of H_2O_2 (with UV irradiation in wavelengths shorter than 300 nm) as follows (Siedlecka and Stepnowski, 2006; Mota et al., 2008):

$$H_2O_2 \xrightarrow{hv} 2HO^{\bullet} \tag{6.13}$$

At higher H_2O_2 concentrations, the following reaction can occur in which H_2O_2 acts as a hydroxyl radical scavenger; however, hydroperoxyl radical ($HO_2^{\bullet}$) is formed (Alfano et al., 2001; Siedlecka and Stepnowski, 2006):

$$H_2O_2 + HO^{\bullet} \rightarrow HO_2^{\bullet} + H_2O \tag{6.14}$$

These radicals can attack the organic compounds, but it is necessary to note that the hydroperoxyl radicals have lower reduction potential (1.7 V) than that of hydroxyl radicals (2.8 V); therefore, their generation is not relevant to the H_2O_2/UV process. According to Lopez et al. (2000), Zhao et al. (2004), and Mota et al. (2008), an increase in the initial concentration of H_2O_2 can enhance the degradation rate of contaminants up to a maximum value, after which they begin to decrease as the concentration of H_2O_2 reaches very high levels because of hydroxyl radicals reacting with excess H_2O_2 to generate the hydroperoxyl radicals, instead of reacting with the organic compounds.

The low- or medium-pressure mercury vapor lamps, both with high intensity, can usually be used for photolysis of H_2O_2. The germicide lamp is a widely applied cheaper alternative; however, the efficiency is lower. In the H_2O_2/UV process, the operational pH should be low ($pH < 4$) (Mota et al., 2008).

The good solubility of H_2O_2 in water solutions, no mass transfer limitation, an effective source of HO•, no need for a separation process after treatment (Mota et al., 2008) or no secondary water pollution by decomposition products, high stability of commodity solutions during storage, and ecological compatibility (Simonenko et al., 2015) are some of the advantages of H_2O_2/UV process.

Stepnowski et al. (2002) investigated the influence of treatment with low concentrations of H_2O_2 combined with stirring and UV light on degradation of organic compounds in the refinery wastewater. They reported that TPHs oxidized at relatively low concentrations of H_2O_2 and additional UV irradiation slightly accelerated the process. It was shown that 1,2-dichloroethane and t-butyl methyl ether degraded in a similar manner, and except for the lowest H_2O_2 concentration used (1.17 mM), the reduction after 24 h was total. In the H_2O_2/UV process, the degradation rate for dichloromethane was the lowest and its maximum reduction was 83% using the highest applied H_2O_2 concentration of 11.76 mM. Philippopoulos and Poulopoulos (2003) studied oxidation of an oily wastewater from a lubricant-production unit using an H_2O_2/UV process. They noted that 20–45% COD removal was achieved with 830–1660 mg/L H_2O_2, and by GC–MS analysis they showed that the organic compounds of the wastewater decomposed to organic acids that were very resistant to photooxidation. Among these compounds, ethylene glycol remained almost unchanged by the attack from hydroxyl radicals. The addition of acidic pH and Fe(III) significantly enhanced the photooxidation of the wastewater. Poulopoulos et al. (2006) treated phenol aqueous solutions using an H_2O_2/UV process. Although the direct photolysis of phenol and its oxidation by H_2O_2 (without UV) were insignificant, the combination of UV and H_2O_2 was extremely effective at phenol degradation. However, the COD was on no occasion entirely eliminated, indicating the resistance of the intermediate products formed to the photooxidation. Increasing the initial concentration of phenol had as a result lower phenol conversions, whereas the increase in H_2O_2 initial concentration significantly enhanced the degradation of phenol. In contrast, COD removal was less sensitive to these changes. Coelho et al. (2006) investigated the performance of several AOPs such as H_2O_2, H_2O_2/UV, UV, photocatalysis, ozonation, Fenton, and photo-Fenton to treat petroleum refinery sourwater. None of the processes, except Fenton and photo-Fenton, led to satisfactory results, reducing at most 35% of the sourwater dissolved organic carbon (DOC). Siedlecka and Stepnowski (2006) investigated treatment of oily-port wastewater effluents using an H_2O_2/UV system. The effect of chemical oxidation on wastewater biodegradability was also examined. The exclusive use of H_2O_2 photolyzed by daylight results in efficient degradation rates for the low-peroxide concentrations used. Higher H_2O_2 concentrations inhibited degradation of organic contaminants in the wastewater.

The degradation rates of all contaminants were relatively high with the UV/H_2O_2 system, but degradation efficiencies were not distinguishably different when 20 or 45 min of UV irradiation was used. Excess H_2O_2 used in the process could inhibit phenolic degradation and could lead to the formation of a new phenolic fraction. The biodegradability of port wastewater did not increase significantly following the application of the AOP. Hu et al. (2008) studied photodegradation of methyl *tert*-butyl ether (MTBE), a gasoline additive and one of the most common contaminants in contaminated underground waters in the United States, due to leaks in gasoline-station storage tanks, by UV/H_2O_2 and UV/TiO_2 in batch-reactor systems. The optimal conditions at an initial MTBE concentration of 1 mM were acidic and 15 mM H_2O_2 in UV/H_2O_2 system, and pH 3.0 and 2.0 g/L TiO_2 in UV/TiO_2 suspended slurries system under 254-nm UV irradiation. Under optimal conditions, MTBE photodegradation during the initial period of 60 min in UV/H_2O_2 and UV/TiO_2 systems reached 98% and 80%, respectively. In both systems, MTBE photodegradation decreased with increasing MTBE concentration. While MTBE photodegradation rates increased with increasing dosage of H_2O_2 (5−15 mM) and TiO_2 (0.5 to 3 g/L), further increase in the dosage of H_2O_2 (20 mM) or TiO_2 (4 g/L) adversely reduced the MTBE photodegradation.

6.4.4.5.3.2 Ozonation Process Ozonation of water is an effective technique to oxidize many organic compounds in aqueous solution due to the strong oxidative properties of O_3. Unlike other oxidizing agents such as Cl_2, oxidation with O_3 leaves no toxic residues that have to be removed or disposed of (Krzemińska et al., 2015). Although the cost of ozone production is still high due to the high demand of energy to generate ozone (Pera-Titus et al., 2004; Mota et al., 2008; Jafarinejad, 2015a,e; Krzemińska et al., 2015), and the efficiency of ozone is extremely dependent on gas−liquid mass transfer, which is impeded by the low solubility of ozone in aqueous solution (Gogate and Pandit, 2004; Mota et al., 2008; Jafarinejad, 2015a,e), interest in the use of ozone in wastewater treatment has increased considerably in the last few years due to the numerous advantages of this process such as:

- No sludge remains;
- Danger is minimal;
- Degradation takes place in one step;
- It is easily performed;
- Little space is required; and
- All residual O_3 can be easily decomposed and converted to oxygen and water (Krzemińska et al., 2015).

Ozone has a high reduction potential (2.07 V), and can react slowly and directly with an organic substrate (R in Eq. 6.15) (Augugliaro et al., 2006; Mota et al., 2008; Jafarinejad, 2015a,e; Krzemińska et al., 2015). However, the use of ozone is only characterized as an AOP when it decomposes to generate hydroxyl radicals (Eq. 6.16), and can be catalyzed by hydroxyl ions in alkaline medium or by transition metal cations (Augugliaro et al., 2006; Pera-Titus et al., 2004; Mota et al., 2008; Jafarinejad, 2015a,e).

$$O_3 + R \rightarrow RO + O_2 \tag{6.15}$$

$$2O_3 + 2H_2O \rightarrow 2HO^{\bullet} + 2HO_2^{\bullet} + O_2 \tag{6.16}$$

The efficiency of ozone in degrading organic compounds is improved when combined with catalyst (Munter, 2001), H_2O_2, UV radiation, or ultrasound (Mota et al., 2008; Jafarinejad, 2015e).

Ozonation reactions can be accelerated by using heterogeneous or homogeneous catalysts. Several metal oxides and metal ions (Fe_2O_3, Al_2O_3—Me, MnO_2, Ru/CeO_2, TiO_2—Me, Fe^{2+}, Fe^{3+}, Mn^{2+}, etc.) have been investigated, and significant acceleration in the decomposition of the target compound has been observed (Munter, 2001).

The addition of H_2O_2 to O_3 (the mixture of ozone and hydrogen peroxide is called peroxone) can initiate the decomposition cycle of O_3 (Munter, 2001), resulting in the formation of hydroxyl radicals as follows (Mota et al., 2008):

$$O_3 + H_2O_2 \rightarrow HO^{\bullet} + HO_2^{\bullet} + O_2 \tag{6.17}$$

O_3 can readily absorb UV radiation at 254 nm wavelength producing H_2O_2 as an intermediate (Eq. 6.18), which can then decompose to hydroxyl radicals under exposure of UV light as shown by Eq. (6.13) (Munter, 2001; Mota et al., 2008).

$$O_3 + H_2O \xrightarrow{hv} H_2O_2 + O_2 \tag{6.18}$$

Utilization of ultrasound and O_3 may also strengthen the generation of hydroxyl radicals due to the reduction of mass-transfer limitations resulting from the turbulence creation by the acoustic current induced by ultrasound (Gogate and Pandit, 2004; Mota et al., 2008).

According to Munter (2001), ozone in combination with GAC can be a good choice for the solution of environmental problems in the petroleum industry. The ARCO Products Company has been treating c.1 million gallons of oily wastewater annually at its Richmond, CA, United States, petroleum-product storage and transportation facility since 1991. This facility was so successful that the company had installed four additional ozone/GAC facilities by 1993.

Kornmüller et al. (1997) studied the ozonation of 3 to 5 ring condensed PAHs in synthetic oil—water emulsions by batch experiments. They reported that PAHs can be oxidized selectively in the presence of high concentrations of dodecane as an aliphatic solvent. No oxidation of dodecane, as a representative of mineral oil, could be observed during experiments, even at pH around 11. At acidic to neutral pH, high oxidation rates of the PAHs were achieved due to a direct reaction with ozone. In the investigated range of 20—40°C, no influence of temperature on the ozonation of benzo(k)fluoranthene could be found. They also noted that during competitive ozonation of five PAHs, the reactions were completed in the sequence of acenaphthene, pyrene and finally benzo(e)pyrene, benzo(k)fluoranthene, and phenanthrene almost at the same time. Kornmüller and Wiesmann (1999) investigated the continuous ozonation of PAHs in a two-stage ozonation system followed by aerobic biological degradation. The highly condensed PAHs benzo(e)pyrene and benzo(k)fluoranthene were oxidized selectively in synthetic oil—water emulsions. The dissolved O_3 concentration was influenced by temperature to a higher degree than the reaction rate of PAH. They expressed that in dependence on pH, PAH oxidation took place by a direct reaction with O_3 inside the oil droplets. They quantified two main ozonation products of benzo(e)pyrene at different retention times during ozonation that could be transformed in the biological treatment step.

Chang et al. (2001) investigated the feasibility of using a UF membrane and O_3 treatment to reuse oily wastewater generated from the automobile-components manufacturing industry. They reported that the UF permeates from the degreasing wastewater could be reused as makeup water. However, the cutting oil formulated with the UF permeates had very different characteristics such as emulsion size and foaming ratio because surfactant existed excessively in the UF permeates. Partial oxidation of surfactants in UF permeates using O_3 makes it impossible to change the emulsion size, foaming ratio, and refractory index, and thus possible to reuse the UF permeates as process water. Garoma et al. (2008) studied the treatment of real groundwater samples contaminated with gasoline components, such as BTEX, MTBE, *tert*-butyl alcohol (TBA), and other gasoline constituents in terms of TPHs as gasoline (TPHg) by an O_3/UV process in a semibatch reactor under different experimental conditions. The O_3/UV process was very effective compared to ozonation in the removal of the gasoline components from these samples. For the various gasoline constituents, more than 99% removal efficiency was achieved for the O_3/UV process and the removal efficiency for ozonation was as low as 27%. The net ozone consumed per mol of organic carbon (from BTEX, MTBE, and TBA) oxidized varied in the range of 5—60 for different types of groundwater samples treated by the ozone/UV process. In ozonation experiments, it was observed that the presence of a sufficient amount of iron in groundwater samples improved the removal of BTEX, MTBE, TBA, and TPHg. Chen et al. (2014) investigated the catalytic ozonation of heavy oil-refining wastewater (HORW) over activated carbon-supported iron-oxide (FAC) catalysts using activated carbon (AC) as the reference. A significant increase in COD removal efficiency was observed in FAC/O_3 compared with AC/O_3 due to more hydroxyl radicals identified by TBA. The composition analysis of organic pollutant in HORW by FT—ICR MS discovered organic pollutants chain scission and oxidation process during the treatment. Great improvement of biodegradability for treated HORW was obtained.

Kiss et al. (2014) evaluated the economics of combined membrane processes and AOPs to model remediation oily wastewater (0.01 wt% petroleum). The AOPs (e.g., preozonation) may increase the membrane-separation process efficiency, especially the retention values. They concluded that the two-stage (MF/UF) membrane-separation process resulted in higher efficiency, but the fixed capital and the working capital costs were about 25% higher than the preozonation combinated MF.

6.4.4.5.3.3 Fenton and Photo-Fenton Processes Fenton's reaction is a nonexpensive and environmental friendly oxidation method, which was discovered by Fenton in 1894 when he strongly improved tartaric acid oxidation with the use of ferrous ion

(Fe^{2+}) and H_2O_2 (Fenton, 1894; Santos et al., 2011). This process is widely used in wastewater treatment. Fenton's reagent is a solution of H_2O_2 and ferrous ions with a complex mechanism, which can be simplified by the following equations (Santos et al., 2011; Mota et al., 2008; Sun et al., 2007; Jiang et al., 2010; Jafarinejad, 2015e):

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + OH^- + HO^\bullet \tag{6.19}$$

$$\text{Organic matter} + HO^\bullet \rightarrow \text{Oxidation intermediates} \tag{6.20}$$

$$\text{Oxidation intermediates} + HO^\bullet \rightarrow CO_2 + H_2O \tag{6.21}$$

$$H_2O_2 + HO^\bullet \rightarrow H_2O + HO_2^\bullet \tag{6.22}$$

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + HO^- \tag{6.23}$$

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \tag{6.24}$$

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe^{III}(HO_2)^{2+} + H^+ \tag{6.25}$$

$$Fe^{III}(HO_2)^{2+} \rightarrow Fe^{2+} + HO_2^\bullet \tag{6.26}$$

Briefly, the reaction between ferrous ions and H_2O_2 produces hydroxyl radicals with high oxidative power (Eq. 6.19) that attack the organic compounds present in the water (Eq. 6.20). Unfortunately, some parallel reactions occur (Eqs. 6.22–6.24), and so the hydroxyl radicals are not only consumed to degrade the organic matter but also to produce other radicals, with less oxidative power, or other species (scavenging effect of HO•). In addition, this leads to the undesired consumption of H_2O_2 (Eq. 6.22). On the other hand, Eqs. (6.25) and (6.26) indicate generation of Fe^{2+} by the reaction between H_2O_2 and Fe^{3+} (Fenton-like process); this way ferrous ion is restored, acting as catalyst in the overall process (Santos et al., 2011; Jafarinejad, 2015e).

In Fenton's reaction system, no energy input is necessary to activate H_2O_2. Therefore this method offers a cost-effective source of hydroxyl radicals, using easy-to-handle reagents. However, the production of a substantial amount of $Fe(OH)_3$, which precipitates and causes additional water pollution by the homogeneous catalyst added as an iron salt that cannot be retained in the process, is a possible disadvantage of this system (Awaleh and Soubaneh, 2014).

According to Motal et al. (2008), the ideal pH in Fenton's reaction is 3. Therefore the pH of wastewater must be adjusted before adding the Fenton reagents. In addition, although a $[Fe^{2+}]/[H_2O_2]$ ratio of 1:2 has a higher degradation rate of organic compounds, it is typically recommended to apply the 1:5 ratio, which yields similar results and needs fewer reagents.

Fenton reaction rates are strongly accelerated by irradiation with UV/visible light which this process is commonly called photo-Fenton system (Munter, 2001;

Mota et al., 2008; Molkenthin et al., 2013; Awaleh and Soubaneh, 2014). In the reaction of the photo-Fenton process, Fe^{2+} ions are oxidized by H_2O_2 to Fe^{3+} and one equivalent hydroxyl radical is generated (Eq. 6.19). In aqueous solutions, the resulting Fe^{3+} act as the light-absorbing species that produce another radical, while the initial Fe^{2+} is reproduced as shown in Eq. (6.27), and the cycle continues (Alalm and Tawfik, 2013).

$$Fe^{3+} + H_2O \xrightarrow{hv} Fe^{2+} + OH^{\bullet} + H^{+} \tag{6.27}$$

H_2O_2 concentration, iron addition, and the operating pH can affect Fenton and photo-Fenton processes. According to Mota et al. (2008), radiation utilization in the photo-Fenton reaction significantly reduces the concentration of the ferrous ions needed compared to the Fenton reaction (in the absence of light). According to Faust and Hoigne (1990), Munter (2001), and Mota et al. (2008), at a pH between 2.5 and 5 (e.g., pH = 3), the dominant species in the photo-Fenton process is the ferric complex $Fe(OH)^{2+}$ which the photolysis of this complex (wavelengths <410 nm) can be the largest source of hydroxyl radicals.

The need for low pH values (normally below 4) and the probable requirement to remove iron after the reaction, are some of the disadvantages of the photo-Fenton process, while the possibility of using solar radiation in this reaction is the main advantage of this process (Mota et al., 2008).

Safarzadeh-Amiri et al. (1997) investigated the UV−vis/ferrioxalate/H_2O_2 process for the treatment of different wastewaters containing chlorobenzene, BTX, 1,4-dioxane, methanol, formaldehyde, and formic acid and compared the efficiency of this process with alternative oxidation processes including the UV/H_2O_2 and UV−vis/Fe(II)/H_2O_2 processes. They reported that in nearly all cases, the UV−vis/ferrioxalate/H_2O_2 process had much higher efficiency (by a factor of about 3−30) than did either the UV−vis/Fe(II)/H_2O_2 process or the UV/H_2O_2 process. They concluded that this process was very efficient and useful for the treatment of moderate to highly contaminated waters.

Tiburtius et al. (2005) studied the efficiency of AOPs for the degradation of aqueous solutions containing BTX and gasoline-contaminated waters. They showed that BTX can be effectively oxidized by the photo-Fenton process, and almost total degradation of BTX and removal of more than 80% of the phenolic intermediates can be achieved at reaction times of about 30 min. Preliminary investigations using gasoline-contaminated waters showed good potentiality of the process for the treatment of large volumes of aqueous samples containing these polluting species. They also reported that heterogeneous photocatalysis and H_2O_2/UV system showed lower degradation efficiency, probably due to the heterogeneous character of the TiO_2-mediated system and loss of photonic efficiency of the H_2O_2/UV system in the presence of highly colored intermediated. Galvão et al. (2006) applied the photo-Fenton process for the treatment of wastewaters contaminated with diesel oil and reported that this process was technically feasible for the treatment of diesel oil-contaminated wastewaters, with total mineralization. As noted before, Coelho et al. (2006) investigated the performance of several AOPs such as H_2O_2, H_2O_2/UV, UV, photocatalysis, ozonation, Fenton, and photo-Fenton to treat petroleum refinery sourwater. None of the processes, except Fenton and photo-Fenton, led to satisfactory results, reducing at most 35% of the sourwater DOC. They reported that the Fenton reaction in batch mode was very fast and reached, in a few minutes, an ultimate DOC removal of 13–27% due to the formation of iron complexes. Radiation for an additional period of 60 min could enhance DOC removal up to 87%. DOC removals above 75% were also reached in a continuous mode, operating one 0.4 L Fenton stirred reactor and one 1.6 L photo-Fenton reactor in series, when the reaction system was operated with HRT higher than 85 min. Mater et al. (2007) evaluated the effectiveness of the use of Fenton's reagent to mineralize organic compounds in water and soil contaminated by crude petroleum. Up to 75% TOC removal efficiency was attained in water and 70% in soil when high H_2O_2 (20%) and low Fe^{2+} (1 mM) concentrations were applied. Besides increasing the degree of mineralization, Fenton's reaction increased the biodegradability of petroleum compounds (BOD_5/COD ratios) by a factor of up to 3.8 for contaminated samples of both water and soil. They showed that low reagent concentrations (1% H_2O_2 and 1 mM Fe^{2+}) were sufficient to start the degradation process, which could be continued using microorganisms, and could lead to a decrease in reagent costs in the treatment of petroleum-contaminated water and soil samples.

Silva et al. (2012) investigated the treatment of produced water containing BTEX by integrating two processes including IAF and photo-Fenton. They reported that degradations above 90% were reached in all cases after 90 min of reaction, attaining 100% mineralization in the optimized concentrations of Fenton reagents. Process integration was adequate with 100% organic-load removal in 20 min. They noted that the results of the integration of the IAF with the photo-Fenton met the effluent limits established by the Brazilian legislation for disposal. Aljuboury et al. (2015) investigated the performance of using Fenton's reagent in the solar photocatalyst of TiO_2 to treat petroleum wastewater from the Sohar oil refinery in Oman, Saudi Arabia. The obtained optimum conditions were reaction time of 90 min, 0.66 g/L TiO_2, 0.5 g/L H_2O_2, 0.01 g/L Fe^{2+}, and pH 4.18. TOC and COD removal rates were 62% and 50%, respectively, and 0.8 ppm residual iron was obtained. They concluded that solar photo-Fenton process was efficient for petroleum wastewater treatment in acidic conditions $pH < 7$ and more economic by free energy. Estrada-Arriaga et al. (2016) evaluated posttreatment using photo-ferrioxalate and Fenton's reaction from real oil refinery effluent with high concentrations of phenols (200 mg/L) as alternative processes to simultaneously reduce COD, phenols, and others pollutants contained in petroleum refinery wastewater. They reported that COD and phenol removals for photoferrioxalate reaction in concentrations of 200 mg/L of oxalate, 20 mg/L Fe^{2+}, and 500 mg/L of H_2O_2, and a pH 5 were 84% and 100%, respectively. The COD and phenol removals for Fenton's reaction in concentrations of H_2O_2 and Fe^{2+} of 300 and 20 mg/L, respectively, and a pH 4 were 55% and 100%, respectively. The reaction time in both AOPs was 120 min. After the treatment with photo-ferrioxalate reaction, the treated wastewater was transferred to a UF hollow-fiber module, with a pressure rate between 8.8 and 18.5 psi (8.8 and 38 mL/min). Removal efficiencies of 66.3% for COD and >99% for TSS were obtained during the UF membrane test. The final concentrations of COD, phenol, sulfides, TSS, turbidity, and color, after photoferrioxalate-UF membrane treatment, were reported to be 22 mg/L (total removal 94%), <0.5 mg/L, <0.2 mg/L, <1 mg/L, 2 NTU, and 254 Pt-Co, respectively.

6.4.4.5.3.4 Heterogeneous Photocatalysis According to Kamboj (2009), Plotnikov noted photocatalysis for first time in the 1930s in his book *Allaemeine Photochemie*. In the 1950s, Markhani and Laidler performed a kinetic study of photo-oxidation on the surface of zinc oxide (ZnO) in aqueous suspensions. By the 1970s researchers began to perform surface studies on photocatalysts like zinc oxide and titanium oxide (TiO_2) (Kamboj, 2009). Heterogeneous photocatalysis has been intensively studied since Fujishima and Honda (1972) discovered the photochemical splitting of water into hydrogen and oxygen in the presence of TiO_2 (Kamboj, 2009; Kaan et al., 2012; Ibhadon and Fitzpatrick, 2013). Since the 1980s, photocatalysis has been examined by many scientists for environmental (air, water, and soil) cleanup (Fujishima et al., 2007; Mota et al., 2008; Kamboj, 2009; Jafarinejad, 2015e).

The acceleration of photoreaction in the presence of a catalyst is called heterogeneous photocatalysis (Ibhadon and Fitzpatrick, 2013). According to Mota et al. (2008), the principle of heterogeneous photocatalysis (Fig. 6.19) is based on the activation of a semiconductor particulate material (CdS, TiO_2, ZnO, WO_3, etc.) by the action of radiation with an appropriate wavelength. With the absorption of photons by the semiconductor particle possessing enough energy to promote the conduction of an electron (e^-) from its valence band (VB) to the conduction band (CB) (a transition called bandgap energy), activation is achieved and creating holes in the valence band (h^+) that will act as oxidizing sites (Mota et al., 2008; Jafarinejad, 2015e). In other words, illumination onto a photocatalyst produces an electron and hole pair

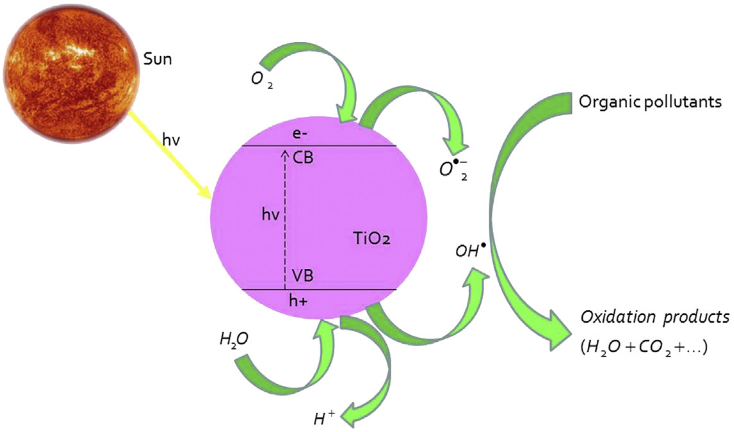

Figure 6.19 General mechanism of TiO_2 in solar photocatalysis process.
Modified from Ibhadon, A.O., Fitzpatrick, P., 2013. Heterogeneous photocatalysis: recent advances and applications, Catalysts 3, 189–218; Zhang, T., Wang, X., Zhang, X., 2014. Recent progress in TiO_2-mediated solar photocatalysis for industrial wastewater treatment: review article, Hindawi Publishing Corporation, International Journal of Photoenergy. Article ID 607954, 12 pp. [Online] Available from: http://dx.doi.org/10.1155/2014/607954.

(e^-/h^+) with high-energy state, which migrates to the particle surface, where it participates in redox reactions with adsorbed species and thus forms superoxide radical anion ($O_2^{\bullet-}$) and hydroxyl radical (OH•), respectively, as shown in Eqs. (6.28−6.31) (Hoffmann et al., 1995; Lee et al., 2003; Mok, 2009; Kamboj, 2009; Zhang et al., 2014; Krzemińska et al., 2015):

$$TiO_2 \xrightarrow{hv} TiO_2\left(e^- + h^+\right) \tag{6.28}$$

$$h^+ + H_2O \rightarrow OH^{\bullet} + H^+ \tag{6.29}$$

$$h^+ + OH^- \rightarrow OH^{\bullet} \tag{6.30}$$

$$e^- + O_2 \rightarrow O_2^{\bullet-} \tag{6.31}$$

According to Bockelmann et al. (1995) and Mota et al. (2008), the addition of H_2O_2 may also favor the heterogeneous photocatalytic process, given that, like O_2, it may act as the acceptor of electrons available in the system, generating hydroxyl radicals as follows:

$$e^- + H_2O_2 \rightarrow HO^{\bullet} + HO^- \tag{6.32}$$

The generated radicals are used as powerful oxidizing agents to convert organic pollutants into H_2O, CO_2 and less toxic byproducts (Hoffmann et al., 1995; Lee et al., 2003; Zhang et al., 2014; Jafarinejad, 2015b,e).

Artificial sources (e.g., UV polychromatic lamps) or the sun can be applied as radiation sources for the photocatalytic processes. Solar light-based photocatalytic degradations can be considered for economics (Banu et al., 2008; Mok, 2009; Krzemińska et al., 2015).

Initial organic load or initial concentration of substrate, catalyst, and state of catalyst, amount of catalyst, reactor's design, irradiation source, UV irradiation time, temperature, solution's pH, light intensity, and the presence of ionic species are the main variables that can affect the heterogeneous photocatalytic process in water and wastewater treatment (Stasinakis, 2008; Mok, 2009; Krzemińska et al., 2015).

A photocatalyst should have the following properties: photoactivity, biological and chemical inertness, stability toward photocorrosion, suitability for visible or near UV light-energy harnessing, low cost, and lack of toxicity (Ibhadon and Fitzpatrick, 2013). Various oxides such as TiO_2, ZnO, SiO_2, SnO_2, WO_3, ZrO_2, CeO, Nb_2O_3, Fe_2O_3, $SrTiO_3$, etc., or sulfides such as CdS, ZnS, etc., have been investigated in photocatalysis (Kaan et al., 2012; Krzemińska et al., 2015), but TiO_2 remained an excellent photocatalyst for its high resistance to photocorrosion and desirable bandgap energy. It is also easily available on the market, chemically inert and durable, and nontoxic (Kaan et al., 2012). It has different crystalline forms, the most common forms being anatase and rutile while the third, brookite, is uncommon and unstable. Anatase is more efficient than rutile in photocatalytic applications because of its more open structure compared with rutile. Degussa P25 is the commercially available form of TiO_2 and consists of two forms of approximating 25% rutile and 75% anatase (Ibhadon and Fitzpatrick, 2013). The utilization of excessive loadings of catalyst may reduce the amount of energy being transferred into the medium due to the opacity offered by the catalyst particles (Stasinakis, 2008; Krzemińska et al., 2015).

Supports play an important role in immobilizing active catalyst, increase the surface area of catalytic material, decrease sintering and improve hydrophobicity, thermal, hydrolytic, and chemical stability of the catalytic material (Ibhadon and Fitzpatrick, 2013). Activated carbon, fiberoptic cables, fiberglass, glass, glass beads, glass wool, membranes, quart sand, zeolites, silica gel, stainless steel, and Teflon have been investigated as TiO_2 supports (Mok, 2009).

Photocatalytic reactors for wastewater treatment may be categorized based on their design characteristics such as state of the photocatalyst, type of illumination, and position of the irradiation source (Mok, 2009). Based on the state of the photocatalyst, the reactors can be briefly divided into two groups: a suspension/slurry type and a thin-film type (Mok, 2009; Kaan et al., 2012; Jafarinejad, 2015b). The main challenge in the design of a photocatalytic reactor is the efficient illumination of the catalyst (Ibhadon and Fitzpatrick, 2013). Photocatalytic reactors can be irradiated using artificial sources (e.g., UV polychromatic lamps) and/or solar light. The irradiation source position determines different configurations such as (1) reactors with an immersed light source; (2) reactors with an external light source; and (3) reactors with distributed light sources. Slurry reactors are extensively applied for treatment purposes (Mok, 22009). In slurry reactors, catalyst loading is an important design variable for the effective use of reactor space and photocatalyst, and a wide range (0.15−8 g/L) of optimal catalyst loading in aqueous suspensions has been reported (Ibhadon and Fitzpatrick, 2013). It is important to note that photocatalytic activity with TiO_2 slurry reactors is larger than with immobilized TiO_2 reactors. Good mass transfer phenomena is the advantage of TiO_2 slurry reactors, while the main disadvantage is that the catalyst requires long settlement times to be separated from the solution and fine filters have to be used. Thus photocatalytic immobilized TiO_2 reactors have been increasingly applied (Mok, 2009).

Minero et al. (1997) investigated the degradation of some crude-oil components (dodecane and toluene) via photocatalysis using seawater media. No chlorinated compounds were found over the course of irradiation, and they reported 100% degradation after just a few hours of illumination. Preis et al. (1997) studied photocatalytic oxidation of phenolic compounds (phenol, p-cresol, resorcinol, and 5-methylresorcinol (5-MR)) in wastewater from oil-shale treatment. Methylated phenolic substitutes (p-cresol, 5-MR) yield better photooxidation than nonmethylated compounds. They compared the results obtained from the experiments with model compounds with the results of photooxidative purification of wastewaters produced from the thermal treatment of oil shale in Estonia. They concluded that being heavily polluted, the wastewater yielded better to photooxidation when slightly diluted with potable water in a 3:1 ratio. The photooxidatively pretreated wastewater also showed better biodegradability and lower toxicity to bacteria than untreated wastewater.

Grzechulska et al. (2000) investigated photocatalytic decomposition of oil in water and reported complete oil decomposition after 2 h of UV illumination with the photocatalyst content of 0.5 g/dm^3. Bessa et al. (2001) studied photocatalytic/H_2O_2 treatment of oil field-produced waters from Campos Basin, Rio de Janeiro, Brazil. They noted that the addition of H_2O_2 in the photocatalytic process was unnecessary and even undesirable due to the corrosive and damaging effects of this substance on the catalysts (TiO_2). Ziolli and Jardim (2002) reported that seawater-soluble crude-oil fractions can be decomposed under the irradiation of nanoparticles of titania using artificial light. Alhakimi et al. (2003) compared photocatalytic degradation using the natural and artificial UV light of 4-chlorophenol as a representative compound in refinery wastewater. They reported that the degradation rate of 4-chlorophenol was 6.4 times and 1.6 times higher when using sunlight compared to the artificial UV lamp for Degussa P25 and Hombikat UV 100, respectively. The degradation rate of it was six times higher, compared to Hombikat UV 100, at the optimal conditions, when using sunlight and Degussa P25 as the catalyst. They measured chloride produced during the reaction and found that it was high for Degussa P25 with sunlight as the energy source. Araújo et al. (2006) studied the photodegradation of three types of soluble and emulsive cutting fluids in an aqueous medium using TiO_2 as catalyst in suspension and UV radiation. They observed the best performance of catalyst at pH 8.0 for all the fluids when most of 70% of the organic load was decomposed. Saien and Nejati (2007) used a circulating photocatalytic reactor with an immersed mercury UV lamp (400 W, 200−550 nm) for removing aliphatic and aromatic organic pollutants in refinery wastewater. They reported that optimum catalyst concentration, fluid pH, and temperature were at amounts of near 100 mg/L, 3, and 318K, respectively. A maximum reduction in COD was also more than 90% after about 4 h irradiation and hence, 73% after about only 90 min. In addition, they observed high-efficiency degradation of all pollutants using GC−MS and a GC analysis systems equipped with headspace injection technique.

Salu et al. (2011) used a novel photocatalytic drum reactor for the treatment of oily wastewater from an interceptor tank typically containing diesel oils obtained from Sureclean, an environmental cleanup company. They reported that TOC reduction was 45% following two 90 min treatment cycles. The TPH reduction was also 45% following 90 min irradiation and a further 25% during a second stage of treatment. They concluded that this reactor can be applied as a polishing technique assembled within a WWTP and allowing for more than one pass-through the reactor improves its efficiency. Soltanian and Behbahani (2011) used a photocatalytic process as tertiary treatment for wastewater from the Bandar Abbas Refinery. The optimized conditions were 3.0 g/L TiO_2 and pH of 6.3. They expressed that the use of H_2O_2 showed no beneficial effect. Phenols, DOC, and O&G removals were 93%, 56%, and more than 50%, respectively, in the catalytic process with UV radiation, improving the quality of the treated wastewater. Diya'uddeen et al. (2011) reviewed treatment technologies for petroleum refinery effluents and concluded that photocatalytic degradation has great potential for replacing other separation and degradation treatment approaches employed at the advanced treatment stage for petroleum refinery effluents. Shahrezaei et al. (2012) treated petroleum refinery wastewater in a photocatalytic reactor using

TiO_2 nanoparticles and reported a maximum reduction in TCOD of more than 83% at the optimum conditions (pH of 4, catalyst concentration of 100 mg/L, temperature of 45°C, and reaction time of 120 min). Ong et al. (2014) evaluated the performance of a submerged membrane photocatalytic reactor (SMPR) consisting of PVDF-TiO_2 hollow-fiber membranes for the separation and degradation of synthetic oily wastewater under UV irradiation. They observed that TOC degradation using PVDF-TiO_2 membrane was remarkably higher than neat PVDF membrane, and it was verified using GC—MS analysis that oil components in the wastewater could be efficiently degraded in the presence of TiO_2 under UV irradiation. The average flux of membrane was reported to be around 73.04 L/h m^2 using PVDF membrane embedded with 2 wt% TiO_2 at 250 ppm oil concentration with module-packing density of 35.3% and air-bubble flow rates of 5 L/min, and under these optimized conditions, TOC degradation and oil rejection were 80% and >90%, respectively. Al-Muhtaseb and Khraisheh (2015) prepared a series of Cu-doped TiO_2 catalysts by a sol-gel method and investigated them for removal of phenol from refinery wastewater under UV irradiation. They reported that undoped-TiO_2 catalysts prepared with ethanol solvent showed the highest phenol degradation rate, even though the surface area of isopropanol was six times higher than ethanol. However, for Cu-doped TiO_2 catalysts, catalysts prepared with isopropanol showed the highest photodegradation rate of phenol. Khan et al. (2015) studied the photocatalytic degradation of real refinery wastewater from National Refinery Limited (NRL) in Karachi, Pakistan, using TiO_2, ZnO, and H_2O_2. The maximum degradation was reported to be 40.68% by using TiO_2 at 37°C and pH of 4, within 120 min of irradiations. As TiO_2 was combined with H_2O_2 the degradation decreased to 25.35%. They concluded that for real refinery wastewater, TiO_2 was comparatively more effective than ZnO and H_2O_2. Real refinery wastewater can also react differently than synthetic refinery wastewater, oil field-produced water, or oil—water industrial effluent.

6.4.4.5.3.5 Electrochemical Oxidation Electrochemical oxidation includes the generation of hydroxyl radicals at the active sites of anode and has the potential to be a distinct economic and environmental choice for wastewater treatment, which has been applied for the decontamination and separation of various inorganic and organic pollutants (Rizzo, 2011; Krzemińska et al., 2015). According to Brillas et al. (1998), cited by Mota et al. (2008), in electrochemical processes, hydroxyl radicals can be produced by two means: anodic oxidation (direct form) and mediated electro-oxidation (indirect form). In anodic oxidation, the hydroxyl radical is formed in the anode of an electrochemical cell from water oxidation (Eq. 6.33). In mediated electro-oxidation, chemical species such as H_2O_2 are continuously produced in the cathode by the reduction of two electrons of dissolved oxygen, as shown by Eq. (6.34) (Brillas and Casado, 2002; Mota et al., 2008).

$$H_2O \rightarrow HO^{\bullet} + H^+ + e^- \tag{6.33}$$

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{6.34}$$

The H_2O_2 generated can act as a reagent for Fenton's system, with the addition of iron, leading to the generation of hydroxyl radicals according to Eq. (6.19). This process, whereby the H_2O_2 from Fenton's reaction is electrochemically produced, is called the electro-Fenton process (Brillas and Casado, 2002; Mota et al., 2008). According to Oturan and Brillas (2007), cited by Mota et al. (2008), the Fe^{3+} obtained with Fenton's reaction (Eq. 6.19) or added to the solution can be continuously reduced to Fe^{2+}, creating an electrochemical catalysis process, as shown in the following equation:

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{6.35}$$

In this system, as UV irradiation is applied to help reduce Fe^{3+} to Fe^{2+}, this technique is called a photoelectron-Fenton process (Wang et al., 2008; Mota et al., 2008).

Electrode and supporting electrolyte types, applied current, solution pH, nature of target contaminant/water matrix, and initial concentration of the pollutants can affect the efficiency of the electrochemical oxidation process (Rizzo, 2011; Krzemińska et al., 2015). Different anodes such as graphite, Pt, TiO_2, IrO_2, PbO_2, doped with SnO_2, several Ti-based alloys, and boron-doped diamond electrodes have been investigated in this system, but the most typically employed as an electrode material is iron or aluminum (Rizzo, 2011; Jafarinejad, 2014b; Krzemińska et al., 2015).

Yavuz and Koparal (2006) investigated electrochemical oxidation of phenol in a parallel-plate reactor using ruthenium-mixed metal-oxide electrode. Removal efficiency of 99.7% and 88.9% were reported for the initial phenol concentration of 200 mg/L and COD of 480 mg/L, respectively. In the same study, specific energy consumption of 1.88 kWh/g phenol removed and, mass transfer coefficient of 8.62×10^{-6} m/s were reported at the current density of 15 mA/cm^2. They also studied electrochemical oxidation of petroleum refinery wastewater at the optimum experimental conditions obtained and reported phenol removal of 94.5% and COD removal of 70.1% at the current density of 20 mA/cm^2. Santos et al. (2006) applied electrochemical technology for the remediation of wastewater from the oil-extraction industry. They noted that electrolysis of the oily wastewater led to a time-dependent reduction in COD in the sample, which could be attributed to: (1) the direct oxidation of oil components at the electrode, by the metal oxide itself, or by hydroxyl radicals available at the electrode surface; (2) the indirect oxidation of oil components by intermediate oxidizing agents formed in parallel reactions (e.g., ClO^-); and (3) the aggregation of suspended oil droplets by electro-flotation. The largest reduction (57%) in COD was reported following electrolysis of an oily sample for 70 h at 50°C with a current density of 100 mA/cm^2. Ma and Wang (2006) treated oil field-produced water by an electrochemical process in a laboratory pilot-scale plant (Fig. 6.20) using double anodes with active metal (M) and graphite (C) and iron as cathode and a noble metal content catalyst with big surface. Because of the strong oxidizing potential of the chemicals generated (Cl_2, O_2, OCl^-, HO•, and so on), when the wastewater passed through the laboratory pilot-scale plant the organic pollutants including bacteria were oxidized and coagulated by produced Mn^+ ion.

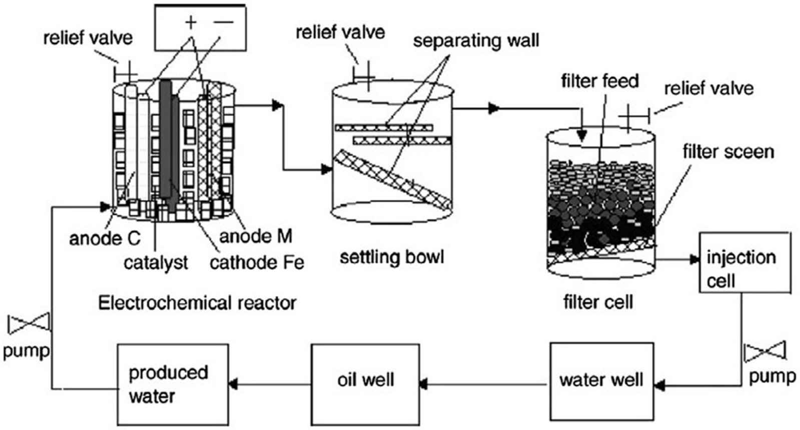

Figure 6.20 Schematic process flow diagram of electrochemical pilot-scale plant in Ma and Wang (2006) work.

They concluded that the catalytic electrochemical treatment of oil field-produced wastewater was effective. Both COD and BOD were reduced by over 90% in 6 min, SS by 99%, Ca^{2+} content by 22%, corrosion rate by 98%, and bacteria (sulfate-reducing bacteria (SRB), saprophytic bacteria (TGB), and iron bacteria) by 99% in 3 min under 15 V/120 A.

Yan et al. (2011) treated petroleum refinery wastewater by an electrochemical process with three-dimensional multiphase electrode, which introduced Fe particle and air into a traditional two-dimensional reactor. An effluent with a satisfactory COD removal efficiency (92.8%) and low salinity (84 μS/cm) was reported when the initial pH was 6.5, cell voltage was 12 V, and fine Fe particle was introduced. In other work, Yan et al. (2014) reported that the effluent with a satisfactory COD removal efficiency (89.91%) and NH_3-N removal efficiency (99.47%) was obtained when the initial pH was 3 and fine Fe particle and air were introduced simultaneously. El-Naas et al. (2014) developed a novel three-step process consisting of an electrocoagulation cell, a spouted bed bioreactor (SBBR) with pseudonymous putida immobilized in polyvinyl alcohol gel, and an adsorption column packed with granular activated carbon produced from agricultural waste, specifically date pits, and evaluated it for the treatment of highly contaminated refinery wastewater. The electrocoagulation cell unit was reported to be effective as a pretreatment step to reduce the large concentrations of COD and SS and reduce the load on the bioreactor and the adsorption column. They concluded that at optimum conditions and unit arrangement, the process was able to reduce the concentration of COD, phenol, and cresols by 97%, 100%, and 100%, respectively.

6.4.4.5.3.6 Wet Air Oxidation Zimmermann (1954) developed the wet-air oxidation (WAO) process (Siemens Water Technologies Corp., 2011) when he looked for an alternative technique to treat special black liquors from papermills. He could burn pulpmill liquors and introduced a technique using air at high pressure leading to the combustion of organic compounds dissolved or suspended in aqueous solution, at relatively low temperatures in the presence of oxygen (Debellefontaine and Foussard, 2000). Since then, WAO has been applied in many applications such as wastewater treatment (Debellefontaine and Foussard, 2000; Siemens Water Technologies Corp., 2011).

The WAO process is a clean technology in which the soluble or suspended organic or inorganic substances are oxidized at elevated temperatures and pressures using oxygen as the oxidizing agent (Copa and Dietrich, 1988; Siemens Water Technologies Corp., 2011). The temperature typically varies from approximately 175–320°C (Copa and Dietrich, 1988) or 150–320°C (Siemens Water Technologies Corp., 2011). System pressures of approximately 10–220 bar (Mota et al., 2008; Siemens Water Technologies Corp., 2011) are applied to restrict the amount of evaporation of water at the desired reaction temperature. Compressed air or pure oxygen is the source of oxygen that serves as the oxidizing agent in the WAO process (Copa and Dietrich, 1988). Hydroxyl radicals are formed in this system (Mota et al., 2008).

The degree of oxidation can determine the products of the WAO process. For low degrees of oxidation, organic matter is turned to low molecular weight organic compounds such as acetic acid. For high degrees of oxidation, organic matter is mainly oxidized to CO_2 and H_2O. Organic or inorganic sulfur is converted to sulfate. Organic nitrogen is turned primarily into ammonia. The halogens in halogenated organics are transformed to inorganic halides (Copa and Dietrich, 1988). Phosphorus compounds are converted to phosphates and chlorine compounds are transformed to hydrochloric acid. Thus the general material balance for the WAO process can be explained with the following reaction where the heat value is close to 435 kJ/(mole O_2 reacted) (Debellefontaine and Foussard, 2000):

$$\begin{gathered}C_mH_nO_kCl_wN_xS_yP_z + [m + 0.25(n - 3x) - 0.5k + 2(y + z)]O_2 \rightarrow \\ mCO_2 + 0.5(n - 3x)H_2O + xNH_3 + wCl^- + ySO_4^{2-} + zPO_4{}^{3-} + \text{heat}\end{gathered} \tag{6.36}$$

The basic flow diagram of a typical WAO unit is shown in Fig. 6.21. In this system, the liquid-waste (feed) stream containing the pollutant material is pumped into the system using a high-pressure pump. The compressed air or oxygen is introduced into the waste stream either at the discharge of the high-pressure pump or at the inlet to the reactor (Copa and Dietrich, 1988). The oxygen flow rate typically does not exceed 110% of the inlet COD flow rate (Debellefontaine and Foussard, 2000). The waste is preheated in a heat exchanger with the hot-treated effluent (Copa and Dietrich, 1988). Auxiliary energy, usually steam, is necessary for startup and can provide trim heat if needed (Siemens Water Technologies Corp., 2011). A vertical bubble column is usually applied as the reactor, which provides the required hydraulic detention time to effect the desired reaction (Copa and Dietrich, 1988). The desired reaction may range from mild oxidation, which needs a few minutes (e.g., 35 min), to total waste destruction, which needs an hour or more detention time (e.g., 36 h) (Copa and Dietrich, 1988; Debellefontaine and Foussard, 2000). According to Eq. (6.3), exothermic heat of oxidation is

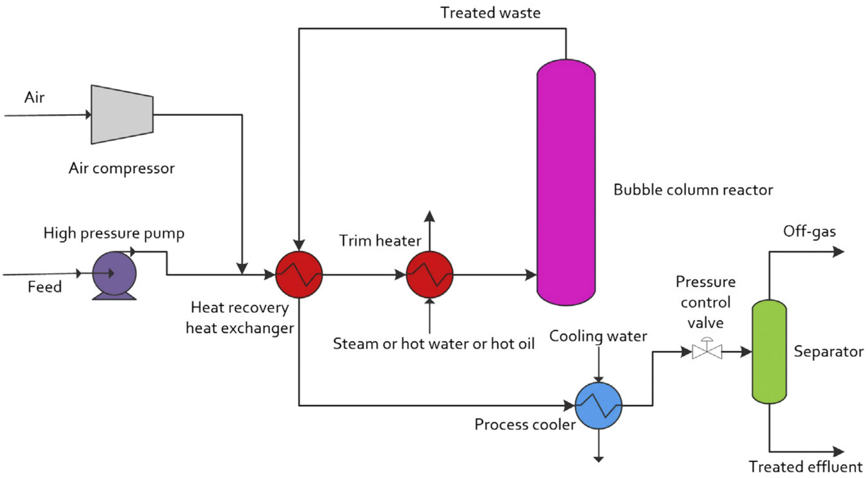

Figure 6.21 Basic flow diagram of a typical wet-air oxidation unit.
Modified from Copa, W.M., Dietrich, M.J., 1988. Wet Air Oxidation of Oils, Oil Refinery Sludges, and Spent Drilling Muds, Zimpro/Passavant Inc., April, 1988. [Online] Available from: http://infohouse.p2ric.org/ref/25/24892.pdf; Siemens Water Technologies Corp., 2011. Can You Treat the Most Difficult Wastewater With Only Air? Zimpro® Wet Air Oxidation Systems: The Cleanest Way to Treat the Dirtiest Water, Answers for Industry, Siemens Water Technologies Corp., GIS-WAO-BR-0111. [Online] Available from: http://www.energy.siemens.com/hq/pool/hq/industries-utilities/oil-gas/water-solutions/Zimpro-Wet-Air-Oxidation-System-The-Cleanest-Way.pdf.

released to the waste stream during oxidation. The temperature of the waste stream is commonly raised to the desired level in the reactor by this heat release. The hot, treated waste exits the reactor and is cooled in the process heat exchangers. The cooled effluent then exits the system through a pressure-control valve. The treated effluent and noncondensable off-gases are separated in a separator tank and discharged through separate lines (Copa and Dietrich, 1988). The gas stream coming out of a WAO treatment facility includes a limited number of VOCs and CO (0.5–25%) together with CO_2, O_2 in excess, and water. A simple postcombustion reactor may be applied as the final oxidation step of these gases before they are vented to the atmosphere (Debellefontaine and Foussard, 2000).

According to Debellefontaine and Foussard (2000), the COD reduction may generally be reached from 90% to 95% for most wastes in the WAO process. The operating cost is typically lower than 95 Euro/$m^{3,}$ and the preferred COD load can vary from 10 to 80 kg/m^3. Due to the required high capital investment and the operating problems, only a handful of industrial reactors are in operation worldwide. Temperature, pressure, inert gas flow rate, pH evolution during oxidation, etc., can affect the performance of a WAO unit and should be considered during reactor design (Debellefontaine and Foussard, 2000).

The efficiency of a WAO can be improved by using homogeneous catalysts (such as Cu^{2+} salts) and heterogeneous catalysts (MnO_2, CuO, $Fe_2O_{3,}$ etc.) in the reaction, which is called catalytic wet-air oxidation (CWAO) (Moat et al., 2008). Various heterogeneous catalysts including noble metals (such as Ru, Rh, Pd, Ir, and Pt) and metal oxides (oxides of Cr, Mn, Fe, Co, Ni, Cu, Zn, Mo, and Ce) have been widely investigated to enhance the efficiency of CWAO (Kim and Ihm, 2011).

Copa and Dietrich (1988) conducted bench-scale WAO studies at the Zimpro/Passavant laboratory facility in Rothschild, Wisconsin, United States, on produced waters, wellhead oils, heavy oils, oily sludges from the refinery, and spent drilling muds. As an example, they prepared a feed material by combining oily sludge, biological sludge, and produced water in a 1:1:2 weight ratio and oxidized it in a shaking autoclave at temperatures of 240 and 280°C, during a 60 min time at those temperatures. They reported that COD reductions of 59.2% and 84.1% were at WAO temperatures of 240 and 280°C, respectively. In addition, the oily nature of the feed was completely eliminated as was evident by the absence of any immiscible oil in the treated effluents. In addition, O&G reductions of 93.6% and 99.1% were reported at oxidation temperatures of 240 and 280°C, respectively. They concluded that this process can be used to dispose of waste oils and oily sludges. It can also be applied to improve the dewaterability of waste-drilling muds, which contain emulsifying agents and oils. Bernal et al. (1999) investigated the feasibility of WAO of the oily wastes generated aboard ships. They noted that it can be a very efficient technology for the treatment of those residual currents, resulting in destruction efficiencies of greater than 90% of initial COD and 99.9% of O&G content.

Zerva et al. (2003) studied the homogeneous WAO of an oily wastewater with a COD of 11 g/L including mainly alcohols and phenolic compounds in a high-pressure agitated autoclave reactor in the temperature range of 180–260°C and oxygen pressure 1 MPa. They reported that among the compounds contained in the wastewater, ethylene glycol showed great resistance to wet oxidation, and temperatures above 240°C were needed for its effective degradation. Organic acids, mainly acetic acid, were the intermediate products of the WAO, and their conversion to carbon dioxide was very slow. Guo and Al-Dahhan (2005) studied the CWAO of phenol in concurrent downflow and upflow packed-bed reactors over pillared clay catalyst. Complete phenol removal and significant TOC reduction were reported at rather mild conditions of temperature (150–170°C) and total pressure (1.5–3.2 MPa) for both operation modes. They expressed that the temperature considerably affected the phenol and TOC conversion, while the air pressure only had minor influence. Total elimination of TOC was difficult due to CWAO-resistant acetic acid as the main intermediate in these conditions. Prasad et al. (2007) investigated CWAO and wet-peroxide oxidation (WPO) of stripped sourwater from an oil-shale refinery. Greater than 70% TOC removal from stripped sourwater was reported using a glass-lined reaction vessel at conditions of temperature (200°C), concentration of $Cu(NO_3)_2$ (67 mmol/L), time (3 h), and oxygen pressure (0.5 MPa). Significant TOC removal (~31%) was also reported in the system without added oxygen. They explained that this was predominantly due to copper-catalyzed oxidative decarboxylation of organics in stripped sourwater based on observed changes in copper-oxidation state. Greater than 80% TOC removal was reported using WPO at conditions of temperature (150°C), concentration of H_2O_2 (64 g/L), and time (1.5 h). They concluded that WPO was a far more effective process for removing odorous compounds from stripped sourwater. Sun et al. (2008) treated heavily contaminated petroleum refinery wastewater by a microwave-assisted CWAO process using GAC (5 wt%) as catalyst under low temperature (150°C) and low pressure (0.8 MPa). They reported that COD removal was more than 90% and the biodegradability of the BOD_5/COD ratio was increased from 0.04 to 0.47 within 30 min, indicating significant improvement of biodegradability for the solution, which was beneficial for the further biotreatment of petroleum wastewater. Yang et al. (2008) investigated the CWAO of phenol over CeO_2-TiO_2 catalyst in the batch reactor and the packed-bed reactor. In the batch reactor, COD and TOC removals were reported to be about 100% and 77% after 120 min in the CWAO of phenol over CeO_2-TiO_2 1:1 catalyst at reaction temperature of 150°C, total pressure of 3 MPa, phenol concentration of 1000 mg/L, and catalyst dosage of 4 g/L. In the packed-bed reactor using CeO_2-TiO_2 1:1 particle catalyst, over 91% COD and 80% TOC removals were reported at the reaction temperature of 140°C, air total pressure of 3.5 MPa, and the phenol concentration of 1000 mg/L after 100 h continue reaction.

Yang et al. (2014) used the graphene oxide (GO) and chemically reduced graphene oxides as catalysts in the absence of any metals in the CWAO of phenol in a batch reactor. Good phenol and TOC removals were reported in the CWAO of phenol using these carbon materials. The GO had the highest catalytic activity, total phenol removal was reported after 40 min, and ca. 84% TOC removal was reported after 120 min at reaction temperature of 155°C, total pressure of 2.5 MPa, and catalyst loading of 0.2 g/L. Parvas et al. (2014) coated nonnoble metal Ni with different loadings on precipitated CeO_2-ZrO_2 support by the sonochemistry method and examined for CWAO of phenol. They reported that the CWAO of phenol with different Ni loadings indicated improvement of phenol destruction at higher amounts of active phase. Removal of phenol was enhanced with increasing catalyst loading from 4 to 9.0 g/L but further increase to 10 g/L decreased the catalyst reactivity. Wang et al. (2014) developed different carbon material catalysts, namely multiwalled carbon nanotubes, carbon fibers, and graphite, to enhance the CWAO of phenol in aqueous solution. Excellent catalytic activity was reported in the CWAO of phenol by these functionalized carbon materials. After 60 min reaction, the removal of phenol was reported to be nearly 100% over the functionalized multiwalled carbon, while it was only 14% over the purified multiwalled carbon under the same reaction conditions. They explained that carboxylic acid groups introduced on the surface of the functionalized carbon materials play an important role in the catalytic activity in CWAO. They can promote the production of free radicals, which act as strong oxidants in CWAO. Fu et al. (2015) carried out the simultaneous WAO of nitrobenzene (NB) and phenol with homogenous catalyst in a stainless autoclave in a temperature range of 150–210°C and at a partial oxygen pressure of 1.0 MPa. They reported that the presence of the homogeneous catalyst greatly improved the conversion of both compounds compared to the noncatalytic cooxidation of NB and phenol. The transition metal ions Cu^{2+}, $Co^{2+,}$ and Ni^{2+} were reported to be effective catalysts, with Cu^{2+} affording the best results. In addition, adding phenol in smaller portions helped to degrade NB more effectively. As an example, two additions of phenol with Cu^{2+} as the homogenous catalyst allowed 95% conversion of NB at 200°C in 1 h. This catalytic cooxidation method incorporating the addition of phenol initiator batches therefore provides an alternative and effective means of removing persistent organic pollutants from the environment. Monteros et al. (2015) studied the catalytic performances of ruthenium and platinum supported on TiO_{2-x} wt% CeO_2 in the CWAO of phenol at 160°C and 20 bar of pure-oxygen pressure. They explained that contrary to expectations, improved oxygen-storage capacities of the materials proved to be detrimental to catalytic performances since they favored the formation of polymers in solution and the accumulation of adsorbed species. However, the presence of Lewis acid sites promoted the phenol total oxidation, which would favor the activation of the hydroxyl function, thus promoting the ortho-oxidation of phenol and finally the formation of CO_2. On the other hand, Pt appeared to be more efficient than Ru for CWAO of phenol.

6.4.4.5.3.7 Supercritical Water Oxidation Supercritical water oxidation (SCWO) is a process that takes place in an aqueous medium at temperatures and pressures above the critical point of water ($T_c = 374°C$ and $P_c = 22.1$ MPa) (Sabet et al., 2014; Jafarinejad et al., 2010a,b; Jafarinejad, 2014a; Wenbing et al., 2013; Fourcault et al., 2009; Bambang and Jae-Duck, 2007; Paraskeva and Diamadopoulos, 2006; Xu et al., 2012). Supercritical water has a smaller amount of hydrogen bonds, a lower dielectric constant, a lower viscosity, and a higher diffusion coefficient compared to normal water (Xu et al., 2012). Under these conditions water becomes a fluid with unique properties that can be applied as a reaction medium to produce nanoparticles, destroy organic compounds, etc. The process usually operates in a temperature range of 400–600°C and pressure range of 24–28 MPa (Sabet et al., 2014; Jafarinejad, 2014a).

The primary application of SCWO is for the destruction of organic wastes (Yu et al., 2013; Jafarinejad, 2014a). Organic substances and oxidants (such as air, or pure oxygen, or H_2O_2) are dissolved into supercritical water completely to create a single-phase environment, which overcomes the interphase mass-transfer resistance and accelerates the whole reaction rate. Supercritical water oxidation rapidly completely destructs organic substances into small molecular compounds such as CO_2, N_2, H_2O, etc., and heteroatoms are also turned into their mineral acids (Xu et al., 2012). Conversion rates higher than 99% can be obtained with residence times shorter than 1 min. Supercritical water oxidation is a clean or green, pollution-free, environmental friendly organic waste-treatment technology. It has a unique effect on treating toxic and biodegradable organic waste, and it will not result in secondary pollution (Bambang and Jae-Duck, 2007; Yu et al., 2013).

A typical SCWO process may consist of feed (aqueous waste, oxidant, fuel (optional), and dilution water (optional)) preparation and pressurization, preheater, reactor, alternate solid removal points, heat exchanger, depressurization, gas/liquid separation, and effluent polishing (Bambang and Jae-Duck, 2007). The flow diagram of an SCWO unit (MODAR type) is shown in Fig. 6.22. The aqueous waste stream containing the organic substances is pressurized and preheated to reactor conditions. The oxidant stream is also pressurized and mixed with the waste stream (Bambang and Jae-Duck, 2007). Under supercritical conditions in the SCWO reactor, organic compounds are completely miscible with supercritical water and with oxidant which the one-phase mixture of water, organic and oxidant

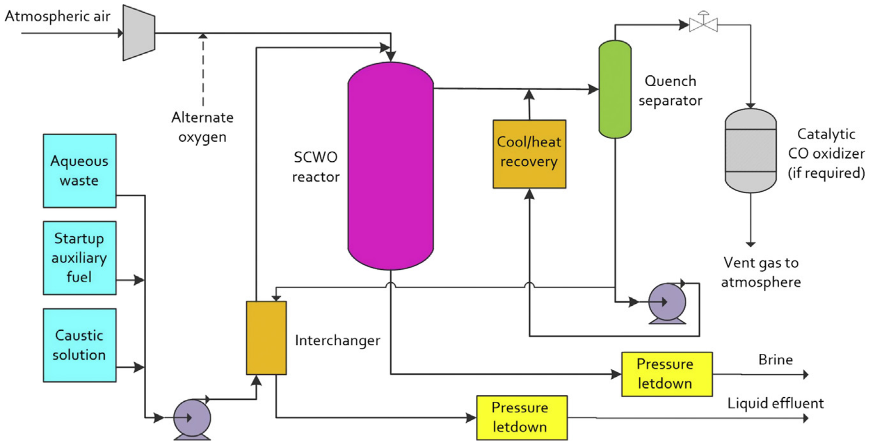

Figure 6.22 Flow diagram of a supercritical water oxidation unit (MODAR type). Modified from Barner, H.E., Huang, C.Y., Johnson, T., Jacobs, G., Martch, M.A., 1992. Supercritical water oxidation: an emerging technology (paper presented at ACHEMA'91). Journal of Hazardous Materials 31 (1), 1−17; National Research Council, 1993. Alternative Technology for the Destruction of Chemical Agents and Munitions, 7 Processes at Medium and High Temperatures. National Academy Press, Washington, DC.

is formed, and the temperature is high enough that free radical oxidation reactions proceed rapidly (Barner et al., 1992; Bambang and Jae-Duck, 2007). The formation of the primary pollutants, NO_x and SO_2, is precluded and in situ acid gas neutralization is accommodated by the process (Barner et al., 1992). Heat-transfer equipment can be applied to recover some of the process heat and to cool products before release. A quench separator is used for gas/liquid separation. If it is required, vent gas can be passed through a catalytic CO oxidizer before release to the atmosphere (National Research Council, 1993).

The technology of sewage treatment by SCWO was first proposed by Medoll (1982). Since then, SCWO has been applied efficiently over a wide variety of toxic and hazardous industrial wastes as reviewed by researchers (Bambang and Jae-Duck, 2007; Xu et al., 2012; Yu et al., 2013). According to Xu et al. (2012) and Bambang and Jae-Duck (2007), today SCWO plants include several famous companies such as General Atomics, MODAR, MODEC, Foster−Wheeler, EcoWaste Technologies, Chematur, SRI International, Hydro-Processing, Hanwha Chemical, and Supercritical Fluids International, etc. (Xu et al., 2012; Bambang and Jae-Duck, 2007). Commercial-scale SCWO plants have been installed in the United States, UK, Japan, China, Sweden, etc., for treatment purposes (Bambang and Jae-Duck, 2007; Xu et al., 2012; Yu et al., 2013). Corrosion, plugging, and high running costs are the main drawbacks of SCWO, which still exist and even cause some commercial-scale SCWO plants to be inactive (Bambang and Jae-Duck, 2007; Xu et al., 2012; Abelleira et al., 2013).

Matsumura et al. (2000) decomposed phenol at a concentration as high as 2 wt% by SCWO at 25 MPa, reaction temperatures range of 623−723K, and residence times of 6.5−26 s. They added oxygen in an equivalent amount to investigate reaction intermediates and reported that although tarry material production was observed, phenol decomposition conversion was predicted well by the reaction-rate equations developed by previous researchers who conducted experiments at lower concentrations. Difference from low concentration phenol oxidation was reported in the reaction product distribution and tarry material production. They explained that the initiation of phenol decomposition was the same regardless of phenol concentration, but that the succeeding radical reactions were different. The additive reaction between aromatic compounds was enhanced by high phenol concentration. Yu and Savage (2000) oxidized phenol in supercritical water at 380−450°C and 219−300 atm using CuO/Al_2O_3 as a catalyst in a packed-bed flow reactor. They reported that the CuO catalyst had the desired effects of accelerating the phenol disappearance and CO_2 formation rates relative to noncatalytic SCWO. It also simultaneously reduced the yield of undesired phenol dimers at a given phenol conversion. The rates of phenol disappearance and CO_2 formation were sensitive to the phenol and oxygen concentrations, but insensitive to the water density. The supported CuO catalyst exhibited higher activity, on a mass of catalyst basis, for phenol disappearance and CO_2 formation than did bulk MnO_2 or bulk TiO_2. However, the CuO catalyst had the lowest activity when expressed on the basis of fresh catalyst surface area. The CuO catalyst exhibited some initial deactivation, but otherwise maintained its activity throughout 100 h of continuous use. Both Cu and Al were detected in the reactor effluent, which indicates the dissolution or erosion of the catalyst at reaction conditions. Portela et al. (2001) tested both normal and promoted hydrothermal oxidation to treat cutting oil wastes (their composition is normally oil, water, and additives (fatty acids, surfactants, biocides, etc.)) in a continuous flow system operating at 300−500°C. They used hydrogen peroxide both as a source of oxygen and as a source of free radicals by introducing it into the reactor with or without previous thermal decomposition, respectively. Organic material oxidation was reported in both cases, obtaining more than 90% TOC reduction in less than 10 s at 500°C. At lower temperatures, the use of promoters clearly increased the oxidation process. Matsumura et al. (2002) used activated carbon as a catalyst for the SCWO of phenol. High concentrations of phenol treatment were reported in supercritical water at 673K and 25 MPa with an equivalent amount of oxygen in a reactor packed with activated carbon. Although activated carbon oxidation was reported in the reaction field, its weight decrease was sufficiently slow for its catalytic effect on phenol oxidation to be observed. The catalytic effect of activated carbon consisted of enhancement of the reaction rate, a decrease in the tarry product yield, and an increase in the gas yield. They also reported that under the conditions used in their study, 65% of oxygen delivered into the reactor was effectively used for phenol oxidation, while only 39% of oxygen was used when no catalyst was applied. They concluded that SCWO using lower operation temperatures and inexpensive carbon catalysts may be possible. Pérez et al. (2004) studied the oxidation of high concentrations of phenol and 2,4-dinitrophenol (DNP) in a pilot-scale SCWO system. Phenol destruction from 94% to 99.98% and TOC destruction from 75% to 99.77% were reported under treatment for approximately 40 s at a pressure of 25 MPa, temperatures of 666−778K, and oxygen excess of 0−34%. They reported that treatment of solution containing 2.4 wt% of 2,4-DNP with 2.1 wt% of ammonium sulfate at under

43 s at 25 MPa, 780K with large oxygen excess resulted in destruction efficiencies of over 99.9996% for DNP and 99.92% for TOC. Mononitrophenols were reported as intermediates, but not in the final effluent, where residuals of ammonium bicarbonate and sulfates were detected. This solution was reported to be extremely corrosive to the Alloy 625 preheaters at temperatures of approximately 370°C. They also reported that treatment of solution including 2.26 wt% of 2,4-DNP, with ammonia but no sulfates at 24.5 MPa, 742–813K, and oxygen concentrations ranging from substoichiometric to 67% excess resulted in destruction efficiencies of over 99.9996% for 2,4-DNP in all cases. TOC destruction efficiencies were reported from 98.98% to 99.98%, while ammonia destruction ranged from 15% to 50%. Picric acid and mononitrophenols were reported as intermediates, but not in the liquid effluent. No CO or NO_x was reported in the effluent gas samples, except in cases with less than stoichiometric oxygen. Wang et al. (2005) studied oily wastewater treatment by SCWO in intermittent equipment at 390–430°C, 24–28 MPa, and reaction residence time 30–90 s. They reported that SCWO was a high-efficiency organic waste treatment and disposal method, and temperature and residence time were the major influencing variables in removing COD from oil-bearing sewage and the removal rate of COD obviously enhanced as temperature and residence time increased.

Marulanda and Bolanos (2010) investigated the SCWO of a real-world mineral transformer oil highly contaminated with PCBs (PCB-contaminated oils). They reported 99.6% organic matter destruction of the complex mixture of hydrocarbons and PCBs under process conditions of 539°C, 350% oxygen excess, and 241 bar. They also reported that the PCB concentration in the aqueous effluent was below the detection limit of the chromatographic method used in the analysis, and a toxicity test for *Daphnia pulex* showed that the liquid effluent of the process was not ecotoxic. They proposed a process flowsheet of an SCWO mobile pilot plant as an alternative to incineration, and by a preliminary economic assessment of the proposed flowsheet they concluded that the process was feasible when compared to treatment by incineration. Wenbing et al. (2013) studied the SCWO of oily wastewater with ethanol. They investigated the cooxidative effect of ethanol on oily wastewater for the initial COD of oily wastewater (4000 mg/L), ethanol concentration (20 mg/L) for a range of temperatures (390–450°C), and a pressure of 23 MPa for the complete combustion of both ethanol and oily wastewater. A 90.26% COD removal was reported after 9 min reaction at temperature of 450°C, hydrogen peroxide excess of 70%, and the initial COD of 4000 mg/L. Ethanol accelerated the destruction of oily wastewater. Significantly higher COD removal with ethanol was found compared to without ethanol (8% increase).

6.5 Oily Wastewater Treatment Plants

As noted before, oily wastewater treatment can typically be classified as process wastewater pretreatment, primary treatment, secondary treatment, and tertiary treatment or polishing (U.S. EPA, 1995; Benyahia et al., 2006; IPIECA, 2010; European Commission and Joint Research Center, 2013; Goldblatt et al., 2014; Jafarinejad, 2015d). A typical oily wastewater treatment system or petroleum refining/petrochemical

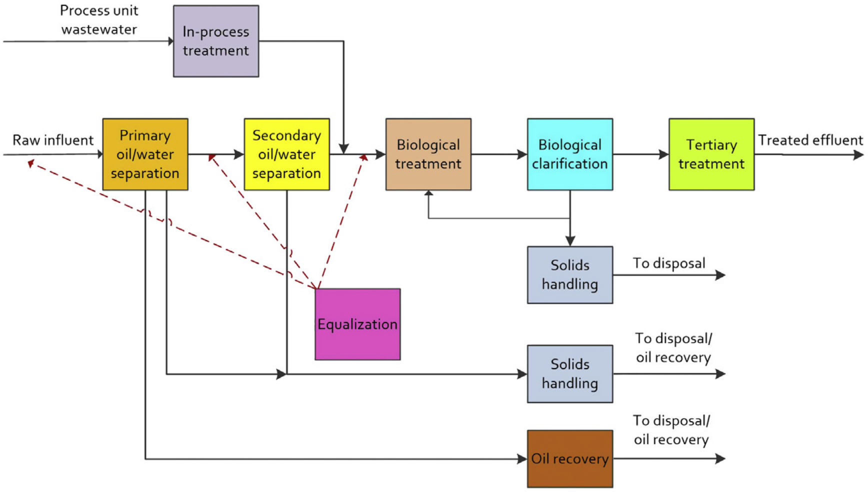

Figure 6.23 Typical oily wastewater treatment system.
Modified from Schultz, T.E., 2006. Petroleum refinery, ethylene and gas plant wastewater treatment presentation, wastewater treatment, treatment options & key design issues. Siemens AG, 1—94. [Online] Available from: http://www.sawea.org/pdf/waterarabia2013/Workshops/Basic-Industrial-Wastewater-Treatment-Workshop.pdf; Siemens Water Technologies Corp., 2009. Total Wastewater Management for the Petroleum Refining and Petrochemical Industries, HP-WWCB-BR-0209, Siemens Water Technologies Corp., pp. 1—16. [Online] Available from: http://www.petroconsult-eg.com/wp-content/uploads/2014/11/siemens_Refinery_Brochure.pdf.

wastewater treatment system is shown in Fig. 6.23, which can consist of equalization, primary and secondary oil—water separation, biological treatment, biological or secondary clarification, and tertiary treatment (if necessary) (Schultz, 2006; Siemens Water Technologies Corp., 2009). In WWTPs, solid wastes are also generated in the form of sludges from a number of treatment units (U.S. EPA, 1995), which must be treated as discussed in detail in Chapter 7.

An equalization system is used to smooth out fluctuations or variations in flow and composition or concentration (Bush, 1980; Schultz, 2006; IPIECA, 2010). Flow equalization smooths out the flow variations, thereby minimizing potential spikes in flow and loads to the downstream units; it may also decrease the size of the downstream units and the cost of the overall WWTPs. Concentration equalization minimizes contaminant shock loading of the downstream units such as biological systems (IPIECA, 2010). Note that the volume and composition of the feed should be fairly constant for the effectiveness of biologically based system (Bush, 1980). The equalization system can be located upstream of the primary oil—water separation (API separator) (IPIECA, 2010), upstream of the secondary oil—water separation (the DAF/IAF) (Bush, 1980; Schultz, 2006; IPIECA, 2010), and downstream of the secondary oil—water separation (the DAF/IAF) (Schultz, 2006; IPIECA, 2010). If upstream of the API separator is chosen for the location of equalization system, due to the separation tendency of the oil and solids contained in the oily wastewater in this tank, hardware

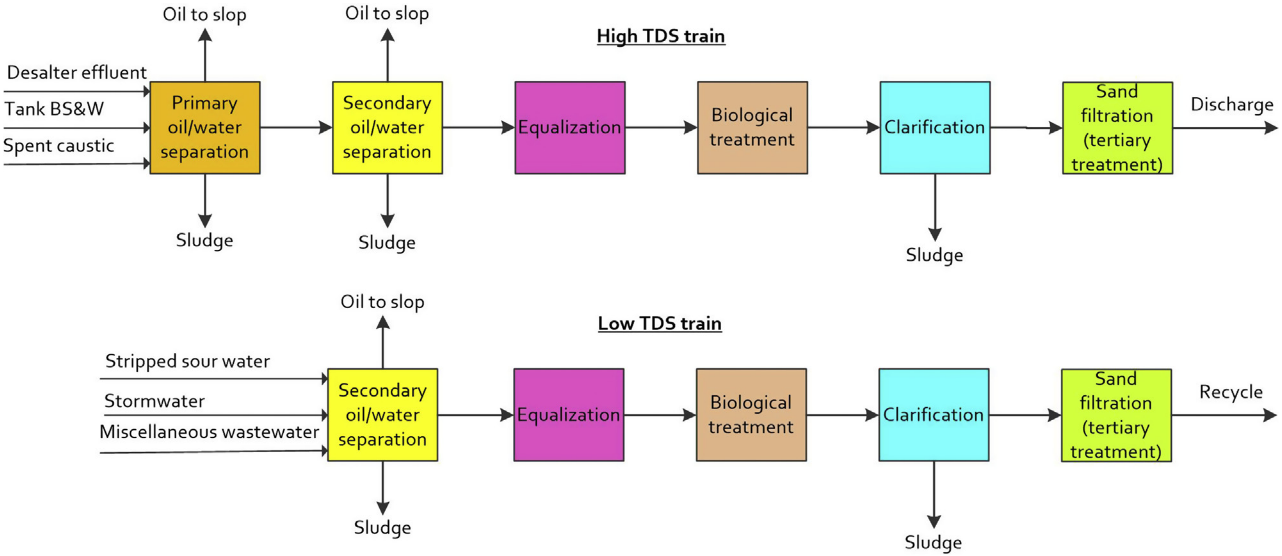

Figure 6.24 Segregated wastewater-treatment system.
Modified from IPIECA, 2010. Petroleum Refining Water/Wastewater Use and Management. IPIECA Operations Best Practice Series, London, United Kingdom.

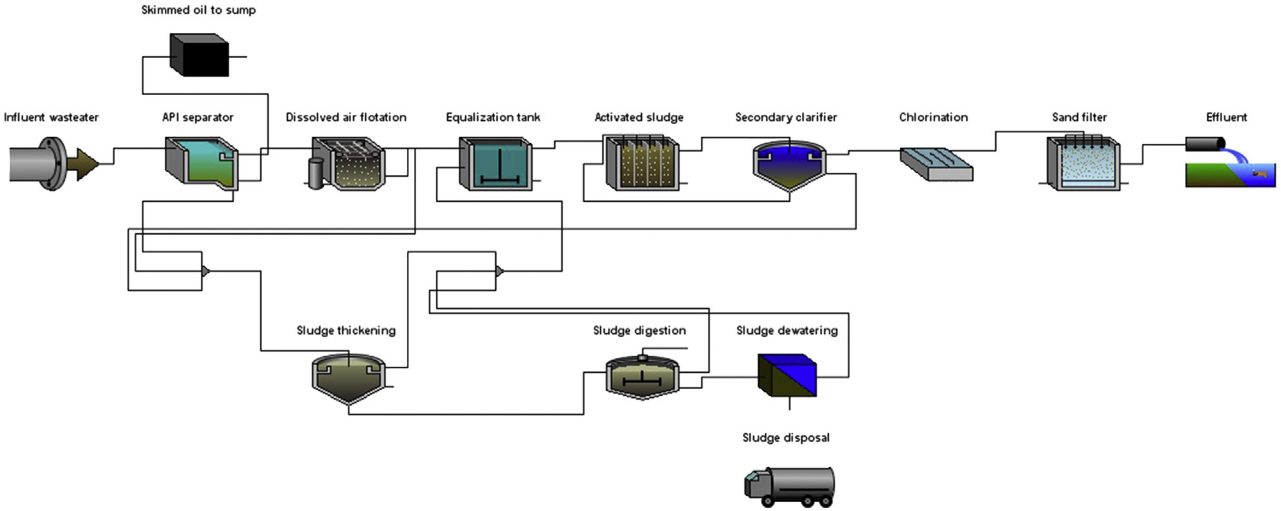

Figure 6.25 Simplified flow diagram of a refinery wastewater treatment plant with sludge handling and disposal.
Modified from Yokogawa Corporation of America, 2008. Refinery Wastewater: Oil & Grease Removal, Application Note, AN10B01C20–05E, Yokogawa Corporation of America. [Online] Available from: http://web-material3.yokogawa.com/AN10B01C20-05E_Refinery_Wastewater_Oil_and_Grease_Removal_Final_1.pdf.

(piping/pumps and controls) must be provided to allow removal of free oil and solids from the tank in order to prevent accumulation of these materials. The equalization system must be cleaned once or twice a year depending on the solids and oil content of the oily wastewater (IPIECA, 2010).

Wastewater segregation and segregated wastewater treatment in the petroleum refineries may be considered in water-scarce areas, but this is not common. Refinery wastewater can be segregated based on the TDS content of the wastewater as follows:

- Low TDS: Stripped sourwater, stormwater, and miscellaneous wastewater; and
- High TDS: Desalter effluent, tank-bottom sediment and water (BS&W), and spent caustic.

Fig. 6.24 shows a segregated wastewater treatment system in a petroleum refinery, which consists of two parallel trains with the same unit operations, except that the low TDS train does not include an API separator due to the low suspended solids content of the wastewater (IPIECA, 2010).

A simplified flow diagram of a refinery WWTP with sludge handling and disposal according to Yokogawa Corporation of America (2008) is shown in Fig. 6.25. This treatment system consists of an API separator, DAF, equalization tank, activated sludge treatment, clarification, chlorination, sand filter, sludge thickening, sludge digestion, sludge dewatering, sludge disposal, and oil sump. Note that the equalization tank and oil sump have been added by the author and that the sludge-handling section of this treatment system is not complete. The simplified flow diagram of the processing wastewater containing oil according to MARINER plus s.r.o. (Flottweg, Solenis) (2016) is shown in Fig. 6.26. This treatment system consists of pH adjustment, API separator, flotation, aeration tank, clarification, oily sludge pretreatment tank, oily sludge tricanter, and sewage sludge decanter (oily sludge pretreatment, decanter, and tricanter are discussed in detail in Chapter 7). Note that the separated oil in the tricanter (still containing water and solids) may need further separation to obtain the

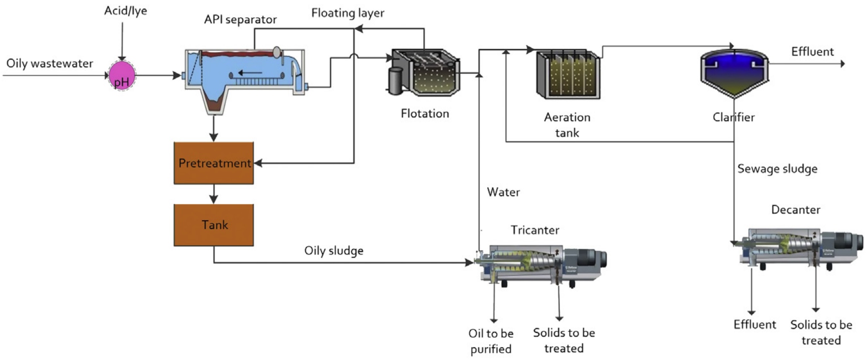

Figure 6.26 Simplified flow diagram of processing wastewater containing oil.
Modified from MARINER plus s.r.o. (Flottweg, Solenis), 2016. Processing and Recycling of Oil Sludge, Processing of Wastewater Containing Oil, MARINER Plus s.r.o. – výhradné zastúpenie Flottweg SE pre ČR a SR, Naftárska 1413, 908 45 Gbely, Slovenská republika. [Online] Available from: http://marinerplus.sk/?page_id=738.

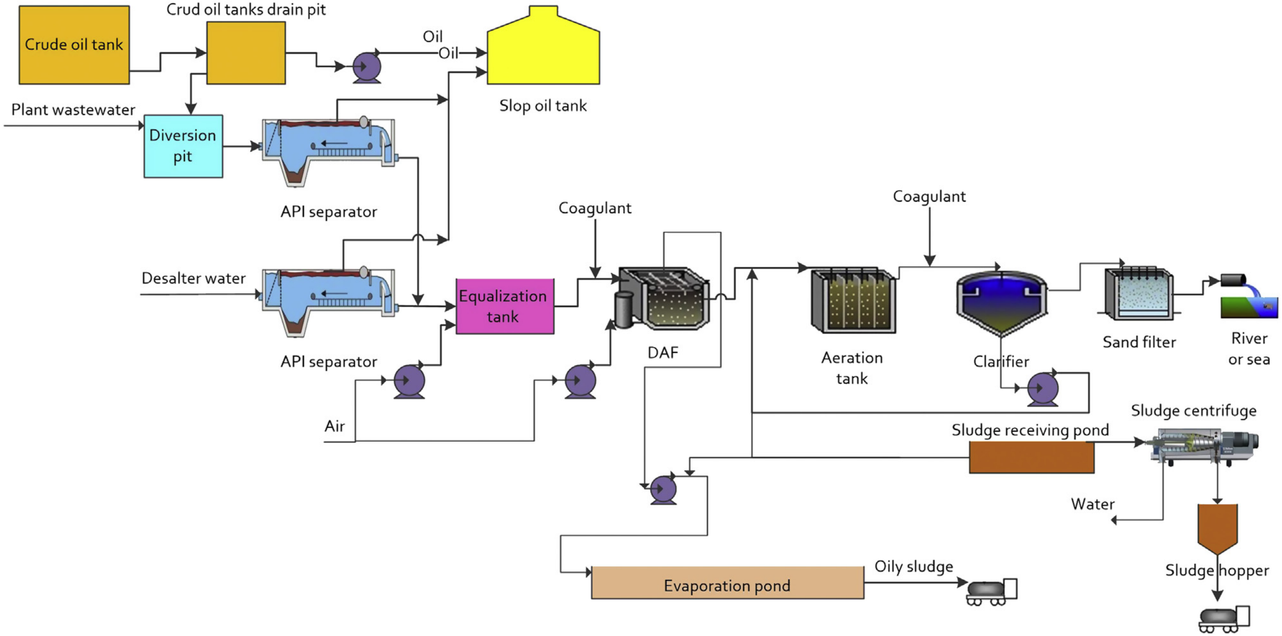

Figure 6.27 Simplified flow diagram of the improvement of existing wastewater treatment system of the refineries in some Middle East countries. Modified from Morita, T., 2013. Technical support for environmental improvement of the refineries in Middle East. In: The 21st Joint GCC-Japan Environment Symposium, February 5–6, 2013. [Online] Available from: https://www.jccp.or.jp/international/conference/docs/23cosmo-engineering-mr-morita-presentation-by-morita.pdf.

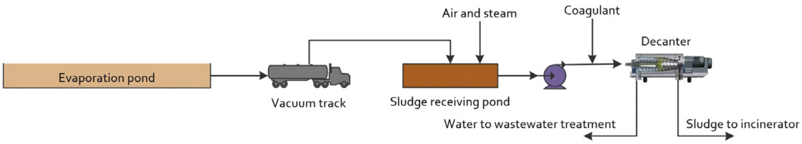

Figure 6.28 Evaporation pond sludge recovery plan.
Modified from Modified from Morita, T., 2013. Technical support for environmental improvement of the refineries in Middle East. In: The 21st Joint GCC-Japan Environment Symposium, February 5–6, 2013. [Online] Available from: https://www.jccp.or.jp/international/conference/docs/23cosmo-engineering-mr-morita-presentation-by-morita.pdf.

recovered oil, and solid residues also need further treatment. Improvements to the existing wastewater treatment systems of refineries in some Middle East countries as presented by Morita (2013) are shown in Fig. 6.27. This treatment system consists of a diversion pit, API separators, equalization tank, DAF, aeration basins, clarification, sand filters, sludge receiving pond, sludge centrifuge, sludge hopper, evaporation pond (discussed in detail in Chapter 7), and slop-oil tank. An evaporation pond sludge recovery plan presented by Morita (2013) is shown in Fig. 6.28, which includes transferring its content to a sludge-receiving pond by vacuum track, oily sludge mixing by air and steam, sludge and wastewater separating by the decanter, retreating of separated wastewater, and burning of sludge by incinerator.

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Solid-Waste Management in the Petroleum Industry

7

7.1 Introduction to Solid Wastes in the Petroleum Industry

Various solid wastes are generated from the activities and processes in the petroleum industry and release of these wastes can have adverse impacts to the environment and human health (E&P Forum, 1993; World Bank Group, 1998; CONCAWE, 1999, 2003; Bashat, 2003; Echeverria et al., 2002; Mokhtar et al., 2011; Lima et al., 2011; European Commission and Joint Research Center, 2013; Ubani et al., 2013; Hu et al., 2013, 2014; Lima et al., 2014; Jafarinejad, 2015a,b). Among the solid wastes, special attention is paid to oily sludges (Kriipsalu et al., 2008). It is important to consider the solid wastes types and sources, characteristics of oily sludge, toxicity and impact of solid wastes, and management of the solid wastes in the petroleum industry.

7.1.1 Solid-Waste Types and Sources

As noted in Chapter 2, the sources of solid wastes from E&P activities are tank/piping sludges, IGF/DGF sludge, waxes, production chemicals, contaminated soils, absorbents (e.g., spill clean up), incinerator ash, oil-based muds and cuttings, pigging sludges, spent catalysts (e.g., catalyst beds, and molecular sieve), industrial wastes (e.g., batteries, transformers, and capacitors), maintenance waste [e.g., sandblast (grits), greases, and filters], produced sand (e.g., from drilling/production operations), scrap materials (e.g., abandoned platforms, used pipelines, used process equipment, used tanks, electrical cables, empty drums, used tubulars, and used casings), medical wastes, domestic refuse, etc. The solid wastes from the E&P of petroleum, environmentally significant components, main sources, and type of operations that generate these pollutants are listed in Table 2.6 (E&P Forum, 1993; Bashat, 2003).

Refinery solid wastes generally include three categories of materials:

- Sludge, both oily (e.g., tank bottoms, residues from oil–water separators such as the American Petroleum Institute (API), parallel plate interceptor (PPI), or corrugated plate interceptor (CPI) separators, sludge from flocculation–flotation unit (FFU), dissolved air flotation (DAF), or induced air flotation (IAF) units, desalter sludges, etc.), and nonoily (e.g., boiler feedwater sludge);
- Other refinery wastes, including miscellaneous liquid, semiliquid, or solid wastes (e.g., contaminated soil, spent catalysts from conversion processes, oily wastes, incinerator ash, spent caustic, spent clay, spent chemicals, and acid tar); and
- Nonrefining wastes (e.g., domestic, demolition, and construction) (European Commission and Joint Research Center, 2013).

The major solid wastes generated in a typical petroleum refinery and their sources are listed in Table 2.16. According to the World Bank Group (1998), refineries

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generate solid wastes and sludges (ranging from 3 to 5 kg per ton of crude processed), 80% of which may be considered hazardous because of the presence of toxic organics and heavy metals (World Bank Group, 1998). The generation rate of solid wastes and sludges should be less than 0.5% of the crude processed, with a target of 0.3% (World Bank Group, 1998; European Commission and Joint Research Center, 2013).

Petrochemical plants also produce a wide variety of solid wastes and sludges, some of which may be considered hazardous because of the presence of toxic organics and heavy metals (MIGA, 2004). There are two main groups of petrochemical solid-waste streams:

- Intermittent wastes such as spent catalysts from certain processing units and product treatment wastes such as spent filter clay, process vessel sludge, storage-tank sediments, vessel scale, and other deposits generally removed during turnarounds; and
- Continuous wastes such as process unit wastes and wastewater treatment wastes.

Steam-cracking process when running on gas or naphtha; generate little solid wastes such as organic sludge, coke, spent catalyst, spent adsorbents, oil filters/cartridges and air-drying adsorbents. Catalysts, clay, adsorbents, sludge/solid polymerization material, oil-contaminated materials, and oily sludge are the major categories of solid-waste generation in aromatics plants (IL & FS Ecosmart Limited Hyderabad, 2010).

Solid waste generated in storage, transportation, and distribution is mainly sludge from the storage and transportation tanks (Cholakov, 2009). Storage-tank-bottom sludge may contain iron rust, clay, sand, water, emulsified oil and wax, phenols, benzene, toluene, xylene, sulfide, sulfate, nitrate, carbonate, ethylbenzene, nephthalene, pyrene, fluorine, cyanide, metals (iron, nickel, chromium, vanadium, antimony, mercury, arsenic, selenium, lead for leaded gasoline storage tanks, etc.), etc. (European Commission and Joint Research Center, 2013).

Either simple oil or sludge, depending on the ratio of water and solids within the oily matrix, can be generated as oily waste in the petroleum industry (Al-Futaisi et al., 2007; Hu et al., 2013). Simple-waste oil typically includes less water than sludge and is highly viscous and includes a high percentage of solids. Stable water-in-oil (W/O) emulsion can be a typical physical form of petroleum sludge waste (Elektorowicz and Habibi, 2005; Hu et al., 2013).

Among the solid wastes generated in the petroleum industry, special attention should be paid to oily sludges (Kriipsalu et al., 2008), but all solid wastes must be managed. Oily sludge is a complex, thick, and viscous mixture of solid particles, water, oil, and petroleum hydrocarbons (PHCs) (Mokhtar et al., 2011; Ubani et al., 2013; Hu et al., 2013, 2014; Lima et al., 2014). Oily sludge is considered hazardous waste because it contains a high concentration of toxic components (e.g., toxic organics and heavy metals), and thus needs proper management (Hu et al., 2014). Note that the accumulation of oily sludge in the petroleum industry can pose serious environmental problems (Lima et al., 2011).

7.1.2 Characteristics of Oily Sludge

Waste characterization is necessary to determine and assign the hazardous nature of waste, waste-stream categories, and select options for segregation, minimization, treatment, and ultimately disposal of waste. Hazardous characteristics and environmental impact ability of the waste can be affected by its physical and chemical properties (Bashat, 2003).

Sludges generally refer to the semiliquid residues from industrial processes and wastewater treatment (European Commission and Joint Research Center, 2013). Oily sludges are hazardous wastes that can be characterized as stable W/O emulsions of water, solids, PHCs, and metals. A protective film, which inhibits water droplets from coalescing with each other, affects the stability of W/O emulsions. This interfacial film is comprised of many natural emulsifiers such as some PHCs constituents (e.g., asphaltenes and resins), fine solids, oil-soluble organic acids, and other finely divided materials. The pH value of oily sludge is typically in a range between 6.5 and 7.5 and its chemical composition can vary over a wide range, depending on the crude-oil source, processing scheme, and equipment and reagents used in the refining process (Hu et al., 2013). Typical chemical characterizations of the sludge taken from tank-field sewers, gasoline-tank-field sewers, distillate-tank-field sewers, API separator, activated sludge, and settling basin plant are listed in Table 7.1. According to Hu et al. (2013), the TPH contents in oily sludge can vary from 5% to 86.2 wt%, but are more frequently in the range of 15−50 wt%, whereas the contents of water and solids are in the range of 30−85 wt% and 5−46 wt%, respectively. Also, according to Mokhtar et al. (2011), oily sludge contains up to 10−30 wt% hydrocarbons, 5−20 wt% solids, and the remainder is water. In addition, according to Liang et al. (2014), it contains 30−50 wt% oil, 30−50 wt% water, and 10−12 wt% solids. The PHCs and other organic compounds in oily sludge can generally be divided into four fractions, including aliphatics, aromatics, nitrogen sulfur oxygen (NSO) containing compounds, and asphaltenes (Mrayyan and Battikhi, 2005; Hu et al., 2013). Oily sludge has high aromatic hydrocarbon content, in the range of 1−40 carbon atoms (US EPA, 1997; Ubani et al., 2013). Up to 75% of PHCs in oily sludge are usually the aliphatics and aromatic hydrocarbons, and their most common compounds include alkanes, cycloalkanes, benzene, toluene, xylenes, naphthalene, phenols, and various PAHs (e.g., methylated derivatives of fluorine, phenanthrene, anthracene, chrysene, benzofluorene, and pyrene) (Hu et al., 2013). The NSO fraction includes polar compounds such as naphthenic acids, mercaptans, thiophenes, and pyridines. The nitrogen content of oily sludge can be less than 3%, most of which is included in the distillate residue as part of asphalt and resin fraction. The sulfur content can be in the range of 0.3−10%, whereas the oxygen content is usually less than 4.8% (Kriipsalu et al., 2008; Hu et al., 2013). Asphaltenes are mixtures of pentane-insoluble and colloidal compounds including polyaromatic and alicyclic molecules with alkyl substitutes (usually methyl groups), and they vary in molecular weight between 500 and several thousand. The stability of oily-sludge emulsion can be attributed to the asphaltenes and resins, because these constituents include hydrophilic functional groups and therefore can act as lipophilic emulsifiers. Oily sludge is typically composed of 40−52 wt% alkanes, 28−31 wt% aromatics, 8−10 wt% asphaltenes, and 7−22.4 wt% resins (Hu et al., 2013).

The physical properties of oily sludge such as density, viscosity, and heat value can vary significantly due to its diverse chemical compositions. The measured properties

Table 7.1 **Typical Chemical Characterizations of the Sludge Taken From Tank-Field Sewers, Gasoline-Tank-Field Sewers, Distillate-Tank-Field Sewers, API Separator, Activated Sludge, and Settling Basin Plant (March Consulting Group, 1991; European Commission and Joint Research Center, 2013)**

Species	Tank-Field Sewers	Gasoline-Tank-Field Sewers	Distillate-Tank-Field Sewers	API Separator	Activated Sludge	Settling-Basin Plant
Solids	92.7%	81.0%	97.0%	90.4%	94.3%	99.7%
Oil	7.3%	19.0%	3.0%	9.6%	5.7%	0.3%
Carbon	26.9%	44.9%	58.0%	25.8%	13.1%	1.7%
Hydrogen	10.2%	7.8%	7.3%	13.1%	51.8%	6.3%
Nitrogen	1.2%	0.4%	0.6%	0.6%	1.7%	0.5%
Sulfur	64,441.0	58,222.0	13,514.0	40,733.0	9479.0	4214.0
Carbonate	29.0	0.3	0.3	0.3%	0.2%	0.1%
Iron	25,000.0	62,222.0	105,326.0	48,269.0	10,900.0	7131.0
Aluminum	4193.0	8148.0	3180.0	43,177.0	2,322.0	4878.0
Calcium	<0.3	13,185.0	11,725.0	11,609.0	4692.0	8104.0
Sulfide	8327.0	4325.9	4238.9	6180.2	2165.9	103.7
Magnesium	9317.0	4430.0	1331.0	4878.0	1351.0	1767.0
Sodium	1,180.0	770.0	445.0	1711.0	3981.0	3971.0
Xylene	746.9	1121.5	4.0	469.5	9.5	3.2
Naphthalene	130.4		25.8	288.2	46.9	16.0

Lead	55.9	308.1	234.5	279.0	49.3	15.2
Phenol	71.4		69.6	265.0	46.9	16.0
Nickel	68.3	500.7	190.8	252.5	37.9	8.8
Nitrate	2290.4	91.9	8.9	228.1	2066.4	194.5
Toluene	478.3	794.1	4.0	138.5	9.5	32.0
Styrene				134.4	47.0	16.0
Vanadium	27.0	49.0	25.0	99.0	18.0	24.0
Ethylbenzene	158.4	106.8	4.0	82.5	9.5	3.2
Chromium	35.4	154.1	81.5	80.0	8.1	11.2
Fluorine	15.5		39.3	59.1	46.9	16.0
Antimony	19.0	15.0	20.0	49.0	14.0	5.0
Benzo(a)pyrene	<7.8		39.3	42.6	46.9	16.0
Phenols	18.6		39.3	40.3	46.9	16.0
Selenium	7.0	4.3	5.0	35.4	26.0	9.0
Benzene	80.7	35.6	4.0	13.2	9.5	3.2
Sulfate	1037.3	19.3	39.7	12.2	2767.8	285.3
Arsenic	5.0	14.5	15.9	6.5	15.2	5.2
Mercury	4.0	9.5	0.2	3.0	1.0	0.0
Cyanide	0.6	0.5	0.7	1.0	7.0	0.7

Figures do not sum to 100% because of double counting; figures quoted on a moisture-free basis; all units mg/kg unless otherwise stated.

of oily sludge can vary with the oily-sludge source, the source location, and sampling time. The polarity and molecular weight of chemical species in sludge are the main factors that affect its physical properties, and empirical modeling and estimation of physical properties based on the chemical compositions of sludge are possible (Hu et al., 2013).

The species and concentrations of heavy metals in oily sludges vary over a wide range similar to organic compounds resulting from different sources (Hu et al., 2013). According to a report from the API (1989), cited by Hu et al. (2013), metal concentrations in oily sludge generated in the petroleum refineries are generally 7—80 mg/kg for Zn, 0.001—0.12 mg/kg for Pb, 32—120 mg/kg for Cu, 17—25 mg/kg for Ni, and 27—80 mg/kg for Cr. Also, according to Bhattacharyya and Shekdar (2003), oily sludge from refineries in India contains phenol (90—100 mg/kg), Ni (17—25 mg/kg), Cr (27—80 mg/kg), Zn (7—80 mg/kg), Mn (19—24 mg/kg), Cd (0.8—2 mg/kg), Cu (32—120 mg/kg), and Pb (0.001—0.12 mg/kg). Oily sludges may contain a very high concentration of heavy metals. According to Admon et al. (2001), Marín et al. (2006), Rocha et al. (2010), Roldán-Carrillo et al. (2012), and Hu et al. (2013), the metal concentration in oily sludge from refineries may be 1299 mg/kg for Zn, 60,200 mg/kg for Fe, 500 mg/kg for Cu, 480 mg/kg for Cr, 480 mg/kg for Ni, and 565 mg/kg for Pb.

7.1.3 Toxicity and Impact of Solid Wastes

As discussed in Chapter 3, the environmental impacts of petroleum are often negative because it is toxic to almost all forms of life (Prasad and Kumari, 1987). Toxicity is a usual measure of the potential environmental impact of a material such as petroleum. It is the degree to which a substance can damage an organism (Reis, 1996). Because of the hazardous nature of oily sludge as a solid waste, there are some regulations in the world such as the Resource Conservation and Recovery Act (RCRA) in the United States, which regulates the management, treatment, and disposal of hazardous wastes (US EPA, 1980; Hu et al., 2013). An RCRA characteristic hazardous waste is a solid waste that exhibits at least one of four characteristics: ignitability, corrosivity, reactivity, and toxicity (US EPA, 2009).

Hazardous wastes can cause soil degradation, groundwater contamination, surface-water contamination, and property value depreciation and can an impact on public health, flora and fauna, and air quality (Shanaa, 2014). Many of the oily-sludge components have been reported to be cytotoxic, mutagenic, and potentially carcinogenic. Physical and chemical alteration of natural habitats and lethal and sublethal toxic effects on aquatics and terrestrial ecosystems are some of environmental impacts of oily sludge (Bojes and Pope, 2007; Ubani et al., 2013).

The physical and chemical properties of receiving soils can be disturbed by oily sludge, which can lead to soil morphological change. Nutrient deficiency, seed germination inhibition, and growth restriction or demises of plants on contact may be the impacts of soil contamination by oily sludge. Because of oily sludge's high viscosity, its components can be fixed in soil pores, adsorbed onto the surface of soil-mineral constituents, or form a continuous cover on soil surface, leading to reduction of hygroscopic moisture, hydraulic conductivity, and water-retention capacity (i.e., wettability) of soils. In particular, the constituents with higher molecular weight in sludge and their degradation products could remain near soil surface and create hydrophobic crusts that reduce water availability and restrict water—air exchange. The activity of soil enzymes (i.e., hydrogenase and invertase) can be diminished by PHCs in oily sludge and the soil microorganisms can also be affected by it. Moreover, after remaining in the terrestrial environment for an extended period of time, the weathered chemical residues of oily sludge may emerge to resist desorption and degradation, and they have significant time to interact with soil constituents. Stable dialkylphthalates, long-chain alkanes, and fatty acids can be formed by covalent bonding between organic compounds in sludge residues and humic polymers (e.g., humin, fulvic acid, and humic acid) in soil, which are resistant to microbial degradation (Hu et al., 2013).

Oily sludge contains heavy metals, which, depending on the metal, its concentration, route of exposure, as well as the age, genetics, and nutritional status of exposed targets, can have a variety of environmental and health concerns (Singh et al., 2011). Oily sludge also contains VOCs and semivolatile organic carbons (SVOCs) (e.g., PAHs) that have been found to be genotoxic (Bojes and Pope, 2007; Ubani et al., 2013). They have a cumulative effect on the central nervous system (CNS) leading to dizziness, tiredness loss of memory, and headache, and the effect depends on duration of exposure. In severe cases, PAH metabolism in the human body generates epoxide compounds with mutagenic and carcinogenic properties, which affects the skin, blood, immune system, liver, spleen, kidney, lungs, and developing fetus, and also causes weight loss (Ubani et al., 2013).

7.2 Overview of Solid Waste-Management Practices

The waste-management hierarchy is shown in Fig. 3.5. As discussed in Chapter 3, waste-management practices include:

- Prevention such as optimizing drilling operations, keeping hazardous and nonhazardous wastes separate (Reis, 1996), research efforts and design of new or modified operations and processes (E&P Forum/UNEP, 1997), and determination of sludge and water content for feedstock (Speight, 2005);
- Source reduction or waste minimization such as using of gravel packs and screening for reduction of volume of solids/sludge generation in E&P sector, proper operation of equipment, and process modifications (E&P Forum, 1993);
- Reuse such as use of hydrocarbon bearing soil for road mix or asphalt (E&P Forum, 1993), and reuse of oily sludge in process units (e.g., coking) as part of the feed due to their oil content (European Commission and Joint Research Center, 2013);
- Recycling/recovery such as recycling drilling muds, recycling scrap metal, recycling paper and plastic, recycling batteries (E&P Forum, 1993), recovery of oil from tank bottoms via centrifuging and filtering (E&P Forum, 1993; European Commission and Joint Research Center, 2013), removal of catalyst from slurry decant oil from process units (e.g., FCC unit) prior to the reuse of it as a feedstock (European Commission and Joint Research Center, 2013), recovery of valuable metals from spent catalyst, recycling catalyst and coke fines, and valuable product recovery from oily sludge with solvent extraction (Speight, 2005);

- Treatment such as thermal, physical, chemical, and biological processes (E&P Forum, 1993; MVLWB, 2011); and
- Disposal such as incineration, biodegradation, composting, landspreading, landfarming, landfilling, etc. (E&P Forum, 1993).

7.2.1 Selection of Treatment and Disposal Methods

Sludges are usually dewatered and/or deoiled (e.g., by centrifugation) prior to final disposal (European Commission and Joint Research Center, 2013). The choice of treatment and disposal methods depends largely on the physical and chemical properties of the waste or the waste characteristics (Bashat, 2003; da Silva et al., 2012), regulatory requirements (Bashat, 2003), and the availability of facilities to process these wastes (da Silva et al., 2012).

7.2.2 Oil-Recovery and/or Removal Methods

Oil recovery involves extracting valuable oil or energy from a waste (oily sludge) for other uses (E&P Forum, 1993; Bashat, 2003; CONCAWE, 2003). It can be accomplished at either on-site production facilities or off-site commercial facilities (E&P Forum, 1993). Oil recovery from sludge can also decrease the disposal volume of hazardous waste outside the industrial zone, prevent the extent of contamination, and reduce the utilization of nonrenewable energy resources (Hu et al., 2013).

Oil recovery is the most desirable environmental option for handling oily sludge because it has high oil concentration (Taiwo and Otolorin, 2009; Liang et al., 2014). Sludge containing recoverable oil less than 40% can be considered as low-oil-content sludge (Islam, 2015), but from an economic point of view, oily sludge containing over 10 wt% oil merits the process of oil recovery (CONCAWE, 2003; Ramaswamy et al., 2007; Zhang et al., 2012; Liang et al., 2014). Several methods such as solvent extraction, centrifugation, surfactant enhanced oil recovery (SEOR), distillation/pyrolysis, microwave irradiation method, freeze/thaw (F/T) treatment, electro-kinetic (EK) method, ultrasonic irradiation method, froth flotation, adsorption, high-temperature reprocessing (HTR) or heating, and filtration have been applied to recover the oil from oily sludge. It is necessary to note that some of these processes such as freeze/thaw treatment, electro-kinetic, ultrasonic irradiation, and froth flotation methods have been used in laboratory scale for the treatment of oily sludge.

7.2.2.1 Solvent Extraction

Solvent extraction is a simple process in which oily waste and solvent are mixed in an appropriate proportion to ensure adequate miscibility of oil in solvent, while most water and solids are rejected as unwanted impurities that may be removed by gravitational settling or centrifugation. The oil and solvent mixture can then be separated by distillation (Hu et al., 2015). A simplified flow diagram of a solvent-extraction process

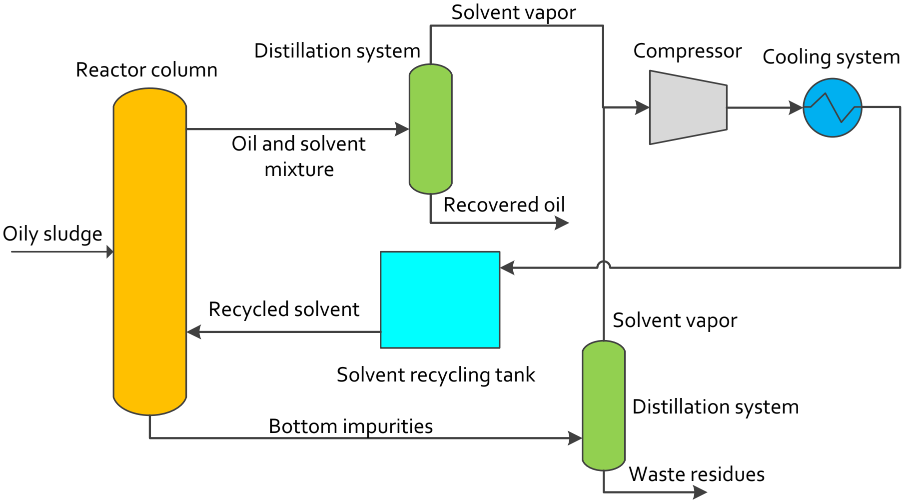

Figure 7.1 Simplified flow diagram of a solvent-extraction process.
Modified from Hu, G., Li, J., Zeng, G., 2013. Recent development in the treatment of oily sludge from petroleum industry: a review. Journal of Hazardous Materials 261, 470–490; Islam, B., 2015. Petroleum sludge, its treatment and disposal: a review. International Journal of Chemical Sciences 13 (4), 1584–1602.

is shown in Fig. 7.1. Oily-sludge waste is first mixed in the reactor column with a solvent, which selectively dissolves the oil fraction of sludge and leaves the less-soluble impurities at the column bottom. The oil and solvent mixture is then transferred to a solvent distillation system where the solvent is separated from oil. The separated oil is considered as oil recovery, while the separated solvent vapor can be liquefied through a compressor and cooling system and sent to a solvent recycling tank. The solvent can be used for repeating the extraction cycle. The bottom impurities from the reactor column are pumped to a second distillation system, and the solvent contained in the impurities is separated and then sent to the solvent-recycling tank, while the waste residue after separation may need further treatment (Hu et al., 2013; Islam, 2015).

The oil-recovery efficiency (R_O) from the oily sludge can be calculated using the following equation:

$$R_O = \frac{\Gamma_{IO} - \Gamma_O}{\Gamma_{IO}} \tag{7.1}$$

where Γ_{IO} and Γ_O are the initial and residue oil contents in the sludge (g/g), respectively (Liang et al., 2014).

The distribution coefficient (K_D), which is used to characterize the solvent-extraction equilibrium, can be defined as the ratio of oil concentration in the solvent phase to that in the solid (sludge) phase at equilibrium (Zubaidy and Abouelnasr, 2010; Liang et al., 2014). For a solvent-extraction equilibrium system, it can be represented by:

$$K_D = \frac{C_O}{\Gamma_O} \tag{7.2}$$

where C_O is the oil concentration in the solvent, which can be calculated from the following equation:

$$C_O = \frac{(\Gamma_{IO} - \Gamma_O)m}{V} \tag{7.3}$$

where m is the mass of sand (g) and V is the solvent volume (mL) (Liang et al., 2014). Zubaidy and Abouelnasr (2010) demonstrated that the K_D enhanced with increasing solid concentration (C_S). Such a phenomenon has been explained as the "solid concentration effect" or "solid effect" (C_S effect). The K_D for a given system under constant temperature, pressure, and medium composition (e.g., pH, ionic strength) should be thermodynamically independent of both oil and solid (sludge) concentrations. The change in K_D with C_S indicates that the experimentally measured K_D is not a thermodynamic equilibrium parameter, or real extraction systems are not ideal (or thermodynamic). Different models have been developed to investigate the fundamental mechanism of the C_S effect and to describe the C_S dependence of K_D, including the solute complexation model (Voice and Weber, 1985), the particle-interaction model (DiToro et al., 1986), the metastable-equilibrium adsorption (MEA) theory (Pan and Liss, 1998), the flocculation model (Helmy et al., 2000), the power function (Freundlich-like) model (Chang and Wang, 2002), the four components adsorption (FCA) model (Wu et al., 2006), and surface-component activity (SCA) model (Zhao and Hou, 2012; Zhao et al., 2012, 2013; Liang et al., 2014).

In solvent extraction, temperature, pressure, solvent-to-sludge ratio or sludge (solid) concentration, mixing, and the solvent itself are the important factors affecting the oil-recovery efficiency. Mixing and heating can improve the dissolution of sludge organic components in the solvent. The extraction process can be accelerated by high temperature but the loss of PHCs and solvent can be caused by it through evaporation, while low temperature would reduce the cost of extraction process but can lead to lower oil-recovery efficiency. Lower pressure is favored during distillation since solvent evaporation can occur at a relatively lower distillation temperature. A lower distillation temperature can not only decrease heating cost, but also prevent thermo degradation of solvents. In addition, increase of the solvent-to-sludge ratio can improve the quantity and quality of recovered oil (Hu et al., 2013). The utilization of various solvents for recovering oil from oily sludge have been reported in many studies. The recovery rates of these solvents are given in Table 7.2.

A large volume of oily sludge can be treated by solvent extraction depending on the extraction-column design. A closed and continuous process capable of retaining the evaporated solvent is suitable to prevent the emission of solvent vapor. The energy costs of the application can be enhanced by the heating required for solvent recycling.

Table 7.2 Applied Solvents for Recovering Oil From Oily Sludge and the Recovery Rates of These Solvents

Solvent	Recovery Rate	References
Propane	In a pilot-plant process with multiple extraction steps, the levels of several aromatic hydrocarbons in the remaining solids were below detection limits.	Poche et al. (1991)
An intermediate-molecular-weight hydrocarbon stream from a petroleum refinery	Using a solvent-to-sludge mass ratio of 0.5, and an extraction time of 1 h, 23–32% of the hydrocarbon material in the sludge was recovered for an overall mass reduction of approximately 10–20%.	Biceroglu (1994)
Isopar-L	Using a solvent-to-sludge mass ratio of 10, and an extraction time of 2 h at 93°C, the removals of most of the hydrocarbons that were analyzed were over 99%.	Trowbridge and Holcombe (1995)
Turpentine	The extracted oil accounted for 13–53% of the original sludge mass.	Gazineu et al. (2005)
Petroleum solvent oil	Petroleum solvent oil with a high percentage of ring compounds (e.g., naphthenics and aromatics) such as catalytic cracking heating oil was highly effective in dissolving asphaltenic components in oily sludge, and the solvent oil with paraffinic character like virgin paraffinic diesel was effective for sludge with more paraffinic (waxy) components.	Meyer et al. (2006)
Supercritical ethane and dichloromethane	The recovered oil ranged from 16–55% of the original sludge mass for supercritical ethane, compared to approximately 50% for dichloromethane.	Ávila-Chávez et al. (2007)
Hexane and xylene	The highest oil-recovery rate of 67.5% was observed by using hexane, with most of them in the range of C_9 to C_{25}.	Taiwo and Otolorin (2009)

Continued

Table 7.2 Applied Solvents for Recovering Oil From Oily Sludge and the Recovery Rates of These Solvents—cont'd

Solvent	Recovery Rate	References
Methyl ethyl ketone (MEK) and liquefied petroleum gas condensate (LPGC)	At a solvent-to-sludge ratio of 4:1, the highest oil-recovery rate of 39% and 32% was obtained by MEK and LPGC extraction, respectively.	Zubaidy and Abouelnasr (2010)
Naphtha cut, kerosene cut, n-heptane, toluene, methylene dichloride, ethylene dichloride, and diethyl ether	Toluene gave the highest PHCs recovery rate of 75.94%.	El Naggar et al. (2010)
Cyclohexane, n-hexanol, n-butanol, and kerosene	Oil-recovery efficiencies from the oily sludge under different solid concentrations at 25 ± 0.5°C for these solvents were in the range of over 50–99.99%. The order of oil recovery for the four solvents was cyclohexane > n-hexanol > kerosene > n-butanol.	Liang et al. (2014)
Cyclohexane, dichloromethane, methyl ethyl ketone, ethyl acetate, and 2-propanol	These solvents (with the exception of 2-propanol) showed a promising oil-recovery rate of about 40%, but the recycling of dichloromethane solvent after oil extraction was quite low.	Hu et al. (2015)

The requirement for a large volume of organic solvents may result in significant economic and environmental concerns. Some alternative methods such as supercritical fluid extraction (SFE) have been proposed to improve the performance of solvent extraction. Extraction can occur more rapidly by SFE in comparison with conventional solvent extraction, and more importantly, the use of organic solvents can be eliminated by this process. However, its use for extracting oil from a large volume of oily sludge can be restricted by low efficiency and high variability (Hu et al., 2013).

7.2.2.2 Centrifugation

Centrifugation provides a basic mechanical separation approach for the treatment of oily sludge (Kotlyar et al., 1999; Huang et al., 2014). In this process, special high-speed rotation equipment is used to generate strong centrifugal force, which can separate components with different densities (such as water, solids, oil, and pasty mixtures in oily sludge) within a short time. For reduction of energy consumption and enhancement of centrifugation performance, sludge pretreatment, such as the addition of organic solvents, demulsifying agents, and tensioactive chemicals, the injection of steam, and direct heating are sometimes used to reduce the viscosity of oily sludge. Potential advantages and disadvantages of centrifugation in oily-sludge treatment are as follows:

Advantages:

- It is generally a relatively clean and mature technology for oily-sludge treatment.
- Oil separation from sludge by centrifugation is effective.
- Centrifugation equipment typically does not occupy much space.

Disadvantages:

- Centrifugation process needs high-energy consumption to generate strong enough centrifugation force to separate oil from oily sludge.
- The application of centrifugation has been limited to small scales due to the high equipment investment and limitations.
- Centrifugation can bring noise problems.
- The use of demulsifying agents and tensioactive chemicals for sludge pretreatment not only enhances the processing cost, but also creates environmental concerns (Hu et al., 2013; Islam, 2015).

A simplified flow diagram of a process of using centrifugation for oily-sludge treatment is shown in Fig. 7.2. Oily sludge is mixed with demulsifying agent or other chemical conditioner. Hot steam is introduced into this mixture in a pretreatment tank to reduce its viscosity. The less viscous sludge is mixed with water at a certain sludge—water ratio for high-speed centrifugation. After centrifugation, the separated water containing a high concentration of PHCs is drained for further wastewater treatment, and the separated oil (still containing water and solids) is sent to a gravimetric separator for further separation to obtain the recovered oil. The separated water from the separator is sent to wastewater treatment. The sediments from the centrifugation and separator are collected as solid residues for further treatment (Hu et al., 2013; Islam, 2015). The solid particles mainly include silicon sand (Al-Futaisi et al., 2007; Pinheiro and Holanda, 2013) and other minerals, iron fragments, heavy metal species, etc., can make this sludge unsuitable for biodegradation (Khan et al., 1995; Huang et al., 2014).

The decanter centrifuge systems are the most suitable centrifuge type for handling oily sludge (CONCAWE, 2003). Two-phase and three-phase horizontal decanter centrifuge systems have been reported for handling oily sludge. Two-phase horizontal decanter centrifuge (Fig. 6.26) can be used for continuous two-phase separation (liquid from solids) (Schwarz Global Consulting, 2011a). The use of two-phase horizontal decanter centrifuge for oily-sludge dewatering results in a dry cake and a liquid consisting of oil and water and some solids (CONCAWE, 2003). The essential part of the decanters is the rotating part, which consists of a cylindrical/conical bowl with a conveyor scroll inside that rotates at a differential speed. The rotating part is driven by electric motors via belt transmission. Feed enters the bowl through a central feed pipe. Through ports in the scroll body, feed passes into the bowl where separation

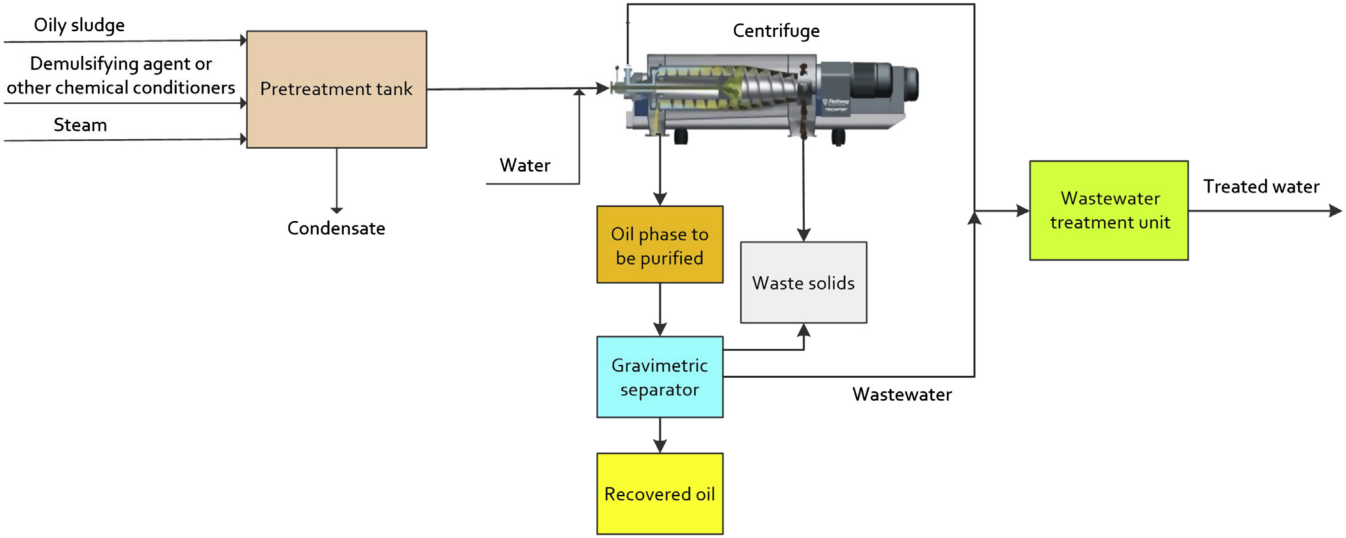

Figure 7.2 Simplified flow diagram of a process of using centrifugation for oily-sludge treatment.
Modified from Hu, G., Li, J., Zeng, G., 2013. Recent development in the treatment of oily sludge from petroleum industry: a review. Journal of Hazardous Materials 261, 470–490; Islam, B., 2015. Petroleum sludge, its treatment and disposal: a review. International Journal of Chemical Sciences 13 (4), 1584–1602.

by centrifugal force occurs. In a decanter, the product is separated into a liquid phase and a solids phase. The discharge of the separated liquid can be under pressure or by gravity. The separated solids are conveyed by the scroll to the conical end of the bowl and are discharged (Schwarz Global Consulting, 2011a; MARINER plus s.r.o. (Flottweg, Solenis), 2016a). The three-phase horizontal decanter centrifuge (tricanter) (Figs. 6.26 and 7.2) can be used for continuous separation of three-phase systems, consisting of two immiscible liquids and a solid material. In a tricanter, the product is separated into a light liquid phase (such as oil), a heavy liquid phase (such as water), and a solid phase (such as organic residues, etc.). The discharge of the separated oil is done by gravity, while the separated water phase is discharged by an impeller under pressure or by gravity. The separated solids are conveyed by the scroll to the conical end of the bowl and are discharged (Schwarz Global Consulting, 2011b; MARINER plus s.r.o. (Flottweg, Solenis), 2016b).

7.2.2.3 Surfactant Enhanced Oil Recovery

The utilization of surface-active compounds (surfactants) has the potential to enhance the biodegradation rates of hydrophobic organic compounds in contaminated media by increasing the total aqueous solubility of these compounds (Cort et al., 2002). Surfactants may be used in mobilizing heavy crude oil, transporting petroleum in pipelines, managing oil spills, oil-pollution remediation, cleaning oil sludge from oil storage facilities, soil/sand bioremediation, and enhanced oil recovery (EOR) (Banat, 1995).

Surfactant is generally an amphiphilic compound, and its molecule consists of a hydrophobic tail and a hydrophilic tail. The hydrophilic tail makes surfactant molecule dissolve in the water phase and enhances solubility of PHCs, while the hydrophobic tail makes it tend to gather at the interfaces to reduces the surface or interfacial tension and thus increase the mobility of PHCs (Mulligan, 2009; Hu et al., 2013). Surfactants that have a greater solubilization ratio give an indication on its ability to enhance the recovery oil from contaminated media (Urum and Pekdemir, 2004).

Surfactants can either be chemically synthesized (synthetic) or microbially produced (biosurfactant). Synthetic surfactants are of petrochemical origin, whereas biosurfactants or biogenic surfactants are produced by bacteria, yeast, and fungi. Synthetic surfactants may be cationic, anionic, nonionic, or amphoteric, although only anionic and nonionic surfactants have been applied as oil dispersants. Biosurfactants are generally categorized based on their biochemical nature and the microbial species generating them. The five main groups of biosurfactants include (1) glycolipids, (2) phospholipids and fatty acids, (3) lipopeptide/lipoproteins, (4) polymeric surfactants, and (5) particulate surfactants (Edwards et al., 2003).

Some synthetic surfactants, such as sodium dodecyl sulfate (SDS), Corexit 9527, Triton X-100, Tween 80, and Afonic 1412-7 have been reported to be able to enhance the concentration of nonpolar compounds in the aqueous phase (Christofi and Ivshina, 2002; Grasso et al., 2001; Cuypers et al., 2002; Prak and Pritchard, 2002; Lai et al., 2009; Hu et al., 2013). However, the problems with applying synthetic surfactants are associated with their toxicity and resistance to biodegradation (Christofi and

Ivshina, 2002; Lai et al., 2009). In comparison with synthetic surfactant, biosurfactants typically exhibit greater environmental compatibility, better surface activity, lower toxicity, and higher biodegradability (Whang et al., 2008; Lai et al., 2009). Furthermore, they could easily be generated from renewable resources via microbial fermentation (Lai et al., 2009). Thus biosurfactants can be better candidates for the application in bioremediation of contaminated soil and subsurface environments (Christofi and Ivshina, 2002; Lai et al., 2009).

Different laboratory- and field-scale studies have been carried out to apply surfactants in oily-sludge treatment. For examples, Abdel Azim et al. (2011) used three sets of demulsifier systems based on nonyl phenol ethoxylates ($n = 9$, 11, 13) (surfactants) to break down petroleum sludge obtained from the main drainage basin of the Al-Hamra Oil Company and found that the best demulsifier composition for complete breakdown of the sludge was the one based on nonyl phenol ethoxylates ($n = 13$). Lima et al. (2011) studied oil recovery from fuel-oil storage-tank sludge using biosurfactants. They isolated five bacterial strains for biosurfactant production, and reported that biosurfactants produced by *Dietzia maris* sp., *Pseudomonas aeruginosa*, *Arthrobacter oxydans*, *Bacillus* sp., and *Bacillus subtilis*, respectively, recovered 95.45%, 93.40%, 91.59%, 88.63%, and 84.09% of the total oily sludge as oil, but only 2.00% of the oil present in oily sludge was recovered when not using biosurfactant. Yan et al. (2012) used a rhamnolipid biosurfactant-producing strain, *Pseudomonas aeruginosa* F-2, to recover oil from oily sludge in laboratory and pilot-scale experiments. They conducted the pilot-scale experiment in the wastewater treatment plant of the Dalian Petrochemical Branch Company. A schematic diagram of the pilot-scale experimental system is shown in Fig. 7.3. This system consists of three identical stainless steel-made tanks (1.1 m long, 0.8 m wide, and 1.1 m high), supported by a steel frame. Three pipelines on the side of each tank introduce sludge, heat steam, and tap water into the tanks, respectively. Control of the addition of material and monitoring of the separation of oil—water/sediment were done by a level gauge on the side of each tank. The temperatures were controlled by temperature controllers connected to the valves of the steam pipelines. The pilot-scale experiments performed under optimum values of the carbon—nitrogen ratio, temperature, sludge—water ratio, and inoculum size of 10, 35°C, 1:4%, and 4%, respectively. The treatment was terminated after 72 h of incubation by adding sulfuric acid to the tanks at a concentration of 0.33% (w/v). Then the treated sample was transferred into a centrifuge. Oil recovery of up to 91.5% has been reported using this system. They concluded that strain F-2 has potential for industrial applications and may be used in oil recovery from oily sludge. Long et al. (2013a) used rhamnolipid for demulsification of waste crude oil in a pilot-scale (100 L) treatment system and reported that rhamnolipid treatment could recover over 98% of crude oil from the wastes. The recovered oil contained less than 0.3% of water and thus could directly reenter the refinery process.

Surfactant-enhanced oil recovery is usually a simple but relatively fast and effective process, and it has the potential to manage a large volume of oily sludge. Effectiveness, cost, public and regulatory acceptance, biodegradability, degradation products, toxicity, and ability to recycle are factors that should be taken into account when

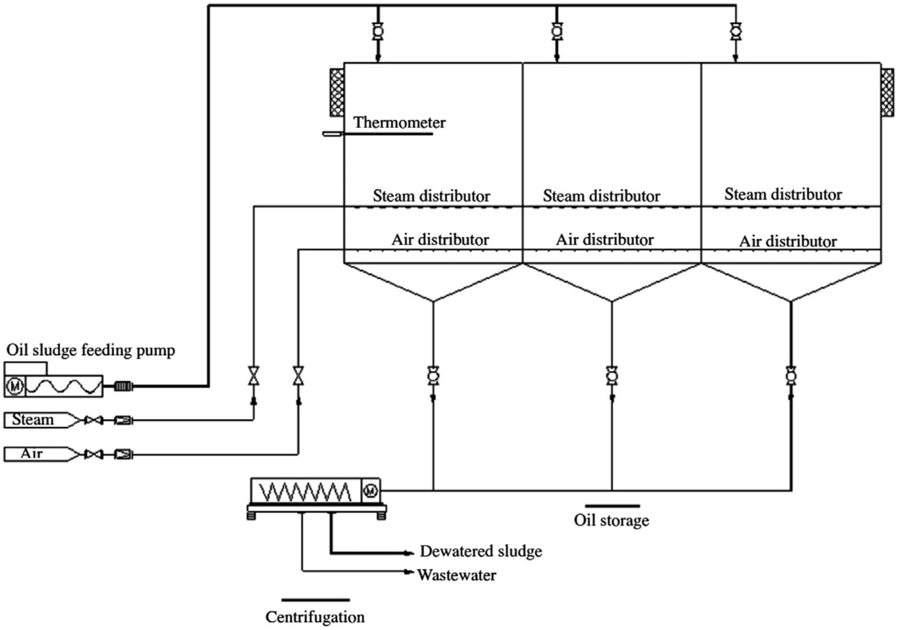

Figure 7.3 Schematic diagram of the pilot-scale experimental system to recover oil from oily sludge (Yan et al., 2012).

selecting surfactants for oil recovery. In particular, the costs of producing biosurfactants may restrict their commercial applications. These costs may be decreased by improving yields, recovery, and using inexpensive or waste substrates (Calvo et al., 2009; Hu et al., 2013).

7.2.2.4 Distillation/Pyrolysis

Distillation may be used to remove light- and intermediate-weight hydrocarbon compounds from the solid—hydrocarbon mixture in a retort furnace (Reis, 1996) or using steam or superheated steam (McCoy, 1977). In this process, the oily sludge as received or in diluted form is pumped by means of a slurry pump into the central or upper part of a heating zone, i.e., a steam distillation tower. The hydrocarbons and water are vaporized by heating the solid—hydrocarbon mixture, and the gases may be removed from the chamber by inert gas, such as nitrogen, or carbon dioxide, but steam is the most economical of the available gases. When the hydrocarbons and water are removed from the sludge, the solids become dry, granular, and noncohesive and fall to the bottom of the tower through a series of grates. A mechanical device, such as a screw conveyor, is then used to remove the solids from the bottom of the tower. The steam and hydrocarbon vapors are withdrawn from the top of the tower to a condenser/heat exchanger in which the vapors are condensed to yield a mixture of oil and water. These are separated gravimetrically in an oil—water separator by centrifugation or any other suitable means. Product oil is drawn off at this point and is suitable for use as a cracking feedstock. In some instances, a portion of the oil may be used as fuel for stripping the steam boiler. A portion of the water from the oil–water separator can be pumped back through the heat exchanger to the stripping steam boiler or freshwater can also be used as makeup for the boiler. Note that the superheated steam can be advantageously utilized. The temperature of the steam used in this process typically varies from about 250 to 700°F and, preferably, will be from about 300 to 600°F (McCoy, 1977).

In this process, the solids may be transformed into a more readily disposable form. Some fractions may be vaporized at relatively low temperatures, whereas the heavy oil fractions need very high temperatures before vaporization takes place. Coking or destructive distillation of the hydrocarbons can result from these high temperatures under other heating conditions (McCoy, 1977). If the distillation temperatures are high enough, pyrolysis will break the hydrocarbon molecules and form coke. The remaining hydrocarbons are solidified by this process and their migration on disposal of the waste can be prevented (Reis, 1996).

McCoy (1977) recovered oil from refinery sludges by steam distillation. The oil recovered from this mixture was suitable for a variety of purposes such as for cracking stock, etc., and the water recovered exhibited a reduced COD. They noted that the dry, free-flowing solids recovered from the heating zone were useful for a wide variety of applications, such as for landfills. Li et al. (2015) proposed an application of oily sludge via a distillation modification treatment. They showed that the separated light oil was higher than 29.2% of the original dewatered oily sludge, such as 33.4% at 493K and 39.2% at 573K for 180 min. In an appropriate range of thermal treatment parameters (distillation temperature 493–533K and time 2–3 h), more desirable results were reported for the residual emulsion. For example, the content of resin and asphaltene in the residual emulsion increased from 29.1% to 47.5% at 493K for 180 min. In addition, the values of penetration and softening point of the residual emulsion were reported as 88 and 48.5°C, respectively. This modification also enhanced its bond capacity. When this asphalt-like emulsion was used as a solidifying or embedding material, an ideal ratio was achieved at 0.5 (m/m) for controlling the release of heavy metals.

According to Reis (1996), several commercial thermal distillation systems are available, but fire hazard due to hydrocarbon vapors at high temperatures, corrosion problems at high temperatures, emission of air pollution, chemical structure alteration of some hydrocarbons at high temperatures, which makes their reuse in some applications impossible, possible formation of a heavy residual tar on the solids due to the distillation lack of heavy hydrocarbon compounds, the high-energy costs of heating, are some of operational limitations of these systems (Reis, 1996).

Pyrolysis is the thermal decomposition of materials at elevated temperatures (500–1000°C) and theoretically in an inert atmosphere. Depending on the operational conditions, it can produce char, liquid, or gas. It is necessary to note that pyrolysis is different from gasification, which converts organic materials to combustible gas or syngas with the existence of 20–40% of the oxygen. Fast pyrolysis is generally a pyrolysis reaction, which is carried out at high heating rates, moderate temperatures

(500°C), short gas residence times (<2 s), and rapid quenching of the vapors. The main product of this process is the pyrolysis liquid, also called biooil or pyrolysis oil, which can be used as a fuel and also as a source of valuable chemical products (Fonts et al., 2012).

Ablative pyrolysis, fluid bed and circulating fluid-bed pyrolysis, and vacuum pyrolysis are three types of pyrolysis configurations (Fonts et al., 2012; Hu et al., 2013). Fluid beds are the most popular configurations because of their ease of operation and ready scale-up (Fonts et al., 2012). The commercial-scale oil-recovery pyrolysis systems are mainly based on fluid beds and circulating fluid beds, which may consist of oily-sludge pretreatment, fluidized bed reactor, char collector, cyclone and fly ash collector, and liquid-condensing system (Fig. 7.4) (Fonts et al., 2012; Hu et al., 2013).

Temperature, heating rate, characteristic of oily sludge (Fonts et al., 2012; Hu et al., 2013), chemical additives (Hu et al., 2013), existence of catalyst, residence time, feeding rate, and reaction atmosphere (Fonts et al., 2012) are various factors that can affect the pyrolysis performance.

Different studies have been carried out to apply pyrolysis for fuel recovery from oily sludge. Chang et al. (2000) investigated the pyrolysis of the oil sludge from the oil-storage tank of a typical petroleum refinery plant located in northern Taiwan by using nitrogen as carrier gas in the temperature range 378–873K. Its heating value of dry basis and low heating value of wet basis were about 10,681 and 5870 kcal/kg, respectively. The main gaseous products (noncondensable gases at 298K) excluding N_2 were CO_2 (50.88 wt%), HCs (hydrocarbons, 25.23 wt%), H_2O (17.78 wt%), and CO (6.11 wt%). The HCs mainly consist of low molecular weight paraffins and olefins (C_1–C_2, 51.61 wt% of HCs). The temperature corresponding to the maximum production rate of HCs was 713K. The distillation characteristics of the liquid product

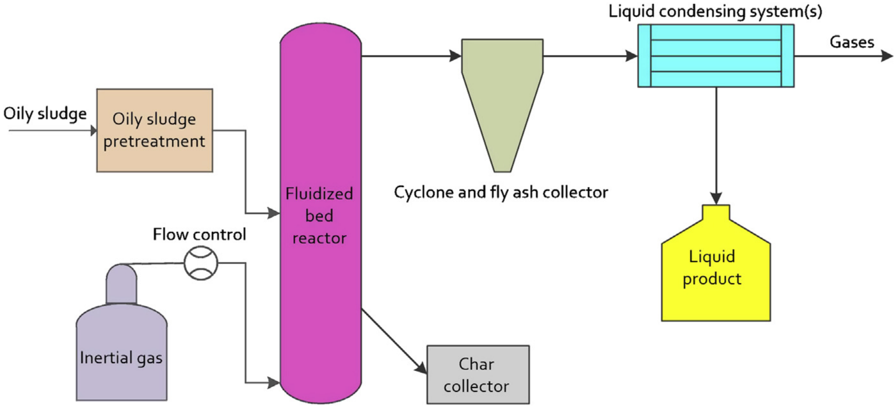

Figure 7.4 Schematic diagram of fluidized bed systems used in sludge pyrolysis treatment. Modified from Fonts, I., Gea, G., Azuara, M., Ábrego, J., Arauzo, J., 2012. Sewage sludge pyrolysis for liquid production: a review. Renewable and Sustainable Energy Reviews 16, 2781–2805; Hu, G., Li, J., Zeng, G., 2013. Recent development in the treatment of oily sludge from petroleum industry: a review. Journal of Hazardous Materials 261, 470–490.

(condensate of gas at 298K) from the pyrolysis of oil sludge was close to diesel oil. However, it contained a significant amount of vacuum residue of about 9.57 wt%. The heating value of the liquid product was reported to be about 10,840 kcal/kg. Schmidt and Kaminsky (2001) studied the pyrolysis of the oil sludge of tanker cleaned in fluidized-bed reactor and investigated the separation of oil from the solids at temperatures from 460 to 650°C. As reported, 70–84% of the oil separated from the solids. Punnaruttanakun et al. (2003) investigated the influence of different heating rates of 5, 10, and 20°C/min on the pyrolysis of API separator sludge obtained from an oil company in Thailand. Hydrogen and acetylene were reported to be the main species in the pyrolysis products. Only a high heating rate of 20°C/min caused significant differences in the thermal-conversion behavior compared to the low heating rates, which, as noted, may be due to the high amount of ash in the sludge. For the reuse, conservation, and recycling of solid wastes, Shie et al. (2004) investigated the effects of using fly ash, oil sludge ash, waste DAY-zeolite, and waste polymer of polyvinyl alcohol (PVA) as additives on the possible improvement of the pyrolysis of oil sludge. For the increase of conversion, two weight ratios of 10 wt% and 5 wt% additives provided the offers in the order of fly ash of 10 wt% > PVA of 10 wt% > oil sludge ash of 10 wt% > DAY-zeolite of 10 wt% > fly ash of 5 wt% > DAY-zeolite of 5 wt% > no additives. The addition of additives reportedly improved the quality of pyrolysis oil (as sum of light and heavy naphtha and light gas oil) in the order of fly ash of 10 wt% > oil sludge ash of 10 wt% > PVA of 10 wt% > DAY-zeolite of 10 wt% > fly ash of 5 wt% > DAY-zeolite of 5 wt% > no additives. Karayildirim et al. (2006) studied the pyrolysis of waste sludges (oil sludge and mixed sludge) using a fixed-bed reactor. They reported that pyrolysis of oil sludge produced a larger amount of oil-containing more aliphatic compounds and a high calorific value. On the other hand, pyrolysis of mixed sludge gave a smaller amount of oil rich in polar compounds. The gaseous products from pyrolysis were reported to consist of a high amount of combustable gases. Landfilling was reported to be the best alternative to dispose of the pyrolytic char obtained from pyrolysis. Wang et al. (2007) carried out pyrolysis of oil sludge first by thermogravimetry/mass spectroscopy (TG/MS) and then in a horizontal quartz reactor with an electrical laboratory furnace under different pyrolysis conditions (heating rate from 5 to 20°C/min, final pyrolysis temperature from 400 to 700°C, various interval holding stage, and catalyst addition). They proved by TG/MS results that pyrolysis reaction of oil sludge started at a low temperature of about 200°C, and the maximum evolution rate was reported to be between the temperatures of 350–500°C. They noted that a higher final pyrolysis temperature, an interval holding stage, and adding catalyst could promote the pyrolysis conversion (in terms of less solid residue production). In all parameters, an interval holding stage for 20 min near the peak temperature of 400°C could increase the yield of oil and improve its quality. Three additives used as catalysts did not improve oil-product quality markedly in spite of enhancing pyrolysis conversion greatly. Liu et al. (2009a) investigated the pyrolysis of tank-bottom oil sludge and found that the pyrolysis reaction was significant in the range of 473–773K. Higher heating rate enhanced the carbon (C) and sulfur (S) content but reduced hydrogen (H) content in solid residues. The main gaseous products excluding N_2 were HCs, CO_2, H_2, and CO. The yield of HCs was reported to be significant in the range of 600−723K. Around 80% of total organic carbon (TOC) in oil sludge could be transformed into HCs in the pyrolysis process.

According to Hu et al. (2013), the potential advantages and disadvantages of pyrolysis in oily-sludge treatment are as follows:

Advantages:

- Liquid product can be easily stored and transported.
- The recovered oil is comparable to low-grade petroleum distillates from commercial refineries and could be directly applied in diesel fueled engines.
- In comparison with the incineration process, pyrolysis of oily sludge produces a lower emission of NO_x and SO_x, and it also enables heavy metals in oily sludge to be concentrated in the final solid product (i.e., char).
- The char generally accounts for 30−50 wt% of the original oily sludge, and it can be used as an adsorbent for the removal of various pollutants such as H_2S or NO_x in gaseous streams and also as a soil conditioner to enhance the nutrient availability for plants.
- The metals enriched in solid char in the pyrolysis process can be more resistant to leaching than those concentrated in the ash obtained from incineration.

Disadvantages:

- The low economic value of liquid products and the relatively complex processing equipment can limit the large-scale implementation of pyrolysis.
- In pyrolysis, the high operational cost is mainly because of the large amount of external energy needed for the endothermic reaction to occur.
- Oily sludge typically contains relatively high water content, and thus the overall cost of pyrolysis may be significantly enhanced by the dewatering of oily sludge before pyrolysis treatment.
- The liquid products of sludge pyrolysis can contain a large portion of PAHs (the well-known highly carcinogenic substances) (Hu et al., 2013).

7.2.2.5 Microwave Irradiation Method

Microwave heating, due to its volumetric heating effects, can offer a faster processing rate than conventional heating techniques (Abdulbari et al., 2011). Microwave energy can directly penetrate the materials through molecular interactions with the electromagnetic field. Microwave heating can result in all individual elements of the material being heated individually, whereas the thermal conductivity of a material restricts the internal temperature distribution of it subject to traditional heating. Thus heating times using microwaves can often be decreased to less than 1% of those needed using traditional heating techniques. The behaviors of materials on interaction with a microwave field are as follows:

- Transparent (low dielectric loss materials): microwaves pass through the material with little absorption;
- Opaque (conductors): the material reflects microwaves; and
- Absorbing (high dielectric loss materials): microwave energy is absorbed based on the electric field strength and the dielectric loss factor.

Microwave heating method can have preferable advantages in the treatment of materials, which include a mixture of absorbers and transparent components. The substances with high dielectric loss absorb microwave energy, whereas microwave energy passes through the low dielectric loss substances, which can result in selective heating. The power absorbed by a material is related to the dielectric properties of the material. The power absorbed per unit volume, or power density (Pd), can be calculated as follows:

$$\mathrm{Pd} = 2\pi f \varepsilon_0 \varepsilon''_{\mathrm{eff}} |E|^2 \tag{7.4}$$

where f is the microwave frequency, ε_0 is the permittivity of free space (8.85×10^{-12} F/m), $\varepsilon''_{\mathrm{eff}}$ is the relative dielectric loss factor, and E is the magnitude of the electric field. The majority of the absorbed power is transformed into heat within the material, hence the heating rate of a particular component is related to the power density, specific heat capacity, and density:

$$\frac{\Delta T}{\Delta t} = \frac{2\pi f \varepsilon_0 \varepsilon''_{\mathrm{eff}} |E|^2}{\rho C_{\mathrm{p}}} \tag{7.5}$$

where T is the temperature, t is the time, ρ is the material density, and C_{p} is the specific heat capacity (Shang et al., 2006).

The microwave frequency ranges from 300 MHz to 300 GHz, with most microwave applications falling between 3 and 30 GHz. The industrial application of microwave heating is usually performed at either a frequency close to 900 MHz or at 2450 MHz (Appleton et al., 2005; Hu et al., 2013).

The concept of microwave heating in demulsification was first introduced by Klaila (1978) and Wolf (1986) in their patent documents (Kuo and Lee, 2010; Islam, 2015). The inner phase in W/O emulsion (such as oily sludge) is water with a relatively higher dielectric loss, and thus more microwave energy can be absorbed by water than oil. By this energy absorption, water can be expanded and the water—oil interfacial film is pressed to become thinner. Water—oil separation can be facilitated without the addition of any chemicals (Tan et al., 2007; Hu et al., 2013). When a W/O emulsion is heated with microwave irradiation, two principal mechanisms generally occur simultaneously. One of these is a rapid increase in temperature, which decreases emulsion viscosity and breaks the outer film of droplets. The other is molecular rotation, which neutralizes the Zeta potential due to rearrangement of electrical charges surrounding water molecules, resulting in movement of ions around droplets (Kuo and Lee, 2010). Underreduced Zeta potential, water and oil molecules can move more freely in the emulsion so that the water or oil droplets can collide with each other to form coalescence, which facilitates water—oil separation (Tan et al., 2007; Hu et al., 2013).

Different factors such as microwave power, microwave duration, surfactant, pH, salt, and other properties of oily sludge such as water—oil ratio can affect the performance of microwave heating on oily-sludge demulsification (Fortuny et al., 2007; Hu et al., 2013).

Several laboratory- and field-scale studies have demonstrated that microwave irradiation is useful for water—oil emulsion treatment. As cited by Hu et al. (2013), Fang and Lai (1995) used a microwave heating method for a field test to demulsify

188 barrels of W/O emulsion in tanks, and their results depicted that the emulsion was separated into 146 barrels of oil and 42 barrels of water, while the water separation yield from emulsions was higher than that when using traditional heating (Hu et al., 2013). Chan and Chen (2002) reported that both the demulsification rate and the separation efficiency enhanced with an increase in droplet size and the concentrations of the carrier (D2EHPA) and acid, but they reduced with an increase in surfactant (Span 80) concentration and the oil phase-to-aqueous phase volume ratio (O/A). As the concentration of electrolyte (NaCl, KCl, $NaNO_3$, and Na_2SO_4) was about 0.5 M, both the demulsification rate and the separation efficiency were maximum. The optimum microwave irradiation power and exposure time were reported to be 420 W and 12 s, respectively. Xia et al. (2003) found that the demulsification efficiency may reach 100% in a very short time under microwave radiation. In another work, Xia et al. (2004) investigated the influence of a very small amount of inorganic salt on the demulsification of W/O emulsions and found that some inorganic salts could effectively enhance the demulsification efficiency and increase the light transmittance of the water separated from the emulsions. Shang et al. (2006) studied the microwave heating technique for the treatment of oil-contaminated drill cuttings (OCDC). For a sample mass of 40 g, it was reported that approximately 20 s of microwave treatment was needed to reduce the residual oil levels close to or below the 1% threshold. They noted that the main limitation in the minimum achievable residual oil levels was the moisture content, but they concluded that increasing the amount of water in the samples could potentially overcome such limitations. Tan et al. (2007) investigated the demulsifying and separation of crude-oil emulsion by the microwave chemical method and found that the separation effect by this method for the high-water-content crude-oil emulsion was better than that of emulsion with lower water content. The separation efficiency of this method was also reported to be about 95 v/v% under the conditions of 50 ppm of demulsifier, 10 s radiation time, and 1 min settling time. Fortuny et al. (2007) studied the effect of a set of crude-oil emulsion variables, including pH and salt and water contents, on the microwave demulsification method. Higher microwave demulsification efficiencies were reported for emulsions containing high water content, except when high pH and salt content were simultaneously involved.

Kuo and Lee (2010) proposed artificial seawater as an economical source of the cations required in microwave process, called seawater-assisted microwave demulsification. The separation efficiencies of a cutting-oil emulsion, an olive-oil emulsion, and a cutting-oil/olive-oil mix were reported to be 93.1%, 92.6%, and 93.2%, respectively, using optimum operating conditions, which were 40 s of microwave irradiation at 700 W, a 60 min settling time, and addition of 12%, 32%, and 20% (all v/v) of artificial seawater, respectively. Using this set of operating conditions, a decrease in solution pH resulted in a significant increase in demulsification efficiency after addition of inorganic acid, whereas an increase in the concentration of surfactant, SDS, resulted in a decrease in efficiency. Abdulbari et al. (2011) studied the influences of Triton X-100, low-sulfur wax residue (LSWR), sorbitan monooleate (Span 83), and SDS on the stability and microwave demulsification of petroleum emulsions. They found that emulsion stability was related to several parameters including the surfactant concentration, water-to-oil phase ratio (10–90%), temperature, and agitation speed. In comparison with conventional heating, the use of microwave heating could significantly increase the demulsification rate, reaching over 90 v/v% for the emulsions. Vazquez et al. (2014) investigated microwave heating and gravity sedimentation for reducing and oil recovering from water-in-oil Mexican oil emulsions and found that microwave heating and gravity sedimentation are alternatives for the separation of these emulsions.

In comparison with the other heating techniques, microwave irradiation can more rapidly raise the energy of molecules inside the medium, leading to higher reaction rates and superheating within several minutes. Because of this short heating time, microwave irradiation is a high energy-efficient and easy-to-control approach for breaking emulsions. In addition to its high demulsification efficiency, the low temperature of the reactor wall during the direct heating inside the bulk medium caused by microwave irradiation could lead to an extended aromatization reaction, which could result in enhanced yield of light aromatic compounds. These light compounds can have a much lower toxicity compared to PAHs with high molecular weight in the liquid products generated during the pyrolysis process. However, the specific equipment required and possible high operating costs restrict the application of microwave irradiation to industrial-scale oily-sludge treatment. Note that this method is unable to treat heavy metals (Hu et al., 2013).

7.2.2.6 Freeze/Thaw Method

One important step in recovering oil from oily sludge is to remove water from a W/O emulsion by separating oil and water into two phases, a process called demulsification (Chen and He, 2003; Hu et al., 2013). A freeze/thaw method applied for sewage-sludge dewatering in cold regions was reported as an effective and feasible method for demulsification (Jean et al., 1999; Chen and He, 2003; Lai et al., 2004; Rajaković and Skala, 2006; Lin et al., 2007; Zhang et al., 2012; Hu et al., 2013). According to Lin et al. (2008) and Hu et al. (2013), there are two different mechanisms for the demulsification. The first mechanism takes place when the water in emulsion becomes frozen ahead of the oil phase as in the following:

$$\begin{aligned}\text{Original emulsion} &\rightarrow \text{Water droplets freezing, expansion, and coalescing}\\ &\rightarrow \text{Gravitational delamination}\end{aligned} \tag{7.6}$$

The second mechanism takes place when the oil becomes frozen ahead of the water phase as in the following:

$$\begin{aligned}\text{Original emulsion} &\rightarrow \text{Oil phase freezing to form a solid cage}\\ &\rightarrow \text{Water droplets freezing and expanding to break the cage}\\ &\rightarrow \text{Emulsion thawing and water droplets coalescing}\\ &\rightarrow \text{Gravitational delamination}\end{aligned} \tag{7.7}$$

The initial oil content (Rajaković and Skala, 2006), freezing temperature, freezing time, thawing procedure and conditions (Rajaković and Skala, 2006; Hu et al., 2013), water content, salinity of aqueous phase, presence of surfactants, and solid contents in emulsion (Hu et al., 2013) can affect the efficiency of demulsification based on freeze/thaw method. Note that according to Hu et al. (2013), the use of the freeze/thaw method for oil recovery from oily sludge might be more promising for cold regions where natural freezing is possible.

Different laboratory-scale studies have used the freeze/thaw method in oily-sludge treatment. For example, Jean et al. (1999) reported that freezing and thawing can separate over 50% of oil from an oily sludge taken from the DAF unit of wastewater treatment plant (WWTP) located in Chinese Petroleum Co., Taoyuan, Taiwan. Chen and He (2003) removed nearly 90% of water from water-in-oil emulsion of lubricating oily sludge by the freeze/thaw method. The optimal freezing temperature was reported to be around −40°C and the best thawing conditions were reported either in ambient air or in water bath at a temperature below 20°C. Rajaković and Skala (2006) separated water-in-oil emulsions by the freeze/thaw method and microwave radiation. The efficiency of oil removal with the assistance of microwave radiation was reported to be up to 90%. Lin et al. (2007) used freeze/thaw treatment to break oil-in-water emulsions and studied the effect of four freezing methods including freezing in refrigerator, cryogenic bath, dry ice, and liquid nitrogen. Freezing in cryogenic or dry ice was reported as the best freezing method for water removal, and its efficiency was over 70% with 60% water content regardless of droplet size and oil phase type. In addition, the volume expansion of water turning to ice and interfacial tension of oil—water interface were determined as the main driving forces of demulsification. Yang et al. (2009) used three thawing types (air or room temperature, a 40°C water bath, and microwave irradiation) in the demulsifying of water-in-oil emulsions in the freeze/thaw method. The significant improved dehydrating ratio was reported with microwave irradiation, which was more than 90 v/v% of the emulsion being separated.

Zhang et al. (2012) studied oil recovery from refinery oily sludge using three different approaches, including ultrasonic treatment, freeze/thaw, and combined ultrasonic and freeze/thaw treatment. The freeze/thaw method alone was reported as a more effective method in terms of the oil-recovery rate (with an oil recovery of 65.7%) than the two other methods. By comprehensively considering oil-recovery efficiency, as well as TPH concentrations in the recovered oil and in the separated wastewater, the combination of ultrasound and freeze/thaw was reported as an effective method with satisfactory performance. An oil-recovery rate of 64.2% and TPH concentrations of 851 mg/g and 200 mg/L in the recovered oil and wastewater, respectively, were reported using this combined treatment system.

7.2.2.7 Ultrasonic Irradiation Method

Cyclic sound pressure (compression and expansion) with a frequency greater than 20 kHz is called ultrasound. Based on the frequency, it can be divided into three regions: power ultrasound (20—100 kHz), high-frequency ultrasound (100 kHz—1 MHz), and diagnostic ultrasound (1—500 MHz) (Pilli et al., 2011).

Ultrasonic irradiation has proven to be an emerging, promising, and effective technique for removing adsorbed materials from solid particles, separating solid from liquid in high-concentration suspensions, and reducing the stability of W/O emulsions (Kim and Wang, 2003; Mason, 2007; Ye et al., 2008; Song et al., 2012; Hu et al., 2013; Li et al., 2013). Solid-particle aggregates can be broken by the oscillating cavitational bubbles and shockwaves resulting from ultrasound, which can lead to the erosion of contaminant films attached to solid particles and thus the separation of pollutants from solids and slurries can be facilitated. Ultrasonic irradiation can reach the inner space of solid matrix that is usually inaccessible when using other separation methods (Li et al., 2013). When an ultrasound irradiation is applied to a fluid medium such as a liquid drop or gas bubble, suspended in a liquid, two major physical effects can be observed. At lower intensities, agglomeration of particles may take place when a particulate suspension is exposed to an ultrasonic sound field. As the intensity of the sound is enhanced, such that its energy is greater than that associated with the attractive forces between the liquid molecules, the phenomenon of cavitation occurs (Dezhkunov, 2002; Check and Mowla, 2013). In a W/O system, the process of emulsification starts when the cavitation threshold is attained. Excess energy for new interface formation can be provided by ultrasound. For any intensity above this threshold, there is a corresponding maximum concentration (restricting) of emulsion, which remains relatively stable, that can be generated. This restricting concentration of emulsion enhances with increasing ultrasound intensity (Gaikwad and Pandit, 2008; Check and Mowla, 2013). The temperature of the emulsion system can be enhanced and its viscosity reduced by cavitation, which the mass transfer of liquid phase can be increased, and thus W/O emulsion can be destabilized. Also, under ultrasonic irradiation, the movement of smaller droplets in emulsion can be faster than the larger ones, and their collision frequency to form aggregates and coalescence of droplets can be enhanced, therefore the separation of W/O phases can be facilitated (Hu et al., 2013).

Different factors such as ultrasonic frequency, sonication power and intensity, ultrasonic treatment duration, temperature, pressure, water content in emulsion, solid-particle size, initial PHCs concentration, salinity, presence of surfactant, and viscosity can generally affect the performance of oil recovery from oily sludge using the ultrasonic irradiation method (Feng and Aldrich, 2000; Canselier et al., 2002; Kim and Wang, 2003; Na et al., 2007; Jin et al., 2012; Hu et al., 2013).

Xu et al. (2009) mixed oily sludge with an initial oil content of 0.130 g/g (dry basis) with water treated in an ultrasound-cleaning tank and then separated oil from the oily sludge by air floatation. The minimum oil content, 0.055 g/g (dry basis), was reported at 40°C after ultrasound irradiation, which was 55.6% less than without ultrasonic irradiation. In addition, 28 kHz ultrasound was reported to be superior to 40 kHz ultrasound. The ultrasonic acoustic pressure amplitude with the 28 kHz ultrasound was 0.085 MPa; the 28 kHz ultrasound also exhibited lower oil content than the 40 kHz ultrasound, which yielded 0.120 MPa acoustic pressure amplitude. In addition, sodium silicate obstructed ultrasound oily-sludge deoiling.

Jin et al. (2012) treated oily sludge from an oil-storage tank using a combined ultrasound and thermochemical cleaning method. The best constituents of detergent solution were reported to be sodium silicate, sodium dodecyl benzene sulfonate, and fatty alcohol ethoxylates in a ratio of 1:1:1. Under the optimum conditions, the oil content of the oil sludge dropped from 43.13% to 1.01%, 0.53% of solids remained in the separated oil layer, and 99.32% oil recovery could be achieved when the concentration of detergent solution was 2 g/L. In comparison with traditional thermochemical cleaning, the oil recovery was 17.65% higher for the combined treatment system. Zhang et al. (2012) observed an oil-recovery rate of up to 80.0% with an ultrasonic power of 66 W and an ultrasonic treatment duration of 10 min when the sludge—water ratio was 1:2 without the addition of biosurfactant and salt. An oil-recovery rate of 64.2% and TPH concentrations of 851 mg/g and 200 mg/L in the recovered oil and wastewater, respectively, were also reported by using combined ultrasonic and freeze/thaw treatment system.

Note that the high cost of equipment and maintenance can inhibit and limit the industrial application of ultrasonic technology, and the oil-recovery performance of a large ultrasonic cleaning tank may be compromised because of the resulted low ultrasonic intensity (Hu et al., 2013).

7.2.2.8 Electro-Kinetic Method

Electro-kinetics (EK) is a developing technology that can be applied for in situ remediation of heavy metals and organic contaminants from saturated or unsaturated media (e.g., soils) (Elektorowicz et al., 2006). The first EK phenomenon was reported at the beginning of the 19th century when Reuss applied a direct current to a clay—water mixture. However, Helmholtz and Smoluchowski first suggested a theory dealing with the electro-osmotic velocity of a fluid and the zeta potential under an imposed electric gradient (Acar and Alshawabkeh, 1993; Virkutyte et al., 2002).

In the EK process, a low-intensity direct current is used across an electrode pair on each side of a porous medium, causing electro-osmosis of the liquid phase, migration of ions, and electrophoresis of charged particles in the colloidal system to the respective electrode (Virkutyte et al., 2002; Yang et al., 2005; Hu et al., 2013). A combination of phenomena such as electro-osmosis, electrophoresis, electro-migration, and electrolysis reactions can generally result in EK remediation (Ranjan et al., 2006).

According to Elektorowicz et al. (2006) and Hu et al. (2013), in the EK technique, different phases (water, oil, and solids) can be separated from oily sludge based on three main mechanisms:

1. An electrical field can break colloidal aggregates in oily sludge, leading to the movement of colloidal particles of oily sludge and solid phase toward the anode area as a result of electrophoresis, and the movement of the separated liquid phase (water and oil) toward the cathode area as a result of electro-osmosis.
2. Following the electro-demulsification process, the electro-coagulation of the separated solid phase could take place near the anode area, leading to an increase of solid phase and sediment concentration (fast coagulation generally generates looser particles, while slow coagulation generates compacted particles).
3. The separated liquid phase (water and oil) can form an unstable secondary oil-in-water emulsion that could be gradually electro-coalesced near the cathode area through charging and agglomeration of droplets where two separated phases of water and oil can be produced (Elektorowicz et al., 2006; Hu et al., 2013).

The demulsification rate of a stabilized W/O emulsion may be described by the following formula:

$$H = H_0 e^{-k_d t} \tag{7.8}$$

where H_0 and H represent the height of the emulsion before and after the experiment, respectively, k_d is the overall demulsification rate constant, and t is the duration of the experiment. According to (Elektorowicz et al., 2006), EK enhances the demulsification rate. The lower the electrical potential is the higher the demulsification rate (Elektorowicz et al., 2006).

Different factors such as resistance, pH, electrical potential, and spacing between electrodes can affect the EK treatment performance. The utilization of surfactants or reagents to enhance the contaminant-removal rates at the electrodes may improve this process. In general, low-treatment capacity and difficulty of application are the limitations of this process. As compared with other oil-recovery methods such as centrifugation and pyrolysis, its use for oil recovery from oily sludge requires a lower amount of energy. However, most EK studies on oily sludge have been carried out at the laboratory level, and the performance and costs at a large-scale still require further investigation. It is expected that the treatment cost may be considerably decreased by application of oily-sludge storage pools as the EK cell at the field-scale (Hu et al., 2013). According to Elektorowicz et al. (2006), the anticipated cost of electrical consumption can be as low as $1.2 CDN/m^3 of sludge. In comparison with the conventional remediation methods, the cost of this process can be much lower, possibly reaching $800 USD/ton of sludge (Elektorowicz et al., 2006).

Yang et al. (2005) investigated EK dewatering of oily sludges, and the highest water removal efficiency (56.3%) at bench scale was reported at a 4 cm electrode spacing and an electric potential of 30 V. Comparison of the water-removal efficiency (51.9%) obtained at the 20 V and 4 cm spacing revealed that further increase of electric potential may be unnecessary. The solids content increase was also reported from an initial 5 to 11.5% and 14.1% for 20 and 30 V, respectively. A larger-scale experimental study using a pair of horizontal electrodes in a cylinder with 15 cm i.d. at 60 V and an initial spacing of 22 cm showed that more than 40.0% of water could be removed and very efficient oil separation from the sludge could be achieved. They concluded that the larger-scale system applying 3.8 to 4 L of sludge affected significantly better dewatering efficiency and oil recovery than all the bench experiments, with an average weight reduction of sludge of 46.5−68.5%. According to Elektorowicz and Habibi (2005), cited by Hu et al. (2013), applying the EK process to treat oily sludge could reduce the amount of water by nearly 63% and light hydrocarbon content by about 43%; the light hydrocarbon content could also be removed by 50% when combining electro-kinetic treatment with surfactant. Elektorowicz et al. (2006) investigated the effect of electrical potential and amphoteric surfactant on the electro-demulsification of oily sludge and found that lower electrical potential (0.5 V/cm) produced a higher demulsification rate, and also application of the amphoteric surfactant did not improve the total efficiency of the process.

7.2.2.9 Froth Flotation

Froth flotation is a widely applied process in mining, metallurgical, and mineral industries, due to its very high throughput and efficiency (Rubio and Tessele, 1997; Ramaswamy et al., 2007). It can also be used for oily wastewater treatment (Al-Shamrani et al., 2002), oil recovery from oily sludge (Ramaswamy et al., 2007), and Bitumen recovery from oil sand (Stasiuk and Schramm, 2001; Al-Otoom et al., 2010). This process is a surface chemistry-based unit operation for fine solid-particle separation from an aqueous suspension. In this process, air bubbles in an aqueous slurry capture oil droplets or small solids, leading to their levitation and collection in a froth layer (Urbina, 2003; Hu et al., 2013). In oily-sludge treatment by this technique, a given amount of water is mixed with it to produce sludge slurry. The generated fine air bubbles by air-injection approach oil droplets in the sludge slurry, and the water film between oil and air bubble can get thinning to reach a critical thickness, leading to the rupture of water film and the spreading of oil to air bubbles. Then, the conglomerate of oil droplets with air bubbles can rise to the top of the water—oil mixture faster than an unattached oil drop due to its reduced density, and the accumulated oil can be skimmed off and collected for further purification (Moosai and Dawe, 2003; Ramaswamy et al., 2007; Hu et al., 2013).

Different factors such as oily-sludge properties (e.g., viscosity, solid content, and density), pH, salinity, temperature, size of air bubble, presence of surfactant, and flotation duration can affect oil-recovery performance by froth flotation. This process is a simple and less-expensive approach for oily-sludge handling, but it is generally unsuitable for treating oily sludge with high viscosity and unable to treat heavy metals. Oily sludge must be pretreated to reduce its viscosity and remove the coarse solid particles. This process requires a large volume of water when treating oily sludge with low moisture and high viscosity, leading to an oily wastewater-treatment problem. In addition, the oil constituents in a skimmed oil/solids mixture still need to be further treated and the recovered oil could also contain relatively high moisture. Therefore a number of restrictions still exist when using it in the field-scale and industrial-scale oily-sludge treatment (Hu et al., 2013).

Ramaswamy et al. (2007) studied the recovery of oil from synthetically prepared sludge containing oil and reported that the maximum oil recovery was about 55%. The optimum time of flotation was reported to be around 12 min and also a maximum of 12% oil-recovery increase was reported as the surfactant amount added increased from 5 to 20 g.

7.2.2.10 Adsorption

Materials such as coal or activated carbon may be applied to remove hydrocarbons from contaminated solids (e.g., soil). A suspension of contaminated soil and the coal in water can be tumbled in a specially designed drum at elevated temperatures to allow the oil to be absorbed by the coal. The oily coal can then be separated from the water and the clean sand by flotation. The oily coal can then be used in conventional coal-fired power plants as fuel and the processed solids can be landfilled either directly or after some additional treatment (ozone treatment or biotreatment) according to the regulations and laws regarding the cleanliness of the product. This process is a relatively low-cost technique (Ignasiak et al., 1990; Reis, 1996). The nature of both the contaminant and the solids can affect the effectiveness of the process (Ignasiak et al., 1990).

7.2.2.11 High-Temperature Reprocessing or Heating

High-temperature reprocessing (HTR) or heating is generally a cost-effective process to recover hydrocarbon and decrease the residual volume of oily materials in any regulatory environment. In the HTR process, influent emulsions or sludges are heated above the boiling point of water and allowed to flash in a separation tower where water and light hydrocarbons are subsequently separated from the heavier hydrocarbons. Heavier hydrocarbons and inorganic substances in the form of slurry are discharged from the separation tower. At high temperatures, water is vaporized from the material in the separation tower, and mass transfer rates of hydrocarbons from the solid inorganic phase are also enhanced due to the reduced viscosities of hydrocarbons. Light hydrocarbons and water can be recovered by condensation, whereas heavier hydrocarbons can be recovered after liquid—solids separation of the slurry phase, and the solid residue needs to be further processed. Note that HTR process uses a flash tower instead of pressurized separation (Hahn, 1994).

According to Hahn (1994), the potential advantages of the HTR process over conventional types of sludge treatment such as filter pressing and centrifugation are as follows:

- HTR facilities are similar to other types of production facilities, which can be considered part of the production process and can be incorporated into existing permits to act. In addition, as part of the production process, the function of HTR facilities is to increase process efficiency through enhanced oil recovery rather than to treat residuals, resulting in fewer permitting requirements, particularly in states where treatment of E&P residuals can be regulated.
- HTR process can find utilization in offshore E&P operations due to the relatively low area requirements.
- Operation of HTR process at temperatures above the melting point of paraffins can allow treatment of materials higher in paraffin content (1%) than those treated in processes that apply pressurized filtration and centrifugation.
- VOCs can be recovered by condensation or vapor recovery during the HTR process, whereas they may cause air-permitting issues in conventional methods.
- The risk of off-site contamination can be reduced due to the materials processing in a closed environment (Hahn, 1994).

7.2.2.12 Filtration

When the hydrocarbon content of the oily sludge or oil-contaminated solids is high, mechanical filtration can be used to separate some of the free hydrocarbons from the solids, but this process is not effective at lowering hydrocarbon concentrations to low levels (Reis, 1996).

The use of sand filtration is not suitable for oily-sludge treatment because the residue resulting from its filtration adheres strongly to a sand filter and the regeneration is difficult. According to Greig and Broadribb (1981), there is a method of oily-sludge treatment that includes filtering the sludge undiluted with recovered oil in a precoated surface filter, treating the filtration residue with a light hydrocarbon solvent, and/or steam stripping the extracted residue. Diatomaceous earth, fly ash, and powdered polymers (e.g., polyurethanes) can be applied as suitable precoat materials. Before filtering sludges with high solids content, water or a light hydrocarbon solvent may be added as a diluent. The filtration may be performed at ambient or elevated temperature. When elevated temperature is applied, conventional means (e.g., steam coils) may be used to heat the oily sludge. Plate, leaf, and tube or candle filters are suitable surface filters and are preferably operated under pressure as opposed to vacuum. In such filters, the precoat is effectively the filter medium and the function of the plate, leaf, and tube or candle, etc., is to act as a support. Kerosene or other solvents such as naphtha can be applied as the hydrocarbon-washing solvent. Filtration aids (chemical and physical conditioners) similar to or identical to the precoat medium may be added to the sludge prior to filtration to ensure longer and improved filtration by enhancing the porosity of the filter cake, lowering the differential pressure per unit cake thickness, and preventing the cake from blinding as follows:

- For a low concentration of up to 1 wt% solids in the feed sludge, the amount of filtration aid applied is preferably in the range 2—4 times the weight of solids;
- For a medium concentration of 1—4 wt% solids in the feed sludge, the amount of filtration aid applied is preferably in the range 1—2 times the weight of solids; and
- For a high concentration (e.g., 4 wt% or higher) solids in the feed sludge, the amount of filtration aid applied is preferably in the range 0.5—1.5 times the weight of solids.

If the particle size of the solids is fine, more filter aid is required. Note that it is advantageous to apply the minimum quantity of filtration aid to achieve satisfactory filtration because too much filtration aid can slow the buildup of filter cake and increase the filtration time. Inserting a drying stage after the filtration and before the solvent extraction may be advantageous and hot or cold air can be used for this purpose. The filtration flow rate can suitably be in the range 0.05—10 $m^3/m^2/h$, but preferably in the range 0.5—2.5 $m^3/m^2/h$. The oil content of the filtered solids can affect solvent consumption and flow rate, and steam consumption and pressure can depend on the boiling point of the solvent. Scraping or centrifugal action may be applied to remove the filtered solids from the filter. With the removal of solid particles, the oil and water can subsequently be separated more easily. However, some oil is retained by the solids and solvent extraction and/or steam stripping can be used to remove it. Greig and Broadribb (1981) reported that using this method it was possible to transform an oily sludge into a dry solid containing less than 1 wt% oil, which was suitable for landfill operations.

Pressure filtration can remove 20—50% of water from oily sludge (Long et al., 2013b). As noted, chemical and physical conditioners can be used to improve oily-sludge dewatering properties (Zall et al., 1987; Qi et al., 2011). Application of chemical conditioners like flocculants and coagulants prior to filtration can improve filterability of oily sludge by enhancing cake porosity of sludge and lowering compressibility of sludge (Buyukkamaci and Kucukselek, 2007; Qi et al., 2011; Long et al., 2013b). Physical conditioners are relatively inert materials that may include minerals and carbonaceous materials. These materials can act as skeleton builders and are able to increase oily-sludge dewaterability and cake properties by adding more incompressible and rigid lattice structures to the sludge solids providing water passages (Zall et al., 1987; Qi et al., 2011).

7.2.3 Water-Removal Methods or Dewatering

Several methods such as percolation ponds, mechanical methods [e.g., shale shakers, hydrocyclones, settling ponds (Reis, 1996), and thickeners (Orszulik, 2008) for preliminary dewatering, centrifugation, filtration such as high-pressure filter presses, vacuum filters, belt presses, and screw presses (Wojtanowicz et al., 1987; Reis, 1996) for further reducing of water from oily sludge or other solid wastes], freeze/thaw treatment (Jean et al., 1999; Guo et al., 2011), EK method (Yang et al., 2005; Guo et al., 2011), ultrasonic irradiation method (Guo et al., 2011), Fenton's reagent combined with sawdust (Guo et al., 2014), chemical treatment (Deng et al., 2015) [e.g., acid conditioning (Guo et al., 2011; Rattanapan et al., 2011), use of surfactants (Long et al., 2013a,b)], and evaporation (Reis, 1996) or heat or drying (Deng et al., 2015) have been used to remove water from oily sludge or other solid wastes. Centrifugation and filtration as well as heat and chemical treatments are applied in industries to dry oily sludge and other waste materials (Deng et al., 2015).

7.2.3.1 Percolation Ponds

A percolation pond is a pond (usually manmade) designed to allow effluent (water) from the wastes to percolate slowly into the ground. The pond acts as a holding facility while gravity allows the water to percolate or seep through porous materials such as the soil or other unconsolidated medium into the local water table (usually the surfacial aquifer) (Ecology Dictionary, 2008).

A percolation pond may be used in arid areas where the water table is very deep (Reis, 1996) and are uncommon in urban settings (Nagy, 2002). These ponds allow dissolved substances in the water (e.g., organic compounds, heavy metals, etc.) to percolate into the local water table and spread into the surrounding soil, posing a potential threat to both human health and the environment (Reis, 1996; Petition Response Section, Exposure Investigation and Consultation Branch, Division of Health Assessment and Consultation, Agency for Toxic Substances and Disease Registry, 1999), thus application is highly restricted (Reis, 1996).

7.2.3.2 Evaporation

Evaporation of water from solid wastes may be the simplest method in arid climates (Reis, 1996). Evaporation ponds are artificial ponds with very large surface areas that use sunlight or solar energy to evaporate water at the ambient temperatures. These ponds are relatively easy to construct and are the least costly means of dewatering, especially in areas with dry and warm weather, high evaporation rates, and lowland costs, and require low maintenance and little operator attention compared to mechanical systems. The large tracts of land needed when the evaporation rate is low or the disposal rate is high, the need for impervious liners of clay or synthetic membranes such as PVC or Hypalon, and the potential for contaminating surrounding land and water sources through seepage from poorly constructed evaporation ponds are some of disadvantages of these systems (Mickley et al., 1993; Ahmed et al., 2000). The risk of groundwater contamination can be decreased by sealing these ponds (Ahmed et al., 2000). Netting or other deterrents should be used to cover these ponds to restrict waterfowl, etc., from coming into contact with pollutants in the waste materials. According to Morita (2013), when an evaporation pond is applied in the wastewater-treatment system of refineries, it may be covered with oily water, leading to restricted evaporation, degraded work environment, and fire risk.

Surface area and depth are two components of the evaporation pond size. The open-surface area of the evaporation pond can be calculated from the following equation:

$$A_{\text{open}} = \frac{V_{\text{reject}} f_1}{E} \tag{7.9}$$

where A_{open} is the open-surface area of the evaporation pond (m^2), V_{reject} denotes the volume of reject water (m^3/d), E is the evaporation rate (m/d), and f_1 denotes a safety factor to allow for lower than average evaporation rates. Evaporation rates may be determined using a standard evaporation pan (class A pan) or water-balance calculations (Ahmed et al., 2000).

According to Mickley et al. (1993) and Ahmed et al. (2000), pond depths ranging from 25 to 45 cm are optimal for maximizing the rate of evaporation. The pond tends to store the reject water during the winter. The following equation can be applied to calculate the minimum depth needed to store the volume of water:

$$d_{\min} = E_{\text{ave}} f_2 \tag{7.10}$$

where $d_{\min}$ is the minimum depth (m), E_{ave} denotes the average evaporation rate (m/d), and f_2 is a factor, which incorporates the effect of the length of the winter. A freeboard, which is described as the depth above the normal reject water surface, must be considered and provided so that reject water does not spill out of the pond due to rainfall and periods of abnormally low evaporation. A freeboard of 20 cm is recommended (Ahmed et al., 2000).

The use of evaporation ponds in the wastewater-treatment system of refineries in Middle East countries was reported by Morita (2013). In addition, dewatering of reserve pits following drilling, produced water, oil-based or salty drilling mud systems, etc., have been reported using evaporation. Note that in dewatering of reserves pits by evaporation, three layers including a free oil layer, water layer, and sludge layer may be formed. A surface crust can be formed by weathering the oil layer, leading to the inhibition of water evaporation and delaying the natural removal of water from the pits (Reis, 1996).

7.2.3.3 Mechanical Methods

Evaporation can be too slow for dewatering of solid wastes, but several mechanical methods are available for this purpose. As noted, mechanical methods such as shale shakers, hydrocyclones, settling ponds (Reis, 1996), and thickeners (holding tank for settling solids through, e.g., gravity, may increase solid concentration from 3% to 10−15 wt%) (Orszulik, 2008) for preliminary dewatering, centrifugation, filtration such as high-pressure filter presses, vacuum filters, belt presses, and screw presses (Wojtanowicz et al., 1987; Reis, 1996) for further reducing of water from oily sludge or other solid wastes in the petroleum industry have been reported. The effectiveness of these mechanical methods to remove water from oily sludge or other solid wastes varies (Reis, 1996). Chemical and physical conditioning of oily sludge and other solid wastes can improve dewatering properties by mechanical methods (Zall et al., 1987; Reis, 1996; Qi et al., 2011).

Centrifugation and filtration are widely applied mechanical methods in industries to dry oily sludge and other waste materials (CONCAWE, 2003; Deng et al., 2015) (centrifugation and filtration were discussed in detail in Sections 7.2.2.2 and 7.2.2.12, respectively). Filtration reduces the transport and disposal costs since there is less water content in sludge. When incineration is selected as the final disposal route of the sludge, leaving more oil in the cake can decrease fuel costs. Note that oil may blind/smear the filter cloth, and filtration aids may be needed to lower plugging tendencies. Pressure filtration can manage feeds with concentrations up to 10% solids and with large proportions of difficult-to handle fines particles (CONCAWE, 2003). This system can remove 20−50% of water from oily sludge (Long et al., 2013b) and cannot achieve the desired effect without some form of pretreatment (Guo et al., 2011). Furthermore, this system can obtain cake solids up to 50% with oil concentrations between 5% and 20%. The performance of the process can be affected by feed temperature, amount and nature of any additives such as lime/spent clay addition, cycle time, cake characteristics, and filtrate characteristics. Effective breaking of solids-stabilized emulsions can be obtained by heating the feed. The screen-belt press can achieve up to 20% solids in the sludge (CONCAWE, 2003) and may be difficult to clean. In comparison with the centrifuge and belt press, the vacuum filtration and screw press are not as effective in solids separation of reserves and production pits due to their low volume reduction of the solid-waste stream (Reis, 1996). High content of solids in the feed (up to 25%) can be handled by two-phase scroll-type decanter centrifuge (CONCAWE, 2003).

7.2.3.4 Chemical Treatment

As is known, application of the especial chemical compounds as settlers of the colloid particles can be a useful technique for separating of sludge from the oil−water emulsion which chemical dewatering can be occurred in this process (Khojasteh et al., 2012). On the other hand, application of chemical conditioners like flocculants and coagulants prior to physical or mechanical treatment can improve sludge dewatering (Hwa and Jeyaseelan, 1997; Buyukkamaci and Kucukselek, 2007; Qi et al., 2011; Long et al., 2013b). The characteristics of the sludges and the type of dewatering devices can affect the selection of chemical conditioners. Lime, alum, ferric chloride, and polyelectrolytes are commonly used chemical conditioners (Hwa and Jeyaseelan, 1997). Application of the chemical method can be more economic than using other physical methods alone (Khojasteh et al., 2012). Note that the final sludge volume can be significantly increased by the large use of chemical conditioners like lime, resulting in uneconomical properties in industrial applications (Hwa and Jeyaseelan, 1997; Long et al., 2013b).

Sludge volume may effectively be reduced by the direct dewatering of oily sludge via acid conditioning without specific mechanical equipment and energy input. In laboratory scale, it was reported that by acid conditioning to an extremely low pH of 1−3, an acceptable dewatering efficiency of 50−80% can be achieved (Guo et al., 2011; Rattanapan et al., 2011; Long et al., 2013b). The dewaterability of oily sludge can be improved significantly as a result of acidification. After 120 min of quiescent settlement, the oily sludge was reported to release more water at lower pH levels. For example, at pH 4.0, approximately 77% of the volume of water in the oily sludge was reported to be separated after acidification. The breakage of the floc skeleton can affect the release of water (Guo et al., 2011). Acidification can also be effective in dewatering of activated sludge, which generally contains similar compositions as oily sludge except for oil and hydrocarbon content (Chen et al., 2001; Guo et al., 2011). The combinational use of surfactants can further improve dewatering efficiency in acidification treatment of activated sludge (Chen et al., 2001; Long et al., 2013b).

Because of either poor cost-efficiency or lack of environmental friendliness, the conventional utilization of physical treatments with or without chemical conditionings may not be feasible in industrial applications. Long et al. (2013b) used biosurfactant rhamnolipid for bench-scale and pilot-scale dewatering of oily sludge from flocculant coagulation and DAF processes in the Shengli refinery of the Sinopec Qilu Petrochemical Corporation (Zibo, China). They reported that rhamnolipid treatments under a concentration of 300−1000 mg/L, pH of 5 to 7, and temperature of 10−60°C could directly separate 50−80% of water from the stable oily sludge, and both mono-rhamnolipid and di-rhamnolipid had equivalent dewatering ability, which is closely related to their equivalent performance in breaking the emulsified oil droplets. The decrease of pH significantly improved the dewatering ability of rhamnolipid, but the alternation of temperature did not affect it. The pilot-scale dewatering system (Fig. 7.5) consisted of oily-sludge tank, dewatering tank (1500 L), blank or control tank, and reception tank. Dewatering and control tanks were subjected to the rhamnolipid treatment with pH adjustment. After sufficient mixing for 3 min, the oily sludge was kept undisturbed at outdoor temperature (5−10°C). After the oily sludge was settled for 120 min, the aqueous phase was pumped to the reception tank. After pilot treatment (1000 L of oily sludge), the settled water with residual oil of 10 mg/L and soluble COD of about 800 mg/L could be directly effluxed into the biotreatment system, while the concentrated oily sludge with a reduced volume by 60−80% could be pumped into coking tower, achieving completely harmless treatment. They concluded

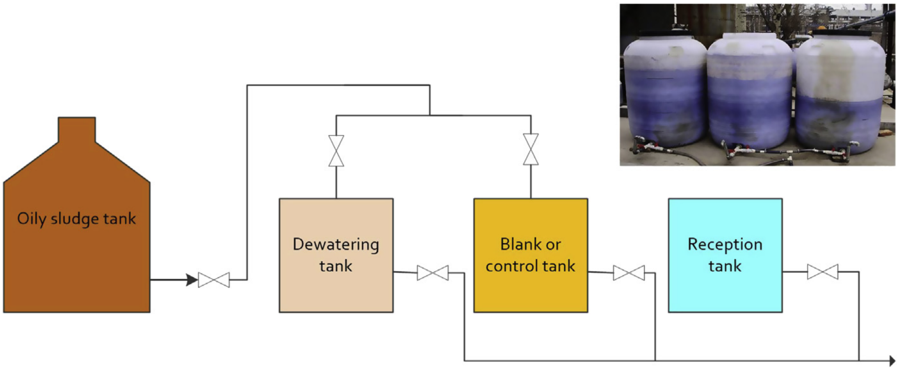

Figure 7.5 Pilot-scale dewatering system of oily sludge with rhamnolipid as the dewatering agent.
Modified from Long, X., Zhang, G., Han, L., Meng, Q., 2013b. Dewatering of floated oily sludge by treatment with rhamnolipid. Water Research 47, 4303–4311.

that rhamnolipid as a dewatering agent may have great potential in the industrial dewatering of oily sludge (Long et al., 2013b).

7.2.3.5 Heating or Drying

Drying is usually a necessary step during the process of sludge treatment that can largely lower the moisture content and enhance the calorific value of the sludge. Dried sludge reduces transport and storage costs and can be used as an acceptable combustible material (Ayol and Durak, 2013; Deng et al., 2015).

In general, conductive heat transfer inside a screw dryer or convective heat transfer directly from the hot gas may be applied to dry sludge (Ohm et al., 2010; Deng et al., 2015). The drying mechanism of sludge can be complicated and during the air-drying process, water from sludge is primarily removed by air convection and free water mainly evaporates (Cai et al., 2013; Deng et al., 2015). Thus convective evaporation is the main mechanism of water removal (Velis et al., 2009; Deng et al., 2015). Drying air temperature, velocity, and different additive agents are factors that can affect the drying kinetics of sludge (Leonard et al., 2005; Tuncal, 2010; Deng and Su, 2014; Deng et al., 2015).

Heating of refinery sludges using a steam coil can remove water and volatile organics. The vaporized materials can be condensed and separated in a drum, into an oil phase and a water phase, and the solid phase can be discharged. Oil-containing sludges may be transformed into low-grade fuel pellets that can be applied in other industries. Biological effluent sludge can also be processed by thermal treatment and can be converted into fertilizer or composting material. Note that either the raw sludge or the solid phase from a filter press or centrifuge can be used as the feed of a thermal treatment unit or sludge-dryer (CONCAWE, 2003).

Deng et al. (2015) studied the effects of different sludge diameters (4–8 mm) and temperatures (105–250°C) on the drying characteristics of long cylindrical oily-sludge drying process made by the sludge shaper. They reported that an increase in temperature and a decrease in diameter accelerated the drying rate and shortened the drying time. The moisture ratio of oily sludge can be significantly decreased by increasing the drying temperature, resulting in a large reduction of total drying time. After drying, fractures appear in the solid skeleton of long, cylindrical oily sludge, resulting in the generation of smaller cylindrically shaped particles.

7.2.4 Disposal Methods

Effective and responsible waste disposal can be one of the key elements of any environmental management system (Bashat, 2003). Disposal methods generally include surface discharge (E&P Forum, 1993), underground storage (CONCAWE, 1999; CONCAWE, 2003), or underground injection (injection well, annular injection, and downhole injection) (E&P Forum, 1993), oxidation (Hu et al., 2013; Ubani et al., 2013; Jafarinejad, 2015a,b; Islam, 2015), incineration, stabilization/encapsulation/solidification, secure landfill, and biodegradation or biotreatment (E&P Forum, 1993; CONCAWE, 1999, 2003; Hu et al., 2013; Ubani et al., 2013; Jafarinejad, 2015a; Islam, 2015).

Disposal can take place either on- or off-site (E&P Forum, 1993; Reis, 1996). Disposal options depend largely on the waste type, characteristics, and regulatory requirements (Reis, 1996; Bashat, 2003). Ecological, technical, or economic factors usually limit the choice of methods (Bashat, 2003). Evaluation of waste-disposal options can generally include environmental considerations, location, engineering limitations, regulatory restrictions, operating feasibility, economics, potential long-term liability, etc. (E&P Forum, 1993; E&P Forum/UNEP, 1997).

Safe disposal of large amounts of oily sludge and other solid wastes generated during the exploration, development, and production, hydrocarbon processing (refineries and petrochemical plants), storage, transportation, and distribution is one of the major challenges faced by the petroleum industry (Srinivasarao-Naik et al., 2011; Ubani et al., 2013). Different techniques such as surface discharge (offshore and onshore), underground injection for slurries, burial (E&P Forum, 1993; Reis, 1996), incineration, stabilization/encapsulation/solidification (E&P Forum, 1993; CONCAWE, 1999, 2003; Hu et al., 2013; Ubani et al., 2013; Jafarinejad, 2015a; Islam, 2015), oxidation (Hu et al., 2013; Ubani et al., 2013; Jafarinejad, 2015a,b; Islam, 2015), secure landfill (E&P Forum, 1993; CONCAWE, 1999, 2003; Ubani et al., 2013; Jafarinejad, 2015a), and biodegradation or bioremediation (e.g., land treatment (landfarming and landspreading), biopile/composting, bioslurry systems, or bioreactors) (E&P Forum, 1993; CONCAWE, 1999, 2003; Hu et al., 2013; Ubani et al., 2013) have been reported for the disposal of oily sludge or other solid wastes in the petroleum industry.

7.2.4.1 Surface Discharge (Offshore and Onshore)

Surface discharge (both offshore and onshore) may be one disposal option for aqueous and solid-waste streams (E&P Forum, 1993; Reis, 1996) as long as their quality meets regulatory standards. Surface discharge is regulated in most areas, but permits for such discharge are needed (Reis, 1996). The sensitivity and capacity of the potential receiving environment, the concentration of potentially contaminants in the waste, and the volume of the discharge stream are factors that should be considered (E&P Forum, 1993).

In some areas, offshore discharge may be applied to dispose treated solids such as drill cuttings and produced solids. For example, in the United States, offshore discharges are forbidden within 3 miles of shore, and this option cannot be applied to dispose oil-based drilling mud wastes (Reis, 1996).

The treated solid wastes (e.g., drill cuttings and produced solids) which their hydrocarbons, salt, or heavy metals contents meet regulatory standards, may be permitted for onshore discharge or spreading over the land surface. The electrical conductivity (EC), sodium adsorption ratio (SAR), the exchangeable sodium percentage (ESP), the O&G levels, and heavy metal content can be assessed for the suitability of a solid waste for surface discharge (Reis, 1996). EC $<$ 4 mmhos/cm, SAR $<$ 12, ESP $<$ 15%, and O&G $<$ 1% are generally the maximum recommended values (Deuel, 1990; Reis, 1996). The maximum recommended accumulations of heavy metals in soil can be 300 mg/kg for As, 50 mg/kg for Be, 3 mg/kg for Cd, 200 mg/kg for Co, 1000 mg/kg for Cr, 250 mg/kg for Cu, 10 mg/kg for Hg, 1000 mg/kg for Mn, 5 mg/kg for Mo, 5 mg/kg for Se, 500 mg/kg for V, 500 mg/kg for Zn, 100 mg/kg for Ni, and 1000 mg/kg for Pb (Reis, 1996).

7.2.4.2 Underground Injection

The pumping of waste fluids or slurries down a well into suitable underground formations or the one-time pumping of wastes down an annulus or to specially monitored wells is called underground injection. Disposal wells are designed to provide a wellbore to transport wastes into underground reservoirs so they do not adversely affect the environment. The underground formations for disposal should be geologically and mechanically isolated from usable sources of water. Injection may be an expensive process requiring extensive planning and control. The injection volume required, the nature of the formation (it should have sufficient permeability, porosity, thickness, and low reservoir pressure in order to receive and handle wastes), the transportation mechanism of the waste to the injection well (e.g., pumping, tank truck, or other means), and the probable requirement for pretreatments before injection (e.g., oil removal, coagulation, and sedimentation, filtration, aeration, oxygen exclusion, bacteria and mineral-scale treatment, and solids grinding to inject them as slurry) should be considered (E&P Forum, 1993).

According to the CONCAWE (1999, 2003), injection into deep rock and clay strata has been considered for some wastes in the petroleum or oil industries. An injection well may be used to manage many liquid wastes such as produced water, process water, blowdown liquids, cooling water, dehydration and sweetening waste liquids, and waste drilling fluids (E&P Forum, 1993).

Annular injection, which refers to the disposal technique where pumpable wastes are injected into the surface casing or production casing annulus, can be applied to manage reserve pit fluids (E&P Forum, 1993) and drilling muds and cuttings (Minton and Secoy, 1993; Bashat, 2003). Note that it is generally a one-time option and is not appropriate for continuous disposal due to the mechanical inability to clean the disposal zone of accumulated debris and the threat of corrosion of the production casing string and the interior of the surface pipe or other casing (E&P Forum, 1993).

Downhole disposal of both oil- and water-based muds and cuttings wastes may be successful in both onshore and offshore drilling operations (E&P Forum, 1993; Shadizadeh and Majidaie, 2008) and it can also be economically favorable (Shadizadeh and Majidaie, 2008). Drill cuttings cannot be injected downhole directly due to the large particle sizes and must be broken up into small particles and slurried with mud or water prior to injection. Grinding machines, pumps, recirculating lines, tanks, and shakers or desanders to remove large solids can be used in these systems (E&P Forum, 1993).

7.2.4.3 Burial

In the past, burial of wastes in pits was a common method for disposal due to its simplicity. The potential for pollutant (hydrocarbons, salts, or heavy metals, chemicals, and other materials) migration from the pit to usable water resources is one of the major concerns with the burial of solids (E&P Forum, 1993; Reis, 1996). Barrier walls around the pit, liners around the pit contents, or a cap to prevent vertical migration may be required and applied as a barrier to pollutants migration and leaching. The depth to groundwater and the type of soil surrounding the pit should be considered prior to wastes burial. Surface gradation to prevent water accumulation and revegetation with native species to decrease the potential for erosion and assist in the full recovery of the area's ecosystem are required after burial and/or pit-closure completion (E&P Forum, 1993).

Burial of drill cuttings and used mud without hazardous materials has been reported (Reis, 1996). Burial can be applied for the disposal of inert unrecyclable materials and stabilized wastes. Dilution burial may be used for wastes with constituents only slightly elevated above levels regulated for disposal (e.g., water-based muds and cuttings). In this method, the pit contents are mixed with soils from the pit and surrounding areas until they meet specifications for burial, and the pit is covered and the surface graded (E&P Forum, 1993).

7.2.4.4 Secure Landfill

The deposition of wastes onto or into land and covering them with soil is called landfilling, and is controlled under legislation (CONCAWE, 1999, 2003). In other words, secure landfills are generally specially designed and monitored land structures that utilize protective measures (clay or synthetic liners) against migration of contained chemical waste via leaching or vaporization and a system of pipes designed for the collection and control of rainwater and leachates from them (E&P Forum, 1993; Bashat, 2003). A landfill may be designed and constructed in a manner that it can be applied as disposal site for toxic and hazardous wastes (E&P Forum, 1993).

Landfilling is one of the cheaper options of disposal in some countries, although the shortage of satisfactory sites and the difficulties in obtaining licenses from regulatory authorities can increase costs (CONCAWE, 1999, 2003). According to the CONCAWE (1999), some European refineries have their own landfill sites that are controlled under European and national waste legislation. However, for most refineries, the material for landfill will go to a commercial, a state-run or an industry cooperative waste disposal facility. Pretreatment of waste, e.g., by dewatering or solidification, is often required before disposal to a landfill (CONCAWE, 1999). Secure landfills are also common in developed countries such as the United States, UK, Canada, and Germany (Bhattacharyya and Shekdar, 2003; Hu et al., 2013).

An impermeable lining of the containment (e.g., clay and plastic sheeting liners and/or multilayer linings with integrated drainage systems), monitoring boreholes, or leachate collection systems in order to inspect the effectiveness of the containment, and special provisions for disposal of liquid wastes or prohibition of liquids disposal are key considerations in the design and operation of a landfill site for protection of groundwater from contamination by the materials contained in the landfill. It is also necessary note that wastes deposited in a landfill are not immediately destroyed but only stored. These materials must not be capable of reacting to produce heat or noxious gases. Special systems may be applied to collect the generated flammable gases, e.g., methane. Because it is likely that an open-ended civil liability exists, it is important that the disposal site be run either by the waste generator who will then retain responsibility for his own waste, or by a properly managed disposal facility (E&P Forum, 1993; CONCAWE, 1999, 2003).

7.2.4.5 Stabilization/Solidification/Encapsulation

Stabilization, solidification, and encapsulation are quick and inexpensive waste-treatment processes (Karamalidis and Voudrias, 2007a; Leonard and Stegemann, 2010a,b; Hu et al., 2013) designed to improve waste handling, reduce surface area across which pollutants can leach, or restrict the solubility of hazardous constituents. Cement, lime, or thermoplastic polymers may be suitable reagents (CONCAWE, 1999, 2003). These processes generally generate dry solids (E&P Forum, 1993). Solidification involves creation of a durable and low leachable solid matrix using a solidifying agent that physically surrounds the contaminant (i.e., cement or lime), or utilizing a chemical fixation process (i.e., sorbents); stabilization involves the conversion of a waste (i.e., by a pH adjustment) to a chemically stable form (monolith or dry granular solid) that resists leaching and encapsulation involves complete coating or enclosure of a waste with a new, nonpermeable substance (CONCAWE, 1999, 2003). In other words, solidification involves generation of a durable solid matrix to encapsulate contaminants, while stabilization involves transforming contaminants into a less toxic and/or less soluble form (Leonard and Stegemann, 2010a). Chemical stabilization is based on the reaction of lime with waste materials and water to create a chemically stable product that is acceptable to immobilize watery sludges to yield a powdery hydrophobic product that can be compacted (CONCAWE, 1999; CONCAWE, 2003). Stabilization/solidification is a common waste-management technique. In fact, the US EPA identified this technique as the best demonstrated available method for over 50 US Resource Conservation and Recovery Act-listed hazardous wastes (Conner and Hoeffner, 1998; Leonard and Stegemann, 2010a), and it has been applied for 25% of US superfund sites (US EPA, 2004; Leonard and Stegemann, 2010a). Depending on the properties and characteristics of the resulting stabilization/solidification product, it may be reused as a construction material (Leonard and Stegemann, 2010a) or applied in foundations, tank bases, bund walls, and road-making (CONCAWE, 1999, 2003).

Microencapsulation is based on the reduction of surface-to-volume ratio of the waste by generation of a monolithic, hard mass with a very low permeability, while macroencapsulation is the enclosing of a relatively large quantity of waste, such as an entire waste container by surrounding it with a stiff, weight-supporting matrix and a seam-free jacket. Encapsulation is an appropriate method for the on-site treatment of disposal sites of accumulated spent acid tars and oily sludges that are difficult to transport and to dispose of by other means. It is necessary to note that the treated product occupies a larger volume than the original sludge. The process is less acceptable for the handling of regularly produced sludges due to the increased mass generated for disposal (CONCAWE, 1999, 2003).

A cement-based stabilization/solidification process was reported to be effective in the treatment of inorganic wastes (Karamalidis and Voudrias, 2007b; Leonard and Stegemann, 2010a,b). As the waste contains metals (because at the high pH of the cement mixture, most metal compounds are transformed into insoluble metal hydroxides), this process can be effective. In the case of spent catalyst, most metal compounds are present as hydroxides and as such may also enhance the strength and stability of the waste containing concrete (CONCAWE, 1999, 2003). The effectiveness of the stabilization/solidification process in treating waste containing substantial quantities of organic compounds remains questionable due to the detrimental effects organic compounds can have on the hydration of binders (Conner and Hoeffner, 1998; Leonard and Stegemann, 2010a,b). In addition, there is little potential for chemical uptake of organic contaminants into hydration products. Thus physical entrapment in the matrix porosity and sorption can affect immobilization of organic contaminants, such that nonpolar (insoluble) compounds are more likely to be retained by the solid, whereas polar (soluble) compounds will remain leachable (Leonard and Stegemann, 2010a,b). Some researchers have reported that organic contaminants can be leached (released) from stabilized/solidified products treated with Portland cement alone (Leonard and Stegemann, 2010b). For example, the release of PAHs (Mulder et al., 2001), methanol and 2-chloroaniline (Sora et al., 2002), polychlorinated biphenyls (PCBs) (Yilmaz et al., 2003), and phenol (Vipulanandan and Krishnan, 1990) have been reported. A Portland cement-only binder system is not generally effective for the immobilization of several common organic contaminants. The effectiveness of the stabilization/solidification process for organic wastes may be improved by using binders that enhance sorption of organic compounds, thereby improving their immobilization and preventing their detrimental effects on binder hydration (Leonard and Stegemann, 2010b).

Caldwell et al. (1990) determined the degree of organic contaminant immobilization obtainable using several generic solidification processes (cement, cement/fly ash, cement/activated carbon, cement/bentonite, and cement/soluble silicates) in a laboratory-scale study. Cement-activated carbon was reported to be effective in stabilization/solidification of a range of organic contaminants. Vipulanandan and Krishnan (1990) investigated the potential of polyester polymer in stabilizing/solidifying phenol and compared the performance of polyester polymer to that of cement with a water—cement ratio of 0.5. Phenol inhibited the setting of cement and polyester polymer. In the case of polyester polymer, higher concentrations of initiator were applied to neutralize the effect of phenol and to initiate the polymerization process. Polyester polymer systems showed no measurable amount of phenol recovery, and phenol recovery from the cement was dependent on the curing time and the initial phenol content. Almost total phenol recovery from the cement was reported by limited toxicity characteristic leaching procedure (TCLP) tests. Phenol also created large voids in the cement microstructure. Increasing the phenol concentration from 0.5% to 2% decreased the compressive strength and splitting tensile strength of polyester polymer and cement. The polyester polymer-solidified phenol waste had substantially higher compressive and tensile strength than cement-solidified waste. Joshi et al. (1995) carried out laboratory studies to determine the feasibility of solidifying and stabilizing oil and gas well sludges from a site in Alberta, Canada using Portland cement, fly ash, lime, and sodium-silicate mixtures. They reported that oil and gas well sludges in a semiliquid state with a solid content greater than 30% and having moderate toxicity can be effectively solidified using cement and fly ash mixtures with 15% of each by weight of solids in the sludge. Addition of 1% sodium silicate by weight of cement accelerated the strength development. Hebatpuria et al. (1999) applied an inexpensive thermally regenerated activated carbon as a preadsorbent in the solidification/stabilization of phenol-contaminated sand. Its use in the solidification/stabilization process decreases the leaching potential of phenol by as much as 600% compared to when no reactivated carbon is applied. Even very low amounts of reactivated carbon added to the mix (1% w/w of soil) efficiently adsorbed most of the phenol and prevented it from leaching. The adsorption of phenol on the reactivated carbon was reported to be partially irreversible over time in the solidification/stabilization waste form, indicating possible chemical adsorption. The formation of a calcium—phenol complex, which further reduced the amount of free phenol present in the pores, was also suggested by pore-fluid analyses of the cement paste containing phenol. The hydration of cement in the presence of phenol was retarded concomitant with formation of amorphous portlandite.

Tuncan et al. (2000) treated petroleum drill cuttings with cement, lime, and pulverized fuel ash (PFA) and reported improved unconfined compressive strength and permeability. Sora et al. (2002) studied the effects of the addition of large amounts of liquid organic streams (mixture of water, methanol, and 2-chloroaniline: 100/76/4 volume ratios, respectively) to cement pastes and in particular the influence of the organics on the hydration process. They reported that the addition of the solution to cement pastes retarded the setting and hardening by some days and slowed down the overall process for many weeks. Moreover, it is likely that the methanol, due to its high vapor pressure, evaporates more completely than water leaving behind in the matrix just the 2-chloroaniline. The dynamic leach testing confirmed that the amount of 2-chloroaniline initially included in the monolith was still there but not firmly bound to the matrix, as it was progressively removed in leachates. The results of this study confirmed the need to use sorbents to capture 2-chloroaniline. Al-Ansary and Al-Tabbaa (2007) applied a stabilization/solidification process to treat two synthetic mixes based on average concentrations of specific contaminates present in typical drill cuttings from the North Sea and the Red Sea areas that contained similar chloride content of 2.03% and 2.13% by weight but different hydrocarbon content of 4.20% and 10.95% by weight, respectively. They tested a number of stabilization/solidification binders such as Portland cement, lime and blast-furnace slag (BFS), microsilica, and magnesium-oxide cement. Despite the significant difference in the hydrocarbon content in the two synthetic cuttings, the measured unconfined compressive strength values of the mixes with the same binder type and content were reported to be similar. This study revealed the reduction of the synthetic drill cuttings to a stable nonreactive hazardous waste, compliant with the UK acceptance criteria for nonhazardous landfills: (1) by most of the binders for chloride concentrations, and (2) by the 20% BFS—Portland cement and 30% Portland cement binders for the low oil content mix. The 30% BFS—Portland cement binder successfully decreased the leached oil concentration of the low oil content mix to inert levels. Al-Futaisi et al. (2007) solidified tank-bottom sludge mixtures using three combinations of selected additives such as ordinary Portland cement (OPC), cement bypass dust (CBPD), and quarry fines (QF). The results of the TCLP analyses revealed that no extracts exceeded the established TCLP maximum limits set by the US EPA. In fact, for several extracts, the metal concentrations were much below the maximum concentration limits. They concluded that the apparent lack of leachability of metals from these sludge applications suggests that metals introduced to these applications are not readily attacked by weak acid solutions and would not be expected to migrate or dissolve into the water. Therefore in terms of trace metals, the suggested sludge applications would not be considered hazardous as defined by the TCLP leaching procedure. Karamalidis and Voudrias (2007a) evaluated the leaching behavior of inorganic constituents from stabilized/solidified refinery oily sludge and ash produced from incineration of oily sludge with cement. Remarkably good immobilization >98% was reported for metals of solidified ash at pH > 6 and >93% of solidified oily sludge at pH > 7. This study revealed that Zn, Ni, and Cu leaching was pH-dependent and a high percent of immobilization (>98%) was reported at pH > 4 for Cu, at pH > 6 for Zn, and pH > 8 for Ni, in both sludge and ash solidified with cement. In fact, the stabilization/solidification process was reported to be more effective, with ash samples, against metal release, considering the initial concentration of metals in each waste. In addition, sulfate leaching was reported to be high at pH range 2—12 and chromate was detected only in solidified oily-sludge samples. In another other work, Karamalidis and Voudrias (2007b) stabilized and solidified real oil refinery sludge samples with various additions of I42.5 and II42.5 cement (Portland and blended cement, respectively) and subjected them to leaching. The waste was confined in the cement matrix by macroencapsulation. The rapture of the cement structure led to an increase of leachability for most of the hydrocarbons, and leaching of n-alkanes from II42.5 cement-solidified samples was reported to be lower than that from I42.5 solidified samples. Leaching of alkanes in the range of n-C_{10} to n-C_{27} was reported to be lower than that of long-chain alkanes (>n-C_{27}), regardless the amount of cement addition. Individual alkane leachability was generally enhanced by increasing the cement content in the solidified waste samples, which indicated that cement addition resulted in destabilization of the waste. Addition of I42.5 cement favored immobilization of anthracene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo[a,h]anthracene; however, addition of II42.5 favored naphthalene, anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, and dibenzo[a,h]anthracene.

Leonard and Stegemann (2010a,b) treated drill cuttings by stabilization/solidification using Portland cement, with the addition of high-carbon powerplant fly ash (HCFA) as a sorbent for organic contaminants. Drill cuttings and HCFA addition both decreased unconfined compressive strength, but HCFA improved hydraulic conductivity, relative to Portland cement-only stabilization/solidification products. The addition of drill cuttings had little effect on the acid-neutralization capacity of products prepared with Portland cement only and improved that of products containing HCFA. Successful formation of a calcium—silicate—hydrate-based matrix with good resistance to acid attack and little detrimental effect from drill cuttings addition were reported. Portland cement, without HCFA addition, was more effective in immobilizing chlorides, but the overall chloride immobilization was poor in all runs. Increased cement addition was reported to enhance the amount of hydrocarbon leached at early curing, possibly due to reactions of the clay content of the drill cuttings at high pH, which affected its sorptivity. However, this effect was mitigated by HCFA addition and binder hydration with time, both of which provided increased surface area for sorption. The addition of HCFA was the most effective factor in hydrocarbon leaching reduction; thus it was concluded that HCFA improved the immobilization of organic contaminants and may represent an inexpensive binder for stabilization/solidification of organic wastes.

7.2.4.6 Incineration

Incineration refers to any process that utilizes combustion to convert a waste to a less bulky, less toxic, or less noxious material (CONCAWE, 1999, 2003). Volume reduction, complete destruction rather than isolation, and possible resource or energy recovery are some of advantages of the incineration method (Bashat, 2003; Zhou et al., 2009; Liu et al., 2009b). An incineration system must generate as complete a combustion as practical by applying an optimum selection of process variables (time, temperature, and turbulence) and preparing air-pollution control devices to reduce and minimize the air-pollutant emission. Many waste materials may be readily combustible and their combustion products can be ash residue and harmless gases, which can be easily disposed of through vents or stacks to the atmosphere. In such cases, this method can often be the soundest technique of waste disposal. Complete combustion, adequate flue-gas treatment, clear stack, low maintenance, minimum materials handling, minimum operating labor, adequate capacity, and adequate availability are some of the factors that characterize incinerators with good performance. In general, the types of incinerators include fixed-hearth incinerators, multiple-hearth incinerators, fluidized-bed incinerators, rotary-kiln incinerators, liquid-fuel incinerators, and gas or fume incinerators (CONCAWE, 1999, 2003).

Complete combustion of oily wastes in the presence of excess air and auxiliary fuels can be possible, and is widely done in large refineries for sludge treatment (Hu et al., 2013). Rotary-kiln and fluidized-bed incinerators are the most commonly used incinerators. In a rotary-kiln incinerator, the combustion temperature is from 980 to 1200°C and the residence time is about 30 min, while in fluidized-bed incinerators, the combustion temperature is from 732 to 760°C and the residence time may be in order of days (Hu et al., 2013; Ubani et al., 2013). Rotary-kiln incinerators can generally incinerate almost any waste, regardless of size and composition (CONCAWE, 1999, 2003). The circulating fluidized-bed technology has been recommended for the incineration of typical low-quality sludge such as oil shale, petroleum coke, sewage, biomass residues, and so on, due to its fuel flexibility, high mixing efficiency, high combustion efficiency, and low pollutant emissions (Zhou et al., 2009; Hu et al., 2013). This technology can be adopted to treat oily sludge (Zhou et al., 2009). The main advantage of fluidized-bed incinerators is its flexibility to accommodate large variations in sludge composition (CONCAWE, 1999, 2003). Note that the incineration process needs sophisticated equipment and experienced operators to achieve adequate combustion of oil sludge. The incineration of oily sludge using fluidized-bed technology usually generates ash scrubber sludge, with low heavy-metal content (Ubani et al., 2013).

Critical parameters and factors that should be controlled during the incineration process are combustion condition, oxygen-to-air ratio, residence time, combustion temperature, waste-feed rates, feedstock quality, presence of auxiliary fuels, and gas emission (Mahmoud, 2004; Hu et al., 2013; Ubani et al., 2013).

Li et al. (1995) applied a batch-type, controlled-air incinerator for the treatment of oily sludge and polyethylene-plastic mixtures. They reported that PAH content in the feeding waste had a strong influence on PAH emission in both stack flue gas and ash residue due to incomplete combustion. For the distribution of individual PAH mean output mass, lower molecular weight PAHs—naphthalene, acenaphthylene, acenaphthene, and fluorene—had >87% of their mass discharged by the stack flue gas. However, the higher molecular weight PAHs—anthracene, fluoranthene, chrysene, benzo(b)fluoranthene, benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3,-cd) pyrene, dibenzo(a,h)anthracene, benzo(b)chrycene, Benzo(ghi)perylene, and coronene—had significant mass fractions (>18%) discharged by the ash residue. The total PAH output/input mass ratios were reported to be between 0.00103 and 0.00360, which indicated that the depletion of PAH mass in the combustion process was very significant. They concluded that the cocombustion of oily sludge with plastic was a potential method of reducing the PAH emission and of saving the consumption of auxiliary fuel. Sankaran et al. (1998) studied the incineration of three different oily-sludge wastes from one of the major refineries of South India in a fluidized-bed incinerator system and reported more than 98% combustion efficiency and 99% incineration efficiencies for all the three types of oily-sludge waste. By observing the flue-gas composition at the stack location, the scrubber sludge generated at the alkali washwater tank, and the ash collected at the postcombustion chamber, they concluded that fluidized-bed incineration technology can be a safe and effective method of treating refinery oily-sludge wastes.

Liu et al. (2009b) investigated cofiring of oily sludge with coal—water slurry (CWS) in a fluidized-bed incineration system and reported that the cofiring of oily sludge with CWS as an auxiliary fuel in this system had good operating characteristics. Coal—water slurry could flexibly control the dense bed temperatures by adjusting its feeding rate. All emissions could meet the corresponding environmental regulations. The CO emission was reported to be less than 1 ppm or essentially zero; the emissions of SO_2 and NO_x were reported to be 120—220 and 120—160 mg/Nm^3, respectively. The heavy-metal analyses of the bottom ash and fly ash revealed that the combustion ashes could be recycled as soil for farming. Zhou et al. (2009) conducted the combustion of oily sludge in a lab-scale circulating fluidized bed and found that the release and combustion of volatiles from oily sludge occurred not only in the dense region but also in the dilute region.

Although oily-sludge incineration has been practiced in a few developed countries, there are some limitations:

- Pretreatment of oily sludge with high moisture is required to improve its fuel efficiency by reducing the excessive water content.
- Auxiliary fuel is typically needed to maintain a constant combustion temperature (Hu et al., 2013).
- Low molecular PAHs, sulfur dioxide, nitrogen monoxide, and carbon monoxide can be fugitive emission of pollutants from incineration and incomplete combustion, which can cause atmospheric pollution.
- Ash residue, scrubber water, and scrubber sludge generated during the incineration process are hazardous and may require further treatment prior to disposal (Srinivasarao-Naik et al., 2011; Hu et al., 2013; Ubani et al., 2013).
- Oily sludge generally contains high concentration of hazardous constituents that are resistant to combustion (Hu et al., 2013; Ubani et al., 2013), and the incineration needs high capital and operating costs (more than $800 per ton of oily-sludge incineration) (Shiva, 2004; Hu et al., 2013).

7.2.4.7 Oxidation Method

Oxidation can be accomplished through chemical oxidation or other enhanced oxidation processes for degrading organic contaminants in oily wastes. Chemical oxidation and advanced oxidation processes were discussed in detail in Chapter 6. Chemical oxidation is carried out by adding reactive chemicals into oily wastes, which oxidize organic compounds to CO_2 and H_2O, or convert them to other nonhazardous substances such as inorganic salts (Ferrarese et al., 2008; Hu et al., 2013; Islam, 2015). Ozone, hydrogen peroxide, permanganate, and persulfate are the oxidants most commonly applied for environmental purposes (Ferrarese et al., 2008). As noted in Chapter 6, advanced oxidation processes can generate radicals in a sufficient amount to oxidize most of the complex compounds present in environmental matrices (Rocha et al., 2010; Jafarinejad, 2015c). In these processes, hydroxyl radicals can react with compounds, exhibiting faster oxidation reaction rates than those of conventional oxidants. It is necessary to note that in these processes the contaminants are destroyed and not transferred to another phase (Rocha et al., 2010).

Several studies have demonstrated that oxidation can be useful for soils and oily-sludge treatment. Watts and Dilly (1996) investigated a number of iron catalysts [iron (III) perchlorate, iron (III) nitrate, iron (III) sulfate, iron (II) perchlorate, iron (II) sulfate, and an iron (III)-nitrilotriacetic acid (NTA) complex] in the remediation of a Palouse loess soil contaminated with 1000 mg/kg diesel using catalyzed hydrogen peroxide. Of the six forms of inorganic catalysts, iron (III) perchlorate and iron (III) nitrate were reported to be most effective in oxidizing diesel in the Palouse loess soil. Iron (III) perchlorate was reported to be the most effective catalyst, but its application for full-scale soil remediation can be restricted due to its commercially unavailability. Although not as effective as iron (III) perchlorate, iron (III)-NTA was reported to catalyze up to 80% TPH oxidation at near-neutral soil pH. Modifications of potassium phosphate (KH_2PO_4) decelerated the rate of Fenton's reaction in soil slurries, probably by complexing soluble iron and other Fenton's catalysts; however, diesel oxidation was not significantly increased. They noted that the chemical cost for the Fenton-like treatment of diesel-contaminated Palouse loess soil can be $52/907 kg (ton), but in other soils, it may be varied by soil characteristics, contaminant properties, and the contaminant concentration. Kong et al. (1998) applied naturally occurring iron minerals, goethite and magnetite, to catalyze hydrogen peroxide and initiate Fenton-like reaction of silica sand contaminated with diesel and/or kerosene in a batch system. They reported that an iron mineral system was less aggressive in contaminant destruction, but it was more efficient than the $FeSO_4$ system. In addition, the magnetite system enabled stronger oxidation than the goethite system due to coexistence of Fe^{+2} and Fe^{+3} and dissolution of iron. Watts et al. (2000) evaluated the relative oxidation of representative aromatic [benzene, toluene, and mixed xylenes (BTX)] and aliphatic (nonane, decane, and dodecane) hydrocarbons found in gasoline to provide the foundation for risk-based treatment of petroleum-contaminated soils and groundwater using modified Fenton's reagent (catalyzed hydrogen peroxide). They reported that oxidation of the aromatic compounds needed less iron and less H_2O_2 than did oxidation of the aliphatic compounds, while proceeding more effectively at near-neutral pH. Greater than 95% of the BTX was oxidized at near-neutral pH using 2.5% H_2O_2 and 12.5 mM iron (III), while only 37% nonane, 7% decane, and 1% dodecane treatment was attained under the same conditions. According to Mater et al. (2007), reagent concentrations of H_2O_2 and Fe^{2+} can affect the reaction time and temperature as well as the degree of mineralization and biodegradability of the soil contaminants. Some H_2O_2/Fe^{2+} combinations (H_2O_2 greater than 10% and Fe^{2+} greater than 50 mM) can result in a strong exothermic reaction, which causes peroxide degradation and violent gas liberation. Up to 70% TOC removal efficiency can be achieved in soil when high H_2O_2 (20%) and low Fe^{2+} (1 mM) concentrations were applied. In addition to enhancing the degree of mineralization, the Fenton's reaction could enhance the biodegradability of petroleum compounds (BOD_5/COD ratios) by a factor of up to 3.8 for contaminated soils. Mater et al. (2007) investigations revealed that low reagent concentrations (1% H_2O_2 and 1 mM Fe^{2+}) could be sufficient to initiate the degradation process, which could be continued by microorganisms; therefore, this can lead to a decrease in reagent costs in the treatment of petroleum-contaminated soils.

Mater et al. (2006) applied sequential steps to treat and immobilize oil constituents of an oil-sludge-contaminated soil. They initially oxidized contaminated soil by a Fenton type reaction (13 wt% for H_2O_2 and 10 mM for Fe^{2+}) with a treatment period of 80 h under three different pH conditions: 20 h at pH 6.5, 20 h at pH 4.5, and 40 h at pH 3.0. Then they stabilized and solidified oxidized contaminated soil (3 kg) for 2 h with clay (1 kg) and lime (2 kg). Finally, they solidified this mixture with sand (2 kg) and Portland cement (4 kg). The results of their study revealed that the Fenton oxidative process could be partially efficient in degrading the oil contaminants in the soil, since residual concentrations were found for the PAH and BTEX compounds. In addition, clay−lime stabilization/solidification followed by Portland-cement stabilization/solidification could be efficient in immobilizing the recalcitrant and hazardous constituents of the contaminated soil. They concluded that these two-step stabilization/solidification processes can be necessary to enhance environmental protection (minimal leachability) and to render the final product economically profitable which the treated waste can be safe enough to be applied on environmental applications such as roadbeds blocks. Cui et al. (2009) carried out the oxidation of oily sludge in supercritical water in a batch reactor at reaction temperatures between 663 and 723K, reaction times between 1 and 10 min, and pressure between 23 and 27 MPa. The results of this study revealed that a COD removal rate of 92% could be achieved in 10 min and could be enhanced as the reaction time, temperature, and initial COD increased. Pressure and O_2 excess were reported to have no remarkable effect on reaction. Rocha et al. (2010) performed oily-sludge treatment using heterogeneous photocatalysis (H_2O_2/UV/TiO_2); this process provided efficient degradation and mineralization of a large part of the organic matter. In addition, this technique also proved to be an alternative treatment for eliminating PAH from oily sludge, removing 100% of all PAH content from the oily sludge after 96 h of irradiation. According to Zhang (2012), cited by Hu et al. (2013), the Fenton oxidation effect on oily-sludge degradation can be enhanced by ultrasonic irradiation, which improves the contact of hydroxyl radicals with PHC compounds (Hu et al., 2013). Jing et al. (2012) evaluated the utilization of wet oxidation for the treatment of oily sludge by using H_2O_2 as oxidant instead of air at high temperature in a batch reactor (Fig. 7.6) and showed that the quantity of oxidant with 250% to theoretical oxygen demand of oily sludge could be comparatively effective. In addition, adding a catalyst, Fe^{3+}, significantly improved the COD removal. They concluded that oxidation of intermediate for oily sludge can be a rate-limiting step for further oxidation of oily sludge.

According to Hu et al. (2013), oxidation generally requires relatively short treatment duration to degrade oily sludge, and is relatively insensitive to external disturbances (e.g., pollutant loading, temperature change, the presence of biotoxic substances, etc.). Products of oxidation are typically more biodegradable than the raw waste materials. However, this technique may require a large amount of chemical reagents to treat a large volume of oily sludge. The treatment costs of advanced

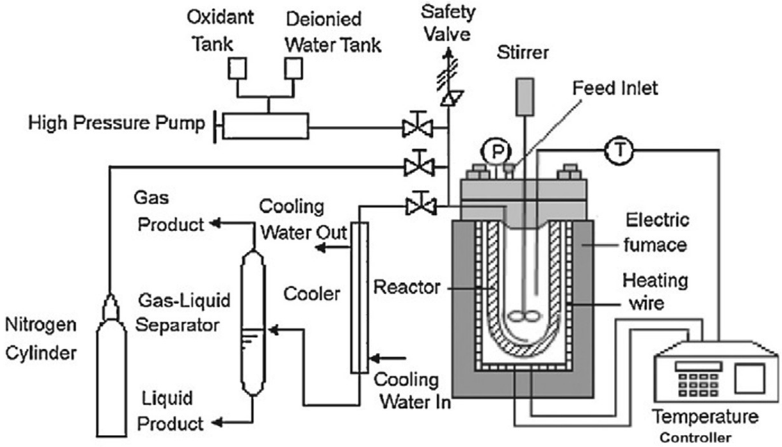

Figure 7.6 Schematic diagram of experimental setup for the wet oxidation of oily sludge (Jing et al., 2012).

oxidation processes such as wet-air oxidation, supercritical water oxidation, and photocatalytic oxidation can also be enhanced by using special equipment and considerable energy inputs (Hu et al., 2013).

7.2.4.8 Biodegradation or Bioremediation

The process in which microorganisms alter or convert organic molecules into other substances (harmless products) such as water, carbon dioxide, etc., is called biodegradation (Congress of the United States, OTA, 1991; CONCAWE, 1999, 2003), while the act of adding materials to polluted environments for accelerating the natural biodegradation process is referred to as bioremediation (Congress of the United States, OTA, 1991; Ubani et al., 2013). In other words, bioremediation is the use of microorganisms for the elimination of environmental pollutants, and is usually applied for the restoration of oilpolluted environments through accelerating the microbial degradation of PHCs (Fernández-Luqueno et al., 2011; Hu et al., 2013). Bioremediation, petroleum biodegradation, and the major oil-degrading microorganisms, effective parameters on bioremediation, nutrient enrichment (biostimulation), seeding with naturally occurring microorganisms (bioaugmentation), and seeding with genetically engineered microorganisms (bioaugmentation with GEMs) were discussed in detail in Chapter 4.

As noted, there are factors that contribute to the biodegradation of hydrocarbons. In other words, bioremediation can be influenced by the type of microorganisms, nutrients, biosurfactants, oxygen, water activity or moisture content, temperature, pH, salinity, time, and the concentration and characteristics of oily waste (e.g., oily sludge and contaminated soils) (Congress of the United States, OTA, 1991; E&P Forum, 1993; CONCAWE, 1999, 2003; Hu et al., 2013; Ubani et al., 2013). Most of these effective factors were discussed in Chapter 4. In general, a sufficient number of microorganisms of the right strains, nontoxic concentrations of contaminants or other compounds, presence of sufficient water (10—15% mass in soil), presence of sufficient nutrients (mainly P and N in ratio 1:10), presence of sufficient oxygen for aerobic processes and a full depletion of oxygen for anaerobic processes, temperature (10—30°C), sufficient availability of contaminants (preferably without high peak concentrations) to the microorganisms, soil pH of 6 to 8 can help the degradation rate (CONCAWE, 1999, 2003). According to Admon et al. (2001) and Yerushalmi et al. (2003), cited by Hu et al. (2013), the elimination of PHCs was observed only after nutrients were amended to oily-sludge-contaminated soil at a C:N:P ratio of 50:10:1 (Hu et al., 2013). Roldán-Carrillo et al. (2012) investigated the biodegradation of oily sludge from Mexican sour gas and petrochemical facilities under different nutrient conditions and found that after 30 days of treatment, the highest hydrocarbon removal was 51% in the sludge that had a C:N:P ratio of 100:1.74:0.5 (Roldán-Carrillo et al., 2012). The degradation of PHCs is generally limited by their high hydrophobicity or low solubility (Hu et al., 2013). The biosurfactants can emulsify petroleum hydrocarbon in oily sludge so that they can be bioavailable to microorganisms for biodegradation in the system. The surface area of the substrates is usually increased by biosurfactants, which enhances their solubility. In general, biosurfactants are important agents that help increase the effective uptake of petroleum hydrocarbons by bacteria and fungi (Ubani et al., 2013). Rahman et al. (2003) studied biodegradation of oily sludge from a crude-oil tank bottom using bacterial consortium, rhamnolipid biosurfactant and nitrogen, phosphorus and potassium solution, and reported maximum degradation after the 56th day of treatment. N-alkanes in the range of nC_8—nC_{11} were reported to be degraded completely followed by nC_{12}—nC_{21}, nC_{22}—nC_{31}, and nC_{32}—nC_{40} with percentage degradations of 83—98%, 80—85%, and 57—73%, respectively. Verma et al. (2006) used three bacterial strains, *Bacillus* sp. SV9, *Acinetobacter* sp. SV4, and *Pseudomonas* sp. SV17 to produce biosurfactants and found that *Bacillus* sp. SV9 degraded approximately 59% of the oily sludge in 5 days at 30°C, whereas *Acinetobacter* sp. SV4 and Pseudomonas sp. SV17 degraded 37% and 35%, respectively. Cameotra and Singh (2008) showed that the use of two additives (a formulated nutrient mixture and a crude rhamnolipid preparation) could be successful in improving the bioremediation of sites contaminated with compounds having limited water solubility. A crude surfactant preparation can enhance hydrocarbon biodegradation in soil, thus the need for costly and time-consuming biosurfactant recovery and purification processes can be eliminated. Cerqueira et al. (2011) used the bacterial consortium for the biodegradation of petrochemical oily sludge and reported an excellent oily-sludge degradation capacity, reducing 90.7% of the aliphatic fraction and 51.8% of the aromatic fraction within 40 days of treatment, as well as biosurfactant-production capacity, achieving 39.4% reduction of surface tension of the culture medium and an emulsifying activity of 55.1%. As the soil moisture and water content for aerobic bioremediation treatment matrix is typically between 50% and 80% of saturation (moisture-holding capacity), optimal activity can take place, while when the moisture content falls below 10% bioactivity can become marginal (Kosaric, 2001; Ubani et al., 2013). In addition, the highest degradation rates usually take place in the range of 30—40°C in soil environments (Zhu et al., 2001; Ubani et al., 2013). When the pH is in the range of 7—7.8, the mineralization of hydrocarbon components in the environment is usually optimal, thus overall biodegradation process is improved (Hamme et al., 2003; Ubani et al., 2013). In general, there are positive correlations between salinity and rates of mineralization of PAHs such as phenanthrene and naphthalene (Leahy and Colwell, 1990; Ubani et al., 2013), but hypersalinity can result in the reduction of microbial metabolic rates (Vincent, 2006; Ubani et al., 2013). The degradation rate of PHCs usually reduces with time, reaching an apparent plateau associated with pollutant residues that are recalcitrant constituents and have very slow degradation (Hu et al., 2013).

Land treatment (landfarming and landspreading), biopile/composting, and mechanized processes or bioreactors or bioslurry treatment are different bioremediation approaches (E&P Forum, 1993; CONCAWE, 1999, 2003; Hu et al., 2013; Ubani et al., 2013). In general, rates of biodegradation can be highest for bioreactors and composting and lowest for the land treatment. Land treatment may be considered a disposal option as well as a treatment, while composting and bioreactors usually transform the waste into a harmless product for subsequent use or disposal (E&P Forum, 1993).

7.2.4.8.1 Land Treatment

A treatment method that includes the controlled application of a waste on the soil surface and the incorporation of that waste into the upper soil zone is called land treatment (Hejazi et al., 2003); it has been applied for the treatment of petroleum industry wastes for many years (E&P Forum, 1993; CONCAWE, 1999, 2003). In this method, biological removal is typically the major degradation mechanism for the most of organic pollutants (Hu et al., 2013), while physical and chemical removal mechanisms such as evaporation, photo-degradation (Hu et al., 2013), volatilization, and dilution may also be important for some compounds. Landfarming and landspreading are different land-treatment approaches (E&P Forum, 1993).

Landfarming involves the controlled application of waste on a soil surface to biodegrade the contaminants using the microorganisms that typically occur under aerobic conditions. Landfarming is different from landfilling or burial, in which the waste is deposited in manmade or natural excavations for an indefinite period of time typically in anaerobic conditions (E&P Forum, 1993; CONCAWE, 1999, 2003). Tilling of the topsoil (for aiding aeration and easy mixture with oily sludge), addition of water, addition of desired nutrients such as organic fertilizers (Ubani et al., 2013; Hu et al., 2013), maintenance of appropriate sludge-application rate and pH (Hu et al., 2013), etc., are needed for proper landfarming. The optimum moisture content, temperature, and pH range for the highest degradation rate in landfarming are 18%, 25−40°C, and 6.5−7.5, respectively, and the most rapid biodegradation of refinery sludge takes place as added nitrogen decreases the C:N ratio to 9:1. Landfarming may not be effective for sites of high component concentrations of greater than 50,000 ppm TPH, and it is difficult to achieve concentration reductions greater than 95% and component concentrations less than 0.1 ppm by this method. This method is not efficient at degrading the heavy constituents of petroleum (Khan et al., 2004) and materials containing significant levels of biologically available heavy metals, persistent toxic compounds, or low specific activity scale (E&P Forum, 1993), and volatile contaminants must be pretreated because they can cause air pollution (Khan et al., 2004). Groundwater should be monitored because the migration of leachate, which may contain PHCs, phenols, and heavy metals, can pollute it (Hu et al., 2013; E&P Forum, 1993). The human health risk associated with a landfarm operation should also be considered because the sludge poses serious carcinogenic risks to workers during the early sludge application period (Hejazi et al., 2003; Ubani et al., 2013).

Landfarming technology requires a large land area for treatment. Compared to other remediation technologies (e.g., incineration, landfilling, and deep-well injection), capital, installation, operation, and maintenance costs for landfarming operations are relatively low (Hejazi et al., 2003; Khan et al., 2004). The cost of this technology for the remediation of petroleum-contaminated soils can range from $30 to $60 US/t and may take from 6 months to 2 years (longer for heavier components of petroleum) (Khan et al., 2004).

The landfarming method lost its popularity in 1984 when the US EPA issued a land-disposal restriction as part of the hazardous and solid-waste amendments to the RCRA, establishing treatment standards under the land-disposal restriction program. This restriction program prohibited the land disposal of untreated oily sludge, which led to treating the oily sludge to meet EPA treatment standards and making sure that there was no migration of hazardous components from the injection zone (Hejazi et al., 2003; Ubani et al., 2013). In most locations, landfarming requires authority permits and approval (E&P Forum, 1993), and in a number of countries the method is not permitted at all. Landfarming is a relatively cost-effective and simple technology that is environmentally acceptable provided that it is properly designed, operated, and monitored (also with respect to leachate and runoff). However, uncontrolled landfarming is unlikely to be acceptable today and has largely been replaced by more controlled operations (CONCAWE, 1999, 2003).

Admon et al. (2001) studied land treatment of refinery oily sludge and reported 70–90% degradation of TPH during 2 months, regardless of initial concentrations (9–60 g/kg soil). Mishra et al. (2001) validated the large-scale use of a carrier-based bacterial consortium and nutrients for the treatment of land contaminated with oily sludge. Their results revealed that the application of a bacterial consortium (1 kg carrier-based bacterial consortium/10 m^2 area) and nutrients degraded 90.2% of the TPH in 120 days, whereas in the control land block (untreated block) only 16.8% of the TPH was degraded (Mishra et al., 2001). Landfarming is an attractive technique for oily-sludge disposal in hot arid climatic conditions (Hejazi and Husain, 2004a). Hejazi and Husain (2004a) in a 12-month field study under arid conditions showed that weathering (evaporation) and not biodegradation was the overall dominant degradation mechanism taking place in landfarms in this area. Their results also revealed that up to 76% of the O&G in the sludge was lost from soil as a result of weathering. However, the primary mechanism for the loss of C_{17} and C_{18} alkanes as compared to branched alkanes was due to biodegradation. In other work, Hejazi and Husain (2004b) studied different effective parameters (moisture content, microbial density and composition, nutrients, and tilling) on the degradation processes in landfarming operations in field experiments. Their results revealed that tilling was very effective at increasing the loss of O&G fractions under arid conditions. However, hydrocarbon loss in the absence of fertilizer and water was mainly due to weathering (volatilization). The microbial counts were found to be low in the absence water and nutrients. The addition of water and fertilizer combined with the tilling contributed to the significant reduction of O&G through both volatilization and biodegradation mechanisms with early reduction of n-alkanes through a biodegradation process followed by weathering. The high loading rate resulted in retaining moisture content in the soil, and it delayed weathering and biodegradation. The high loading rate caused bacterial counts to increase, as it provided them with a plentiful source of food and water; however, it did not stimulate the biodegradation process for almost 6 months after the highest rate of sludge application to the soil. Marin et al. (2005) investigated the possibility of refinery sludge bioremediation by landfarming in semiarid conditions and reported an 80% biodegradation of total hydrocarbons in 11 months (half of this reduction occurring during the first 3 months).

Landspreading is similar to landfarming, but it refers to the one-time application of waste to a site. Landspreading sites only receive a single application of waste, and the potential for the accumulation of waste constituents in the soil is reduced by this practice. It is seldom required for landspreading sites to construct a containment system (liners) or monitor the leachates from the site. However, site topography and hydrology, physical and chemical composition of the waste, and waste-application rates should be considered. Landspreading can be used as a disposal method for E&P wastes such as drilling fluids and cuttings with low levels of hydrocarbons and salts (E&P Forum, 1993).

7.2.4.8.2 Biopile/Composting

As landfarming technology requires a large land area for treatment, biopile/composting can be an alternative technology for it (Hu et al., 2013). Biopile technology refers to piling contaminated masses and amendments into heaps or cells or mounds usually to a height of 2−4 m and stimulating aerobic microbial activity by upflow pneumatic aeration (Jфrgensen et al., 2000; Kriipsalu et al., 2007). Note that masses or the mixture should be as homogeneous as possible prior to placing it into biopiles. In comparison with windrow composting, aerobic biodegradation in static forced air biopile is simple and presents better control over the process (Kriipsalu et al., 2007). General guidelines suggest that the biopile technique may not be effective on petroleum concentrations greater than 50,000 ppm (Khan et al., 2004; Kriipsalu et al., 2007), and toxic metal concentration should be below 2500 mg/kg dry matter (Kriipsalu et al., 2007). Bulking agent, nutrients, moisture adjustment, air blowing (Wang et al., 2012), and minerals (E&P Forum, 1993; Khan et al., 2004) can enhance the activities of indigenous or extraneous microorganisms for treatment, and control of heat and pH can also be helpful. Soil characteristics such as texture, permeability, moisture content, and bulk density can play a significant role in the success of biopiles (Khan et al., 2004). In biopiling oily-sludge or oil-contaminated soil, a bulking agent can be applied for adsorbing moisture, enlarging the porosity of the compost mixture, and supporting biological processes. Optimal porosity of 30−35% (Kriipsalu et al., 2007) can be attained by using inexpensive bulking agents, such as wood chips, sawdust, peat, or bark (Jφrgensen et al., 2000; Kriipsalu et al., 2007). This technology is called composting if organic material is added (Jφrgensen et al., 2000; Marín et al., 2006; Hu et al., 2013). The degradation of PAHs during bioremediation of contaminated soils can be enhanced by addition of organic matter (Jφrgensen et al., 2000; Kriipsalu et al., 2007). Organic matter can initially absorb excessive moisture and free moisture during the composting process, compensating for the moisture loss to some extent that takes place in the case of forced aeration (Kriipsalu et al., 2007). Careful control of temperature, moisture, aeration, particle size, macro- and micronutrients in the mass to be composted, C:N:P ratio of the materials, etc., can be helpful for optimizing the composting process (Marín et al., 2006). Optimal biodegradation can take place between 20 and 40°C. Under optimal conditions, the treatment period may be from 6 months to 2 years (Khan et al., 2004). However, the biodegradation process may be accelerated to a few months or even few weeks in contained areas with controlled climate (in housings) (CONCAWE, 1999, 2003).

Ouyang et al. (2005) compared two bioremediation technologies (microbial bioaugmentation and composting) for restoration of the oily sludge and oil-polluted soil from the Shengli oil-production plant (Dongying, China). After 56 days treatment under ambient temperature, bioaugmentation with microbe preparation was reported to decrease the oil contamination of oily sludge by 45–53% after three-fold application of the preparation, while composting of the same sludge was reported to reduce the oil contamination by only 31%. In addition, the planting of tall fescue (*Festuca arundinace*) revealed a decrease of sludge toxicity after application of both bioremediation technologies and additionally reduced the total hydrocarbon content by 5–7%. Marín et al. (2006) evaluated the efficacy of composting as a bioremediation method for reducing the hydrocarbon content of oily refinery sludge with large total hydrocarbon content (250–300 g/kg) in semiarid conditions, which involved open-air piles turned periodically over a period of 3 months. The results of this study revealed that when the bulking agent (wood shavings) was added, the initial hydrocarbon content was decreased by 60% in 3 months, while a 32% reduction was attained without the bulking agent. The inoculation of the mass with pig slurry (a liquid organic fertilizer that adds nutrients and microbial biomass to the pile) did not significantly improve the degree of hydrocarbon degradation (56% hydrocarbon degraded). In addition, the composting process led to the biodegradation of toxic compounds. Delille et al. (2007) quantified the effects of temperature on the hydrocarbon mineralization rate during mesocosms, biopiles, and field-pilot studies carried out on artificially contaminated sub-Antarctic soil. The results of field tests under natural sub-Antarctic conditions demonstrated that up to 95% of the contaminants could be degraded within 1 year, showing that low temperatures (0–7°C) can still accommodate oil biodegradation by indigenous microorganisms. Covering the soil with a plastic sheet induced an annual mean increase of temperature of only +2.2°C. The results of mesocosm studies and pilot biopile experiments also proved that constant heating of soil could be an effective way to speed up bioremediation of diesel-contaminated sub-Antarctic soils; however, the microbial response was always improved by a complementary fertilizer addition. Kriipsalu et al. (2007) studied the aerobic biodegradation of oily sludge generated by a flotation–flocculation unit of an oil-refinery WWTP. The results of this study revealed that reduction of TPHs in sand, mature oil compost, kitchen-waste compost, and shredded waste wood after 373 days of treatment was 62%, 51%, 74%, and 49%, and the reduction of PAHs was 97%, +13% (increase), 92%, and 88%, respectively.

Liu et al. (2010) carried out in situ bioremediation of oily-sludge-contaminated soil by biostimulation of indigenous microbes through addition of manure at the Shengli oilfield in China. After about 1 year of bioremediation, the TPH content reduction was 58.2% in the treated plots compared to only 15.6% in the control plot. They concluded that although there were distinct decreases in TPH and toxicity and marked improvements in the physicochemical properties and microbial activity of the soil after bioremediation, the TPH content in the soil was still as high as 101 g/kg in treated plots and further remediation (e.g., phytoremediation) may be needed. Wang et al. (2012) reported that after 220 days, 49.62% of TPHs could be removed from the middle layer of the bulking agent pile, whereas only 20.44% could be removed from the inner layer of the control. However, the quantity of TPHs in the middle layer of the bulking agent pile was still high and required subsequent treatment. In addition, the application of a large amount of nutrients (urea) led to a suppressing effect on both metabolic activity and diversity.

Relatively low capital and maintenance costs, simple design and operation, and some (but incomplete) removal of oil pollution are some of the advantages of biopile/composting (Ouyang et al., 2005). It can also be engineered to fit different products and site conditions (Khan et al., 2004). Temperature in the piles may be increased due to the heat generated by intense microbial activity, resulting in the use of this technology for PHC degradation under extreme climatic conditions such as in sub-Antarctica areas (Delille et al., 2007; Hu et al., 2013). In comparison with landfarming, biopile/composting can more efficiently remove PHCs in oily sludge and treat more toxic compounds (Hu et al., 2013), although contaminant reductions of more than 95% are difficult to attain (Khan et al., 2004). When the attempted biological treatment in biopile/composting proves to be unsuccessful, mixing noncontaminated amendments to contaminated material (compost mixtures) produces a far greater quantity of contaminated masses that can cause a major concern; finally, some bulking agents can be recycled and applied in subsequent runs (Kriipsalu et al., 2007). In biopile/composting, a closed system can control vapor emissions. In other words, VOC emissions can be controlled by auxiliary collection units. The treatment capacity of this technology is much smaller than that of land treatment and it still requires a relatively large area of land and long treatment period for oily-sludge degradation, although the area needed is less than for landfarming (Khan et al., 2004; Hu et al., 2013). The contaminant, the procedure used, pre- or posttreatment, or the need for emission-control equipment all affect the cost of biopiles. This method requires few personnel for operation and maintenance, and the cost of this technology for the treatment typically ranges from $130 to $260 US per cubic yard (Khan et al., 2004).

7.2.4.8.3 Bioslurry Systems or Bioreactors

Bioslurry systems are also called bioreactors (E&P Forum, 1993; Woo and Park, 1999; Ward et al., 2003; Khan et al., 2004; Machın-Ramırez et al., 2008; Hu et al., 2013; Ubani et al., 2013), fermenters, and mechanized processes (CONCAWE, 1999, 2003). In bioslurry systems, solid wastes are mixed with water in various ratios (i.e., 5–50% w/v), and rates over solids treatment are greatly enhanced by maximizing the contact between microorganisms, hydrocarbons, nutrients, and oxygen (Machın-Ramırez et al., 2008; Ward et al., 2003). Mass transfer restrictions are minimized and contaminant desorption from solids is enhanced, resulting in much higher hydrocarbon removal rates than observed in landfarming and other solid-phase systems (Ward et al., 2003). In these systems, biodegradation takes place at a rapid rate with typical treatment times ranging from less than 1 month to more than 6 months (Khan et al., 2004). After treatment, the slurry is usually dewatered and treated solids can be disposed of (Zhang et al., 2001; Khan et al., 2004). Depending on the components and regulations, liquids may be transported to a WWTP, injected, or discharged (E&P Forum, 1993).

Bioslurry systems may usually be operated as a batch or semicontinuous process (E&P Forum, 1993). According to Ward et al. (2003), the first bioreactor systems for treatment of oily sludges required batch-cycle process-times of 1–3 months, but there are now accelerated processes that can be completed in 10–12 days. In these processes, up to 99% of TPHs may be degraded and the sludges can be transformed from hazardous to nonhazardous according to the US EPA's toxicity characteristic leachate-procedure criteria (Ward et al., 2003). On the other hand, control of temperature, moisture, pH, oxygen, nutrients, addition of surfactants, supplementation of microorganisms, monitoring of reactions and conditions, and control of VOC emissions are possible in closed systems (Khan et al., 2004).

There are different designs for bioreactors such as rotating drum equipped with lifters to provide internal mixing or vertical tank equipped with an impeller or air sparger for mixing (Woo and Park, 1999; Machın-Ramırez et al., 2008). Rotating drum bioreactors are alternatives to slurry bioreactors, since they can handle wastes with high solid contents (Woo and Park, 1999). According to the CONCAWE (1999, 2003), there are commercial bioreactors and fermenters with vacuum or pressure operation equipped with humidity control and mechanical stirring of the entire charge with a capacity up to 200 tons for a single charge that can operate under aerobic or anaerobic conditions. In these bioreactors, residence times are between a few hours and few days depending on the type and grade of contamination. Typical hydrocarbons require a few hours to degrade, whereas PCBs need several days (CONCAWE, 1999, 2003).

The Petrozyme process is a reactor-based microbial process that applies advanced fermentation technology to degrade petroleum hydrocarbons in sludge, generating a nonhazardous effluent with very low levels of hydrocarbons. This process has been successfully demonstrated at pilot- and full-scale in different petroleum refineries in Canada, the United States, Venezuela, and Mexico and has been used in commercial operations in the United States and Venezuela. In the bioreactor, up to 90% of TPHs in the sludge can be degraded at 28–32°C and pH 6.6–7.6 within 6–12 days depending on the composition of sludge and the required treatment standards (Singh et al., 2001). The Petrozyme process can operate with a much shorter residence time of 12 days, with the extent of degradation of TPHs up to 99% (Ward and Singh, 2000; Singh et al., 2001; Ward et al., 2003).

According to Coover et al. (1990), cited by Ward et al. (2003), a bioreactor system (with a capacity of 4.55×10^6 L and float-mounted mixers and aerators) was utilized to remediate petroleum-impounded sludges at a major Gulf coast refinery. Operating nominal solids contents in the bioreactor and the average temperature were about 10% and 22.6°C, respectively. Reduction in oil and grease was 50% after 80−90 days, and the overall extent of removal of PAHs was 90%. Woo and Park (1999) applied a laboratory-scale drum bioreactor system to investigate the engineering aspects of soil bioremediation and reported that over 95% of PAHs with three or four rings (fluorene, phenanthrene, anthracene, pyrene) could be degraded at 270 mg/kg soil within 20 days. In addition, the degradation rate of PAHs in the suspension phase was higher than that in the sediment phase.

Maga et al. (2003) reported that a 10,000-gallon sequencing batch reactor was used for the on-site degradation of oily sludge and the hydrocarbons in oily sludge were degraded within 2 weeks, from 20,000 ppm to less than 100 ppm. Furthermore, the concentrations of heavy metals (primarily zinc and copper) and total suspended solids in treated sludge residuals were reported to be well below discharge limits. Ayotamuno et al. (2007) reported that bioaugmentation in the bioremediation of oily sludge [from the Bonny-Terminal Improvement Project (BTIP) for Bonny Island, near Port Harcourt, Nigeria] reduced the total hydrocarbon content of the sludge from 40.7% to 53.2% and 63.7−84.5% within 2 and 6 weeks of treatment, respectively. But only a 12.8% total hydrocarbon content reduction was attained in the control reactor after 6 weeks of treatment. In addition, the total hydrocarbon content reduction of the two strains of bacteria (*bacillus* and *pseudomonas*) applied in the mixed culture during the bioaugmentation process was higher than that of individuals strains in the pure culture. Between the two strains, *pseudomonas* was reported to be the better degrader. Machın-Ramırez et al. (2008) reported that abiotic loss of TPHs in the oily-sludge waste was insignificant in the slurry-phase system, and degradation rates under the various treatment conditions ranged between 666.9 and 2168.7 mg/kg/day over a 15-day reaction period. In addition, biostimulation with a commercial fertilizer [the Fertilizer Peters NKP (15:15:15)] resulted in 24% biodegradation of the TPH in the oily waste. Addition of nonindigenous adapted consortium did not increase the removal of TPH from the oily waste. They concluded that the complexities of the constituents of the alkylaromatic fraction of the waste restricted the biodegradation rate even in a slurry system.

In general, the bioslurry/bioreactor system can be a rapid and effective method for oily-sludge disposal. Unlike other land-based biological treatment processes, bioreactors generally require less space (E&P Forum, 1993; Hu et al., 2013). The nonhomogeneous oily-sludge slurry and clayey mixtures may cause serious handling and operational problems and require pretreatment. All of these pretreatments and/or subsequent posttreatments (e.g., solid dewatering and wastewater treatment) can significantly enhance the overall cost (Khan et al., 2004; Hu et al., 2013). Thus the relatively high treatment cost is a disadvantage of this technology. The treatment cost of bioslurry/bioreactors can typically range from $130 US to $200 US per cubic meter. The cost can be increased by gas treatment due to the generation of volatile compounds (Khan et al., 2004). The price for capital equipment, design, and construction of these systems can range from $125,000 US to $2,000,000 US (Khan et al., 2004; Zhang et al., 2001).

7.2.5 Concerns of Spent Catalysts in the Petroleum Industry

7.2.5.1 Spent Catalysts

The process by which chemical reaction rates are changed by the addition of the catalyst is called catalysis (Erust et al., 2016), and it played an important role during the second half of the 20th century in the development of the petroleum industry. Heterogeneous catalysts are the major categories of catalysts and include acid, metal, sulfur, and bifunctional catalysts and, to a lesser degree, oxide phases (other than supports) (Marcilly, 2003; Akcil et al., 2015).

Petroleum industry (e.g., refinery) catalysts usually include metals supported on an inert carrier such as alumina, silica, or activated charcoal. The metals may be precious, such as platinum or rhenium in a reformer catalyst, or heavy base-metal elements such as nickel, molybdenum, cobalt, tungsten, and vanadium, e.g., nickel-molybdenum for a hydrotreater catalyst (CONCAWE, 1999, 2003). In fact, hydrotreating catalysts usually consist of molybdenum supported on an alumina carrier with promoters such as cobalt or nickel (Marafi and Stanislaus, 2008). Sometimes nonmetal catalysts are applied such as phosphoric acid in the catalytic polymerization process. During application, the catalysts can be contaminated by metals such as lead, arsenic, nicke,l and vanadium, nonmetals like sulfur and carbon, and significant quantities of hydrocarbon products and residues (CONCAWE, 1999, 2003). Overheating, pore blockage, and fouling of the active surface with coke, deposition of carbon, sulfur, and contamination with heavy metals like lead, arsenic, and vanadium from the feedstock are some of the possible reasons for deactivation of the catalysts (Marafi et al., 2008; Barik et al., 2012).

Consumption of industrial catalysts was up to 800,000 ton/year in 2012 (Li et al., 2016), and among them, the refining catalysts account for about 24% of the world market and the catalysts for hydrotreating and fluid catalytic cracking contribute the largest share of refining catalysts (Silvy, 2004; Li et al., 2016). Spent refinery catalysts correspond to about 4 wt% of the overall refinery waste (Liu et al., 2005; Akcil et al., 2015), and based on estimation, the total amount of spent hydrotreating catalyst generated worldwide is 150,000−170,000 ton/year (Dufresne, 2007; Marafi and Stanislaus, 2008; Li et al., 2016).

Spent catalysts may be generated in the production and maintenance operations of the E&P sector (E&P Forum, 1993; Bashat, 2003); catalytic cracking, catalytic hydrocracking, hydrotreating/hydroprocessing, polymerization, residue conversion, and catalytic reforming units of refiners (Speight, 2005; European Commission and Joint Research Center, 2013); steam-cracking process and aromatics plants of petrochemicals (IL & FS Ecosmart Limited Hyderabad, 2010). The amount of fresh catalysts applied, their life, and the deposits formed on them during use in the reactors can extensively affect the quantity of spent catalysts discharged from different processing units. Due to the use of large quantities of catalysts in the hydrotreating process for the purification and upgrading of various petroleum streams and residues, hydroprocessing units are often the major spent catalyst waste-generating units in most refineries (Marafi et al., 2008).

Spent catalysts in the petroleum industry typically include about 4−12% molybdenum, 15−30% aluminum, 1−5% nickel, 0−4% cobalt, 5−10% sulfur, 1−5% silicon, and 0–0.5% vanadium (Barik et al., 2012). In particular, spent hydrodesulfurization catalysts generally consist of 10–30% molybdenum, 1–12% vanadium, 0.5–6% nickel, 1–6% cobalt, 8–12% sulfur, 10–12% carbon, and the balance is alumina, which makes it economically viable for recovery of valuable metals (Biswas et al., 1986; Akcil et al., 2015).

Spent catalysts are considered secondary resources that can reduce the consumption of primary resources and provide economic benefits (Erust et al., 2016; Akcil et al., 2015). The US EPA classified spent catalysts as hazardous wastes (US EPA, 2003; Marafi et al., 2008; Shen et al., 2012; Erust et al., 2016; Akcil et al., 2015), and a viable but economical solution must be found to solve this serious environmental issue (Marafi et al., 2008).

7.2.5.2 Management of Spent Catalysts

Spent catalysts can be managed through the following approaches:

- Regeneration such as oxidative regeneration (Ferella et al., 2016).
- Rejuvenation: Rejuvenation removes metal-contaminant deposits or alkali and other metal ions from used or spent catalysts and allows for reactivation of catalysts. Demetallization may be applied. In this process, metals undergo oxidation, sulfidization, and chlorination in a specific reactor. Some rejuvenation processes include chemical extraction or leaching (Ferella et al., 2016). Cho et al. (2001) studied three different rejuvenation methods to recover the catalytic activity of spent fluid catalytic cracking catalysts. In particular, carbochlorination, metal carbonyl, and washing techniques were tested on spent equilibrium catalyst with the aim to remove nickel, vanadium, and iron (Cho et al., 2001; Ferella et al., 2016).
- Reuse as cement and mortar additive (Antiohos et al., 2006; Ferella et al., 2016); reuse as catalyst for fuel synthesis from biomass, conversion of plastics into fuels, and zeolite production (Ferella et al., 2016); use of spent catalysts in the manufacture of other products such as use of those containing nickel, cobalt, and molybdenum in the production of ceramic tiles; combination of spent catalysts with waste products from other industries to make useful products such as mixing of catalysts containing phosphoric acid with aluminum industry waste alkali mud to make a soil amendment product; combination of spent catalysts with asphalt and use as a road base; use of spent catalysts containing activated charcoal, or highly contaminated with hydrocarbon residues as fuel in, e.g., cement manufacture (CONCAWE, 1999, 2003).
- Recovery of metals (Ferella et al., 2016) using hydrometallurgical (metals are leached by catalysis with acids or bases), pyrometallurgical (using a heat treatment), and biohydrometallurgical (microorganisms, bacterial, or fungal leaching) methods (Asghari et al., 2013; Akcil et al., 2015). In other words, leaching with ammonia and ammonium salt solutions, leaching with acids, alkali leaching, two-stage leaching (leaching with an alkali in the first stage and an acid or ammonia in the second stage, or the other way around), bioleaching, roasting with alkali compounds (sodium salts and potassium salts), chlorination, electrolytic cells (Marafi and Stanislaus, 2008), chelation using ethylene diamine tetra acetic acid (EDTA) or another similar agent to complex the metal ions may be applied to recover metals from spent catalysts. The advantages and disadvantages of bioleaching compared to chemical leaching, thermal treatment, and other traditional processes for metal extraction are listed in Table 7.3 (Asghari et al., 2013). Commercial processes include either leaching out metals or roasting to make metals soluble in water (Marafi and Stanislaus, 2008). In fact, there are several

Table 7.3 Comparison of Bioleaching With the Chemical Leaching, Thermal Treatment, and Other Traditional Processes in Metal Extraction (Asghari et al., 2013)

Method	Advantages	Disadvantages
Chemical leaching, thermal treatment, and other traditional processes	Shortest process time	Needs complex process plant and maintenance cost; Needs large amount of acid and alkali; High-energy requirement; High operational cost; Liability of hazardous chemical usage during the treatment; Needs sufficient (high) concentration of elements in ores; Not applicable for highly contaminated materials; and Hazardous emissions.
Bioleaching	Environmentally friendly (green technology); Low cost; Low-energy requirement; Simpler and cheaper to operate and maintain than traditional processes; Conditions of operation at ambient pressure and nonexcessive temperatures close to ambient; Most efficient method in terms of heavy metal solubilization; Higher removal efficiency for heavy metals; Without strict requirements of raw material composition; Applicable for highly contaminated materials; and Safety emissions.	Longer process time; and dependency on several atmospheric conditions.

methods to separate the different metals, including selective precipitation and solvent extraction, which are most common. Pyrometallurgical and biohydrometallurgical methods were also suggested in the scientific literature but do not yet have industrial utilization (Akcil et al., 2015).
- Disposal such as landfilling (CONCAWE, 1999, 2003; Asghari et al., 2013; Ferella et al., 2016).

Disposal in landfills is environmentally limited due to the leaching of chemicals such as vanadium, molybdenum, nickel, and cobalt present in the catalysts by water after disposal and subsequent pollution of the environment (Furimsky, 1996; Marafi et al., 2008). In the United States, the RCRA governs the disposal and treatment of spent catalysts that holds not only the approved dump-site owner liable, but also the owner of the buried waste. This environmental responsibility continues for the life of the dump site. Current RCRA regulations require landfills to be constructed with double liners as well as with leachate collection and groundwater-monitoring facilities, resulting in higher costs. Furthermore, landfills have continuing environmental liability. In some cases, treatment before landfilling is required, which can further increase costs. In recent years, interest in the development of processes for recycling/reclaiming of waste-catalyst materials has increased (Marafi et al., 2008).

7.3 Handling of Heavy Metals

Metals such as vanadium, nickel, iron, copper, etc. (nickel and vanadium < 1000 ppm) are some of the impurities found in crude oil (Jafarinejad, 2016). In fact, the amount of metals in crude oil typically varies from a few ppm to more than 1000 ppm. In crude oil, metals such as zinc, titanium, calcium, and magnesium are usually present in combination with naphthenic acid as soaps and metals such as vanadium, copper, nickel, and part of the iron are present as oil-soluble porphyrin-type compounds (Ali and Abbas, 2006).

Contamination of products, poisoning and fouling of catalyst, and corrosion of equipment by metal chelates, and the tendency to form particulate emissions in the submicron range are some of the negative effects of metals in petroleum. Ali and Abbas (2006) reviewed the methods for the removal of metals from heavy oils and residuum fractions and these methods include physical processes (distillation, solvent extraction, and filtration), chemical treatment with acids and alkali, and catalytic treatment or catalytic hydroprocessing (e.g., hydrodemetallization process). Several methods such as chemical treatment with acids and alkali, selective oxidation/solvent extraction, the photocatalytic method, electrochemical treatment, and novel thermal and catalytic methods have been reported in the literature for metals removal from residual oil. According to Ali and Abbas (2006), hydrotreating and gasification may be the only processes capable of effecting substantial removal of metals. Hydrotreating may not be economical or practical for heavy, high-metal content resids. When a pretreatment step by one of the above methods can be used to remove metals, then heavy resids can be more economically upgraded by conventional techniques of catalytic cracking (Ali and Abbas, 2006).

Incineration of oily sludge can generate oily-sludge ash and fly ash enriched with heavy metals, which can result in further environmental concerns (Hu et al., 2013). On the other hand, the morphology, growth, and metabolism of soil microorganisms and the oil-product concentrations can be influenced by heavy metals during the bioremediation of oily sludge (Zukauskaite et al., 2008; Hu et al., 2013). An increase in C:N ratio in microbial biomass following a relative enhancement in fungal communities may be a specific indicator of soil contamination by heavy metals (Dai et al., 2004). According to Maliszewska-Kordybach and Smreczak (2003), the combined effect of PAHs and heavy metals on soil microorganism activity and on some plants at an early stage of their development can be stronger than in soils with heavy metals or PAHs alone (Maliszewska-Kordybach and Smreczak, 2003). According to Shen et al. (2005), the action and interaction between heavy metals and PAHs can strongly depend on the time of pollution. The existence of heavy metals in PAH-contaminated soils not only reduces the diversity of the microbial population but also presents a few distinctive species by exerting selective pressure. Investigation of microbial activity and diversity in long-term mixed contaminated soils with respect to PAHs and heavy metals can have major implications for the bioremediation of organic pollutants in metal-organic mixed contaminated sites (Thavamani et al., 2012).

The purpose of most current oily-sludge treatment technologies is recovery and/or removal of petroleum hydrocarbons, and these technologies have no or limited effects on the removal of heavy metals in oily sludge (Hu et al., 2013). The stabilization/solidification technology may be applied for oily-sludge incineration byproducts such as sludge ash and fly ash to prevent heavy metals from leaching (Karamalidis and Voudrias, 2008; Hu et al., 2013). Removal of heavy metal from oily sludge using ion-exchange textiles (Elektorowicz and Muslat, 2008); removal of metals from the residual fuel oil and residuum fractions using centrifugation, solvent extraction, and contacting the material with various chemicals and chelating agents (Abbas et al., 2010); extraction of metals from fly ash by different solvents such as ammonium nitrate, ethylenediaminetetraacetic acid, sodium acetate, ammonium oxalate, and NaCl (Al-Ghouti et al., 2011); and leaching extraction of oily-sludge fly ash by sulphoric acid solution and then vanadium recovery from leaching solution using emulsion liquid membrane (ELM) (Nabavinia et al., 2012) have been reported in the literature.

Elektorowicz and Muslat (2008) pretreated bottom-tank oily sludge from the Shell Canada refinery in Montreal, Canada with an organic solvent (acetone) and then applied ion-exchange textiles to remove heavy metals. Total removal of vanadium was reported while the removal of cadmium, zinc, nickel, iron, and copper was 99%, 96%, 94%, 92%, and 89%, respectively.

According to Abbas et al. (2010), the water-soluble salts of sodium, calcium, iron, zinc, aluminum, and chromium was reduced substantially by the centrifugal method, whereas the oil-soluble compounds of heavy metals (vanadium and nickel) were not affected; the sodium/vanadium mass ratio decreased from about 0.5 to about 0.1. The extraction method using polar solvent (e.g., ethyl acetate) was very effective for the removal of oil-soluble metals from heavy residual fractions. Chemical treatment using sulfuric acid presented the most promising results. Although sulfuric acid was reported to effectively remove sulfur and metals along with the resinous and asphaltic substances from petroleum, the formation of an emulsion is always a serious concern; when broken it yielded darkened oil and a lot of acid sludge. Chemical treatment was effective for the demetallization of heavy oils and residue. Maleic acid in dimethylformamide was reported to be the most effective reagent. Contact of heavy residual fractions with aqueous solutions of $FeCl_3$ and $SnCl_4$ (0.1−0.5 M range) in acidic solution was also found to be effective. Abbas et al. (2010) recommended solvent-extraction methods as a pretreatment step before traditional hydroprocessing methods of upgrading heavy oils.

Nabavinia et al. (2012) investigated the ELM method for vanadium recovery from oil-refinery sludge in two stages which included contact of fly ash of this sludge with a sulfuric-acid solution followed by purification and enrichment with the ELM technique. The results of this study revealed that more than 65% of vanadium in fly ash could be extracted in one stage of leaching by sulfuric acid, and under the optimum operating conditions of ELM method, more than 86% of vanadium could be extracted in 1 h at ambient temperature.

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