Zarook Shareefdeen *Editor*

Hazardous Waste Management

Advances in Chemical and Industrial Waste Treatment and Technologies

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Dedication to
My family and friends

Preface

The rapid advances in the discovery of new chemicals, modernization of treatment and disposal technologies, and stringent environmental regulations demand continuous updating of knowledge related to hazardous wastes. This book contributes toward covering recent advances in hazardous waste management methods and innovative treatment and disposal technologies while also presenting the fundamental materials of the subject. The chapters are carefully selected such that they can be covered in an elective course of an undergraduate or first-year graduate level in several disciplines, including chemical engineering, environmental engineering, civil engineering, environmental science, and environmental management. This book will also be a valuable resource to industrial professionals and environmental regulators who work in the area of hazardous waste management.

Chapter 1 gives an overview of hazardous waste management and control. In this chapter, the definition of hazardous wastes, major environmental laws, incidents due to mismanagement of hazardous wastes, and liability issues resulting from mishandling of hazardous wastes are covered. Moreover, hazardous waste symbols, listed wastes, past contaminated sites, hazardous waste identification methods, and hazardous waste management and treatment methods are summarized. Chapter 2 provides a detailed analysis of 15 hazardous waste accidents that have taken place worldwide over the last few decades. From this chapter, students will learn that human error, improper disposal practices, faults in safety equipment, runaway reactions, failure to follow safety procedures, etc. cause tragic consequences including loss of life, environmental damage, and financial liabilities. Chapter 3 covers conventional and emerging practices in hazardous waste management. The sources, classification, characteristics of hazardous waste, health and environmental impacts of hazardous waste, hazardous waste minimization strategies, recent advances, and emerging scientific methods are discussed in detail. Chapter 4 presents the importance of pollution prevention, waste management hierarchy, and pollution prevention methods including source reduction, reuse, recycling, and equipment modification. This chapter also covers environmental regulations related to pollution prevention and discusses several industrial case studies that emphasize the benefits of pollution prevention. Chapter 5 covers the definition of medical waste, medical waste constituents, medical waste regulations, and conventional and advanced methods used in medical waste management and control. The medical waste treatment methods, including autoclaving, chemical disinfection, microwave disinfection, plasma gasification, and pyrolysis are discussed in detail. Furthermore, medical waste management and control during COVID-19 pandemic are examined through recent case studies. Chapter 6 covers advances in waste collection, storage, transportation, and disposal techniques. In this chapter, different storage systems, inventory management methods, transport vehicles used in waste disposal, transport modeling and risk analysis, and type of waste incinerators including liquid injection, rotary kiln, fluidized bed, starved air, and multiple hearth incinerators are discussed. Chapter 7 covers advances in land, underground, and ocean disposal techniques. In this chapter, the site selection and design of landfills, deep-well injection systems, underground geologic repositories, and limitations of ocean disposal methods are discussed. Chapter 8 presents waste-to-energy (WtE) technologies. In this chapter, the three main WtE processes (incineration, gasification, and pyrolysis) are reviewed along with design conditions and different reactor configurations used in WtE plants. Chapter 9 covers gaseous and solid waste management in WtE plants, which generate unwanted by-products including dioxins, furans, ash, slag, and other volatile and nonvolatile compounds. This chapter reviews air pollution control (APC) methods used in the elimination of solid particles, acid gases, NOx gases, and volatile organic compounds (VOCs). The chapter also presents methods used in producing useful products from the unwanted by-products generated within the WtE processes. Chapter 10 covers classical and advanced technologies used in the treatment of hazardous wastes. The technologies that are coved in this chapter include adsorption, absorption, filtration, Fenton treatment, ozone treatment, membrane technology, plasma treatment, and accelerated carbon technology. Chapter 11 presents hazardous waste transport in the three main mediums: air, subsurface, and water. This chapter covers a number of case studies including the transport of pollutants from incineration, oil spills, cyanide release, wastewater discharge, and illegal dumping of wastes. The chapter also highlights how mathematical modeling and software could deliver effective warning systems on the spread of toxic contaminants. Chapter 12 covers Internet of Things (IoT) applications in the field of waste collection, waste sorting, and wastewater. This chapter summarizes how the sensors and connectivity of IoT are implemented to tackle waste-related issues by introducing the digital world to city infrastructure that can revolutionize the waste management methodology. Chapter 13 presents types of hazardous petroleum waste and an overview of the major waste management and control applications using physical, chemical, and biotechnological methods in the petroleum industry. This chapter highlights that innovative biological treatment technologies, in addition to traditional physical and chemical methods have become important in providing new strategies and approaches to waste treatment in the petroleum industry.

Sharjah, United Arab Emirates Zarook Shareefdeen

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About the Editor

Zarook Shareefdeen is a professor of chemical engineering at the American University of Sharjah (AUS) and the United Arab Emirates. He is a registered professional engineer in Ontario, Canada, and received his Ph.D. in chemical engineering from the New Jersey Institute of Technology (NJIT), USA. He has also worked as a visiting professor at the University of Waterloo, ON, Canada (2014, 2021); director of research at Biorem Technologies Inc. (2000–2006), ON, Canada; research fellow at the University of California (1999), USA; assistant professor at the King Fahd University of Petroleum and Minerals (KFUPM) (1994–1999), Saudi Arabia; and postdoc at NJIT (1994). He has been teaching hazardous waste management and air pollution control for over 15 years at the AUS. Professor Shareefdeen has written several book chapters, published many peer-reviewed journal and conference papers, coedited the book Biotechnology for Odor and Air Pollution Control (Springer, 2005), and has two several patents in the United States related to industrial air pollution control. His research and teaching interests include hazardous waste management, medical waste management, waste-to-energy technologies, air pollution control, biofiltration, and bioreactor modeling.

Chapter 1
Introduction to Hazardous Waste Management and Control

Zarook Shareefdeen and Ali Elkamel

1.1 Introduction

Hazardous waste, also known as "industrial waste" or "chemical waste," is harmful to human health and the environment. Hazardous wastes are generated as a result of manufacturing activities; however general public only sees the benefits of manufactured goods but not the hazardous wastes which are generated as a result of the manufacturing process. Public perceptions on hazardous wastes can be easily influenced by nontechnical factors such as social media, news media, movies, etc. In general, opinions from environmental experts are different because of their knowledge on the nature of the chemical constituents forming the hazardous wastes, which are present at disposal and manufacturing sites.

It is important to realize that the treatment cost of hazardous waste is several folds higher than the treatment cost of municipal solid waste (MSW), which mainly consists of general throw away trash such as product packaging, grass clippings, furniture, clothing, bottles, food scraps, newspapers, appliances, etc. (Municipal Solid Waste n.d.). Industrial production will continue to expand in order to meet the demands of the population; hence the generation of hazardous wastes will continue to increase. Additionally, in order to meet the consumer demand on food, the agriculture industry will continue to manufacture different types of fertilizers, pesticides, and insecticides which are toxic to human beings as well as to the environment.

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In addition to health and the environmental-related damage, mishandling of hazardous wastes can also cause severe liabilities and a loss of millions of dollars to the industry; therefore, engineers must show responsibility and ethics in dealing with hazardous waste, in terms of adequate management and treatment activities. Engineers, environmental professionals, and regulators must understand the legal definitions of hazardous waste, in order to design and manage treatment and disposal systems, to demonstrate the efficiency of the treatment systems, and to identify potential violations in case of hazardous waste releases into the environment.

1.2 Hazardous Waste

A hazardous waste is any waste with a chemical composition or other properties that can cause illness, death, or some other harm to humans and other life forms, when mismanaged or released into the environment. The US Environmental Protection Agency (US EPA) has established hazardous waste identification regulations that outline a process to determine whether any particular material is a hazardous waste or not (Hazardous Waste Identification (40 CFR Parts 261) n.d.).

Hazardous waste can be in any forms such as solids (i.e., contaminated soil), sludge (i.e., activated sludge from a biological reactor), liquids (i.e., solvent residues from the containers), and containerized gases (i.e., a propane gas cylinder). Hazardous waste can have one or more of these characteristics: flammable, reactive, explosive, corrosive, radioactive, infectious, irritating, or bioaccumulative. Radioactive and infectious wastes are not commonly generated within industrial wastes; therefore, the management, treatment systems, and regulatory methods are different for these two types of wastes (LaGrega et al. 2001).

1.2.1 Definitions

The Resource Conservation and Recovery Act (RCRA) has created a foundation for the proper management of hazardous waste (Resource Conservation and Recovery Act n.d.). According to RCRA definition, the hazardous waste has one or more of these characteristics: toxicity, reactivity, ignitability, or corrosivity (TRIC). Toxic wastes such as arsenic, cadmium, etc. are very harmful. Reactive wastes are normally unstable and can react violently with air or water or form explosive mixtures with water. The reactive wastes also include wastes that emit toxic fumes, when mixed with water and materials capable of detonation. The ignitable wastes are liquids, with a flash point below 60 °C, or solids capable of causing fire under standard temperature and pressure. The flash point is the lowest temperature at which it can vaporize to form an ignitable mixture in the air. Corrosive wastes are aqueous wastes with a pH ≤ 2 or ≥ 12.5 or the wastes that corrode steel at a rate in excess of

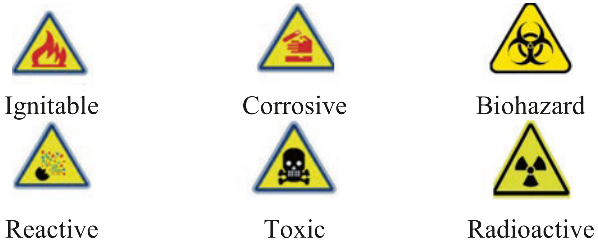

Fig. 1.1 Hazardous waste symbols

0.25 in per year. The symbols used to identify hazardous waste characteristics are shown in Fig. 1.1.

Different physical and chemical tests are required to identify waste characteristics, discussed above, so that the suitable treatment and disposal guidelines can be selected. Physical state of the sample (i.e., aqueous, solid, volatile, sludge, multiphase), sample types (i.e., organic, inorganic, metals, ion), analytical sensitivity of the measurements needed, purpose of testing, sampling duration time, volume of the sample collected, type of sample containers used, etc. are some of the basic information required for testing and analysis. In a recent study, Shukla et al. (2020) reviewed and summarized EPA testing methods.

In the United States, according to RCRA, a mixture made up of a hazardous waste mixed with a nonhazardous waste becomes a hazardous waste by definition. However, hazardous waste mixing rules differ from country to country; for example, in France, a special authorization is required before mixing the hazardous waste, while in the Netherlands, mixing is forbidden (LaGrega et al. 2001). According to RCRA, any substance derived from hazardous waste (i.e., from a treatment, disposal, etc. of a listed wastes) is also a hazardous waste. The derived-from wastes are materials that are produced by treating or changing a hazardous waste. For example, if you have a hazardous waste and you send it to a burner, the resulting ash material is considered as a waste derived from the initial waste; thus ash material in this case becomes a hazardous waste.

1.2.2 *Listed Wastes*

US EPA has prepared hazardous waste listings which categorize wastes from different industrial processes, wastes from specific sectors of industry, or wastes in the form of specific chemical formulations. Before developing a hazardous waste listing, EPA carefully examines particular waste streams that can pose threat to human health and the environment. If the waste poses enough of a threat, EPA includes that waste in one of the lists. Thereafter, any unknown waste fitting the description is considered to be a hazardous waste, regardless of its chemical composition (Hazardous Waste Identification, 40 CFR Parts 261).

Based on the characteristics of hazardous wastes, US EPA has compiled four main lists (F, K, U, and P). These lists include all types of wastes commonly found in industries. The list allows one to easily determine whether the waste is hazardous or not hazardous. Thus, these lists can be used to avoid costly analytical testing, needed to identify hazardous waste characteristics. The F list includes chemical wastes (i.e., spent solvent wastes, wastes from production of certain chlorinated aliphatic hydrocarbons, wastes from wood preserving, etc.) from nonspecific industries; K list includes wastes from specific industries (i.e., pesticides manufacturing,); P list includes acutely toxic, unused, or discarded chemicals (i.e., arsenic acid, calcium cyanide, etc.); and U list includes unused or discarded chemicals (i.e., methylene chloride, vinyl chloride) that are acutely toxic and have one or more of the four hazardous waste characteristics (TRIC, toxicity, reactivity, ignitability, and corrosivity). To indicate its reason for listing a waste, EPA also assigned a hazard code to each waste listed on the F, K, P, and U lists. Hazard codes are given in Table 1.1.

The seven categories of F-listed wastes are as follows: spent solvent wastes (F001–F005), wastes from electroplating and other metal finishing operations (F006–F012, F019), dioxin-bearing wastes (F020–F023 and F026–F028), wastes from the production of certain chlorinated aliphatic hydrocarbons (F024, F025), wastes from wood preserving (F032, F034, and F035), petroleum refinery wastewater treatment sludges (F037 and F038), and multisource leachate (F039). The 13 industries that can generate K list wastes are as follows: wood preservation, inorganic pigment manufacturing, organic chemical manufacturing, inorganic chemical manufacturing, pesticide manufacturing, explosives manufacturing, petroleum refining, iron and steel production, primary aluminum production, secondary lead processing, veterinary pharmaceuticals manufacturing, ink formulation, and coking activities (processing of coal to produce coke, a material used in iron and steel production) (Hazardous Waste Identification, 40 CFR Parts 261). EPA uses the P and U lists to label hazardous wastes consisting of highly concentrated forms of known toxic chemicals. P and U listings apply only to a very narrow group of wastes. For example, an unused pesticide containing pure toxaphene is a listed waste (P123) when discarded (Hazardous Waste Identification (40 CFR Parts 261) n.d.). Table 1.2 shows examples of the listed wastes (Defining Hazardous Waste 2021).

Table 1.1 Hazardous codes (Hazardous Waste Identification (40 CFR Parts 261) n.d.)

Type of waste	Code
Toxic waste	(T)
Acute hazardous waste	(H)
Ignitable waste	(I)
Corrosive waste	(C)
Reactive waste	(R)
Toxicity characteristic waste	(E)

Table 1.2 Listed wastes (Defining Hazardous Waste, 2021)

F001	The spent halogenated solvents used in degreasing: tetrachloroethylene, trichloroethylene, methylene chloride, 1,1,1-trichloroethane, carbon tetrachloride, and chlorinated fluorocarbons
F010	Quenching bath residues from oil baths from metal heat treating operations where cyanides are used in the process
K005	Wastewater treatment sludge from the production of chrome green pigments
K035	Wastewater treatment sludges generated in the production of creosote
P005	Allyl alcohol
P068	Methyl hydrazine
U081	2,4-Dichlorophenol
U227	1,1,2-Trichloroethane
U227	1,1,2-Trichloroethane

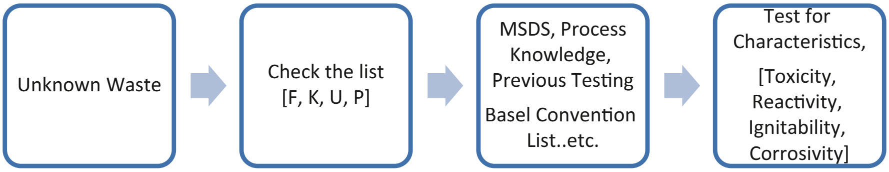

Fig. 1.2 Hazardous waste identification steps for an unknown waste

1.2.3 *Hazardous Waste Identification*

Waste can be identified as hazardous or nonhazardous by means other than testing its characteristics. For example, Material Safety Data Sheet (MSDS) gives a lot of information about a chemical (MSDS for Ethylbenzene n.d.). The information in an MSDS includes physical and chemical properties, fire and explosion hazard data, reactivity hazard data, health hazard data, control and protective measures, spill or leak procedures, and hazardous material identification data (Defining Hazardous Waste 2021). As explained above, a waste derived from any hazardous compound is also a hazardous waste. Therefore, the chemical nature, the previous waste testing reports, and the process knowledge on how the waste is produced also help in determining whether the waste is hazardous or nonhazardous. The Basel Convention hazardous waste list is adopted by 116 countries of the UN Environment Program (UNEP) (discussed further in Sect. 1.3). This hazardous waste list is also a useful source in hazardous waste identification. The steps in determining whether a waste is hazardous or nonhazardous is illustrated in Fig. 1.2.

1.2.4 Hazardous Waste Generators

Hazardous wastes can originate from industrial, agricultural, commercial, and household activities. Industrial activities and operations result in the generation of hazardous wastes including undesired by-products, sludge from treatment process (i.e., industrial wastewater treatment sludge, spent activated carbon after the treatment, etc.), residues from containers, accidental spills, liquids resulted from cleanup of process equipment, chemicals that do not meet specifications, chemicals that have outdated shelf life, etc. Depending on the nature of the industries, the quantity and composition of hazardous wastes significantly can differ from place to place within the same country and also from country to country. Hazardous waste generators either manage the wastes on-site or off-site, by transporting it to a commercial waste treatment facility. Most of the hazardous wastes generated are in aqueous form, which is consequently released into the sewer or water bodies after treatment.

In addition to major industries, there are many service industries such as dry cleaners, automobile maintenance shops, analytical laboratories, photographic film processors, etc. that also generate hazardous wastes. According to the US environmental laws, the requirements are different for small quantity generators (i.e., those that generate more than 100 kg but less than 1000 kilograms of hazardous waste/month). Common households also generate hazardous wastes that include cleaners, automotive products, paint products, fertilizers, and pesticides. US federal law specifically exempts household hazardous waste from regulations; however local and state governments have programs to educate the public about the management and disposal of household hazardous wastes.

Healthcare industries and hospitals also generate medical or biohazardous wastes, which are wastes that contain an infectious substance and are generated from the diagnosis, treatment, or immunization of human beings or animals. Examples of medical wastes include soiled or blood-soaked bandages, discarded surgical gloves, removed body organs, and surgical instruments such as scalpels, needles used to give shots or draw blood, etc. One of the more common medical waste treatment techniques is incineration, which is basically a controlled burning process. Incineration process reduces the mass and volume of wastes significantly. However, many waste items present within the by-products of incineration may contain toxins such as mercury, dioxins, furans, etc.

1.2.5 Hazardous Waste Sites (Superfund Sites)

Many toxic chemicals such as dichlorodiphenyltrichloroethane (known as DDT), polychlorinated biphenyls (PCBs), dioxin, trichloroethylene (TCE), etc. were found in contaminated sites as a result of past practices. These hazardous waste disposal incidents and their toxic effects are well known, and they include exposure of dioxin at Love Canal, Niagara Falls, New York (LaGrega et al. 2001), hexavalent chromium (Hinkley Groundwater Contamination), perfluorooctanoic acid, PFOA (DuPont C8 Lawsuit), etc.

Many of the hazardous waste incidents of the past are well documented through news media. For example, in the book of Silent Spring, Carson et al. (1962) documented the detrimental effects of pesticide DDT on the environment and health. DDT has been found to cause reproductive problems and death. Carson et al. (1962) accused the chemical industry of spreading disinformation, as well as the public officials, who accepted industry claims uncritically. Similarly, the "Erin Brockovich" movie of 2000 dramatized the true story of legal clerk Erin Brockovich, who fought against the energy corporation Pacific Gas and Electric Company (PG&E) regarding its liability for the Hinkley groundwater contamination incident with hexavalent chromium. Hexavalent chromium compounds are associated with many diseases including lung cancer, respiratory tract irritation, nose bleeds, etc. Furthermore, the 2019 movie called "Dark Waters" dramatized Robert Bilott's case against the chemical manufacturing corporation DuPont which contaminated a town with unregulated chemicals, namely, perfluorooctanoic acid (PFOA) (Dark Waters, 2021). The details of these incidents as well as other incidents from the past to the present are covered in a separate chapter. A large amount of money, in billions of dollars, had to be spent in order to remediate the contaminated sites which resulted from past malpractices and to compensate the people who suffered from diseases such as fertility problems, neurological disorders, cancer, etc. or even fatality as a consequence. Liability is a major driving force of the regulatory control system in the United States; however this is not the case in most of the developed countries (LaGrega et al. 2001). Hazardous chemicals are persistent (i.e., difficult to biodegrade with long half-life) and dangerous; thus, contaminated sites due to past malpractices pose serious threats to the human lives and the environment.

The hazardous waste sites due to past malpractices in the United States, referred to as "National Priorities List (NPL)" or "Superfund Sites," receive funds for remedial investigation and site cleanup under the federal Superfund program, which is funded through tax money received from petroleum, chemical, and environmental industries. The Environmental Protection Agency (EPA) can also compel the responsible party (i.e., generators of the hazardous waste) to fund their own remediation and site cleanup activities. EPA has a formal process for evaluating hazardous waste sites before placement in the NPL. As of June 12, 2019, there were 1344 Superfund sites on the NPL in the United States (NPL sites n.d.). From the NPL sites, one can acquire information about remediation activities and the treatment methods used for cleanup of hazardous contaminants from the sites. Table 1.3. shows a sample description of a recent NPL site in the state of New Jersey, USA.

Table 1.3 Description of a recent NPL site (Pioneer 2021)

Site location	The Pioneer Metal Finishing Inc. (Pioneer) Franklinville, Gloucester County, New Jersey
History	Pioneer began operation as an electroplating facility in 1955 and discharged untreated waste from the facility. Wastes reportedly consisted of metallic salts, untreated process sludge, rinse water, cleaning solutions, and plating wastes. Electroplating activities were ceased in around 2005, and the facility is currently used for powder coating operations
Site contaminants	Sampling indicates that the soil adjacent to the Pioneer facility is contaminated with chromium, copper, and nickel above risk levels. Soil is also contaminated with polychlorinated biphenyls (PCBs)
Potential impacts	Two employees were exposed to the contaminated soil at the facility. The contamination threatened Timothy Lake, which is approximately 1 mile downstream of the site and is utilized for swimming, boating, and fishing
Response activities	In July 2018, the New Jersey Department of Environmental Protection (NJDEP) asked the EPA for help. In response, the EPA collected samples for field characterization which indicated that flammables, acids, and corrosive materials were present within the facility. Between August 2018 and August 2019, the EPA removed over 100 tons of hazardous waste from the facility, which included approximately 20,000 gallons of liquid waste
Need for NPL listing	The state of New Jersey referred the site to the EPA because both the soil and sediment were contaminated with metals, which require cleanup to protect human health and the environment. The EPA received a letter of support from the state for placing the site on NPL

1.2.6 Toxicology

Management and control of hazardous wastes requires an understanding of toxicology, which is a study that deals with the undesirable effects caused by the exposure of living beings to toxic chemical substances. The effect of toxic substances on natural systems (i.e., plants, organisms, etc.) is termed as ecotoxicology, which is a scientific discipline that extends the principles of toxicology to natural systems (LaGrega et al. 2001). Toxicology is largely supported by the toxicity data obtained from experiments with laboratory animals (i.e., mice, fish, birds). When the data from experiments on animals is extrapolated to humans, the data can carry a considerable degree of uncertainty.

Normal physiological functions of our human body are affected by the exposure to chemicals at various degrees, concentration levels, duration time, etc. The exposure level should be maintained below the “threshold limit level (TLV),” which is defined as the amount of intake at which no harmful effects on the human body are observed. The threshold levels are represented by various terms such as no observed adverse effect level (NOAEL), acceptable daily intakes (ADI), reference doses (RfD), etc. A number of databases for TLVs, RfDs, ADIs, and other toxicological data for both noncarcinogenic and carcinogenic substances have been established (LaGrega et al. 2001; IRIS n.d.). The toxic dose or lethal dose (LD50) of a chemical is expressed as milligrams of a pollutant exposed per kilogram of body weight; thus

LD50 represents dose at which only 50 percent of the organisms (i.e., number of mice used in the experiment) remained alive. The equivalent for inhaled pollutants, i.e., the median lethal concentration (LC50), is used, and it represents the concentration at which 50 percent of the organisms used remained alive.

Toxic pollutants can enter the human body mainly through three exposure routes which are ingestion (gastrointestinal tract), dermal contact (skin), and inhalation (respiratory tract). Most toxic substances, except for corrosive materials, nerve agents, etc., do not cause harmful effects at the point of entry. In order for the harmful effects to take place, the chemical agent or its biotransformation products must reach the critical site in a target organ (i.e., kidney, liver, etc.) at a sufficiently high concentration and for a sufficient length of time. Although the amount of pollutant entering a human body through any of the three routes may be high, the amount of the toxic material absorbed and reaching the target organ, termed as effective dose, is a major factor. In addition to the amount of pollutant exposed, exposure period is also important. Depending on the duration of exposure, exposure periods on human body are categorized as acute (1 day), subacute (10 days), sub-chronic (2 weeks-7 years), and chronic (7 years-lifetime). If the human body cannot deactivate or eliminate the toxicants received for a prolonged period during a chronic exposure, the toxic materials can accumulate and cause serious diseases such as cancer, liver failure, kidney damage, etc. Based on the exposure routes, frequency and duration of exposure, and intake and reference dose levels, assessment can be performed to identify factors that have the potential to cause risk or harm and subsequently eliminate and control the hazards (LaGrega et al. 2001).

1.2.7 Environmental Chemistry

Since most of the hazardous wastes are organic, it is important to know the chemistry of hazardous compounds. Organic chemicals can be divided into three basic groups related to volatility: volatile organics, semi-volatile organics, and nonvolatile organics. Volatile organic compounds (VOCs) have a high vapor pressure. In general, VOCs are relatively low molecular weight compounds. Examples of VOC include acetone, benzene, toluene, and phenol. Highly volatile VOCs can be measured using purge and trap technique. At first, an inert gas, such as helium, is bubbled through an aqueous sample containing VOCs, followed by trapping using an adsorbent. The adsorbed VOC is later analyzed using an instrument, such as gas chromatography (GC). Semi-volatile and nonvolatile organics can be analyzed using solvent extraction technique, in which the aqueous sample is first acidified and then the sample is extracted using a compound such as phenol. Subsequently, extracted sample is analyzed using an appropriate instrument.

Hazardous organic pesticides and herbicides are chemicals which are used to control the spread of insects, rodents, parasites, and undesirable plants or herbs. Organic pesticides are grouped as chlorinated and organophosphate pesticides. Chlorinated pesticides such as DDT have harmful effects as they do not readily degrade in nature and tend to accumulate in the fatty tissues. Organophosphate pesticides such as parathion are toxic to both humans and animals. Organic herbicides inhibit photosynthesis and disrupt other phytochemical activities of plants. Inorganic pesticides and herbicides include toxic compounds such as zinc, copper, arsenic, mercury, sulfuric acid, sodium arsenate, sodium thiocyanate, etc., and they are persistent in soil and highly toxic. Over time, organisms become resistant to organic pesticides and herbicides; thus the use of inorganic pesticides and herbicides may become necessary. Another type of hazardous organic compounds is polychlorinated biphenyls (PCBs), and it has a widespread use in electrical transformers and capacitors. EPA has banned the manufacture, processing, and distribution of PCBs due to their high toxicity level. A thorough knowledge on the toxicity levels, physical-chemical properties, and chemistry of hazardous compounds will help in selecting adequate remediation and treatment technologies (LaGrega et al. 2001).

1.2.8 Physical–Chemical Properties of Hazardous Wastes

Physical-chemical properties of the hazardous chemicals determine how pollutants are transported within the phase or between phases in the environment and also how effectively they can be removed. For example, the solubility, which is a function of temperature and the particular chemical species, determines how the pollutant is distributed between phases (i.e., air/water phase) and how the pollutant can be separated by changing the pH, etc. For instance, the solubility product constant, concentration of the hazardous substances in aqueous systems, and pH levels help in the determination of the concentration of toxic metals that precipitate.

Air-water partition of a pollutant is represented by Raoul's law, which states that the partial vapor pressure is directly proportional to the mole fraction of the pollutant in water. For a pollutant which has a very low solubility, the partition between air and water phases is represented by Henry's law. Henry's law constant, which is the ratio of partial pressure to the concentration of the pollutant, is used to determine the pollutant distribution for dilute systems.

Other important partition coefficients represent partitions between soil/water, organic carbon portion of the soil/water, and octanol-water partition. In the determination of octanol-water partition coefficient, the organic solvent octanol is used as a substitute for natural organic matter present in the soil. This parameter is used in many environmental studies to help determine the distribution and the fate of chemicals in the environment. Another important partition coefficient which is usually used in risk assessments is the bio-concentration factor, which represents the tendency of a pollutant to be absorbed by aquatic organisms. Diffusion coefficients and adsorption parameters also play an important role in the movement of pollutants in the air, water, and subsurface environment.

1.2.9 Fate and Transport of Hazardous Wastes

For successful management of hazardous waste, it is important to understand the fate and transport of contaminants in the environment. In general, the release of contaminants from industries is managed or controlled to ensure that the concentration levels are below the TLV levels. These contaminants can be in any form including air emissions (i.e., VOCs emission from a storage tank), liquid wastes (i.e., pollutant levels in the treated wastewater effluent), and solid wastes (i.e., contaminated soil with PCBs). However, uncontrolled releases also occur due to incidents such as pipeline breakdown, industrial accidents, etc. Whether it is a controlled or an uncontrolled release, the pollutants that are transported to the receptor points (i.e., humans, plants, birds, environment, etc.) in their original or altered form need to be monitored and managed.

Processes in the Subsurface

Movement of the pollutants in the subsurface, i.e., below the surface of the soil, is slowdown or retarded due to processes such as sorption, ion exchange, precipitation, and filtration. Sorption of pollutants onto soil surfaces occurs due to hydrogen bonding (chemical), van der Waals forces (physical), and coulombic attractive forces (electrostatic). Sorption is reversible; however desorption of pollutants from the soil may take a very long time for pollutants, such as PCBs to desorb. Because of the affinity to the natural organic portion of the soil, organic compounds such as PCBs are attached to the soil, which contains a high fraction of organic content. The organic portion of the soil comes from decayed materials such as plants, animals, etc. Thus, the organic content decreases with respect to the soil depth. Furthermore, as the particle size of the soil decreases, adsorption increases due to an increase in the adsorption surface area. The concentration of contaminants is linked to the amount of contaminants adsorbed per mass of soil or any other adsorbent material such as carbon, zeolite, etc. Such relations are termed adsorption isotherms which can be linear or nonlinear such as Freundlich or Langmuir isotherms. The soil has a capacity to exchange cations. For example, sodium ions in the clay can replace calcium ions present in the water. Ion exchange also plays a role in slowing down the movement of pollutants in the water. Furthermore, precipitation process, which is the opposite of dissolution, retards the movement of pollutants in the water. Toxic heavy metals such as nickel, mercury, chromium, and lead can be easily precipitated, at high pH levels, as hydroxides. Filtration is also considered a retardation process, as it traps the movement of the pollutant in the pore spaces (LaGrega et al. 2001).

The processes that increase the movement of pollutants include co-solvation, ionization, dissolution, and complexation. By introducing large quantities of an organic solvent to the polluted area of the subsurface, the pollutant movement can be enhanced. When a pollutant is subject to simple ionization, its mobility can be enhanced; for example, hexavalent selenium is more mobile than trivalent selenium. Complexation occurs by tying up free metallic ions, and this process is shown to enhance the movement of the pollutants in the subsurface. Pollutants can be transformed in the subsurface through various reactions including chemical oxidation and reduction reactions, biological oxidation, hydrolysis, etc. Hexavalent chromium is toxic; however by reducing it to trivalent chromium, it can be easily precipitated; thus its movement in the subsurface can be controlled (LaGrega et al. 2001).

Transport in the Subsurface

The pollutants that are released in liquid form can be leached into the subsurface environment and can be transported due to the movement of water. Water movement in the subsurface environment occurs due to the difference in the hydraulic heads (or pressure difference measured in water levels), which is described by the Darcy law. Darcy law relates the flow rate to the pressure gradient, the cross-sectional area, and the hydraulic conductivity or permeability of the subsurface soil material. Additionally, Darcy law aids in the calculation of pollutant movement in the subsurface. For example, a contaminant travel time is given by the distance traveled by a pollutant over seepage velocity, which is the ratio of Darcy velocity to porosity of the soil. The permeability of the soil varies depending on the type of soil constituents (i.e., clay, very low; gravel, very high). For instance, the pollutants can take a longer time to reach the receptor points if the permeability of the soil is very low. In an unsaturated region of the soil, pollutants also disperse or spread into the soil through diffusion process, due to the difference in concentration levels (LaGrega et al. 2001).

Transport in the Air

Pollutants released into the air are transported by the wind and dispersed. Transport and dispersion of the pollutants in the air depend on many variables including the stability of the atmosphere, wind direction, wind magnitude, surrounding buildings, landscape, type of sources (i.e., point, line, area, volume, puff sources), and contaminants. It is important to assess the quantity and concentration levels of air emission releases especially from hazardous waste sites, lagoons, industrial sources, etc. Air quality models are used to evaluate the impact of releases of air contaminants from hazardous waste sites and are used to provide valuable information in design, risk analysis, decision-making, etc. (LaGrega et al. 2001). The models allow us to predict the concentrations that would result from any specified set of pollutant emissions, for any specified meteorological conditions, at any location, for any time period, with total confidence in our prediction. For instance, by using the models, one can estimate how much must emissions from an existing power plant need to be reduced, so that the emission levels are within the regulatory limits. However, the models are based on several assumptions, and hence, they represent simplifications to reality (de Nevers 2000).

The US EPA has developed a number of air quality predictive models, and they can be downloaded from the EPA website (Air Quality Models 2021). Air quality models are widely used by agencies to identify sources that contribute to air quality issues, as well as to assist in the design of effective strategies to reduce harmful air pollutant generation. The computer models, such as SCREEN3, ISCST3, etc., developed by US EPA were used widely in the assessment of many types of contaminant releases. For example, Azlah et al. (2018) used the CALPUFF model to predict pollutant concentrations and dispersion under various atmospheric conditions, and they investigated the influence of wind directions, plume paths, and removal efficiency of a full-scale biofilter which was used to treat emissions from a meat rendering plant located in Ontario, Canada.

US EPA in its Guideline on Air Quality Models recommends CALPUFF as the preferred model for assessing long-range transport of pollutants and their impacts (LaGrega et al. 2001). The American Meteorological Society and US EPA introduced another important model AERMOD which incorporates air dispersion based on planetary boundary layer turbulence. This model is also used widely and can be applied to surface and elevated sources (i.e., stack emissions), regardless of the types of terrains (Air Quality Models 2021).

1.3 Hazardous Waste Regulations

1.3.1 Resource Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

Due to improper waste disposal practices of the past, severe health and environmental problems arose, as described in Sect. 1.2.5. Hence, the establishment of regulations on hazardous wastes became necessary. The US Congress endorsed two major laws known as Resource Conservation and Recovery Act (RCRA), in 1976, to manage the currently generated hazardous waste, and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) in 1980, to manage and remediate contaminated sites that resulted from past malpractices.

RCRA facilitated the management process for the entities performing the following activities: waste treatment and disposal facilities, waste recovery and recycling, and waste transportation from the point of generation to final disposal sites. CERCLA, also known as the Superfund Act, facilitated the identification of hazardous waste-contaminated sites, as well as the implementation of remedial activities (i.e., site cleanup). Although RCRA and CERCLA greatly influence the waste management and control practices in the United States, it is important to note that these regulatory systems do not describe the concentration, physical and chemical characteristics, and the suitable treatment methods (LaGrega et al. 2001). However, without this information, it is impossible to evaluate the treatability of the waste, or its potential for recycling. In addition, alternative classification systems, such as engineering classification, exist. The engineering classification systems include the phases of wastes (i.e., gas, liquid, solid, mixed, aqueous, etc.), type of wastes (organic and inorganic wastes, metals, etc.), and constituents of hazardous wastes.

1.3.2 Hazardous and Solid Waste Amendments (HSWA)

RCRA was revised in 1984, and the revised version is known as Hazardous and Solid Waste Amendments (HSWA), which prohibits the disposal of non-containerized liquid hazardous waste into landfills. Furthermore, HSWA prohibits the transportation of hazardous waste without obtaining proper documentation and permit. The documentation must include the details on the hazardous waste generator, transporter, and receiver, as well as details regarding the type of waste, quantity of wastes, etc.

1.3.3 Superfund Amendment Reauthorization Act (SARA)

In December of 1984, one of the world's worst industrial disasters occurred in Bhopal, India. The disaster was attributed to inadequate maintenance by a US company known as Union Carbide and poor monitoring by the Indian authorities. The malfunctioning of safety devices, the location of the plant, and the toxic nature of the emitted gas (i.e., "methyl isocyanate, MIC") worsened the effects of the accident and ended the lives of more than five thousand people. More than 250,000 people were exposed to MIC and about 65,000 people suffered from severe diseases. The Bhopal disaster also raised questions about the implications of the transfer of potentially hazardous technology to the developing countries (LaGrega et al. 2001; Varma and Varma 2005). At that time, the US EPA was severely criticized because it had not listed MIC as one of the hazardous pollutants. This tragic accident that happened in Bhopal led the US Congress to revise CERCLA. Thus, CERCLA was revised in 1986, and this revised law is currently known as Superfund Amendment Reauthorization Act (SARA).

1.3.4 Emergency Planning and Community Right-to-Know Act (EPCRA)

One of the main outcomes of the revision to CERCLA is the Emergency Planning and Community Right-to-Know Act (EPCRA) which requires industry, local, state, and federal governments to plan for emergencies. Furthermore, it provides the right to the community to know about the chemicals stored in industrial facilities, their use, and releases to the environment. The Community Right-to-Know provision of EPCRA increased the public's awareness as a result of the access to information. By working with industrial facilities, people can use the information to improve chemical safety, to avoid accidents, and to protect the public health and the environment (EPCRA 2021).

1.3.5 Other Environmental Regulations Related to Hazardous Wastes

While RCRA and Superfund Act are the major US laws dealing with hazardous wastes, several other environmental laws have applications to hazardous waste management. Some of the most important laws are discussed below (Laws and Regulations n.d.).

Toxic Substances Control Act (TSCA)

US Congress passed the Toxic Substances Control Act (TSCA) in late 1976, and it addresses the production, import, use, and disposal of specific hazardous chemicals, such as hexavalent chromium used as a water treatment chemical, dibenzo-para-dioxins and dibenzofurans, and polychlorinated biphenyl (PCBs) used as a transformer fluid, lead-based paint in residential structures, asbestos in schools, etc. TSCA requires an industrial facility to keep records on the quantities of the chemicals it imports, manufactures, and uses (Laws and Regulations n.d.).

Occupational Safety and Health Act (OSHA)

The Occupational Safety and Health Act (OSHA) of 1970 addresses health and safety-related issues in a workplace. Its main aim is to ensure that employers provide their workers with an environment free from dangers to ensure their safety and health. It discusses regulatory measures regarding the exposure to toxic chemicals, excessive noise levels, mechanical dangers, heat or cold stress, or unsanitary conditions (OSHA n.d.). OSHA gives workers the right to safe and healthy working conditions. It is the duty of employers to ensure that the workplaces are free of any dangers that could harm their employees. OSHA also gives workers the right to participate in activities and to ensure their protection from job hazards. These rights include the following:

- File a complaint with OSHA to have their workplace inspected
- Receive information and training about the OSHA standards that apply to the workplace, workplace hazards, methods to prevent harm, etc

- Review the records of work-related injuries and illnesses that may occur in their workplace
- Receive copies of the results from tests and monitoring done to assess hazards
- Get copies of the workplace medical records
- Participate in OSHA inspections and speak, in private, with the inspectors.
- File a complaint with OSHA if they have been retaliated against or mistreated by their employer as the result of requesting an inspection
- File a complaint if punished or retaliated against for acting as a "whistle-blower," etc

According to OSHA regulations, employers also have the responsibility to provide a safe workplace for their employees. Employers must:

- Inform workers about hazards through training, labels, alarms, color-coded systems, chemical information sheets and other methods
- Train workers in a language they can understand
- Keep accurate records of work-related injuries and illnesses
- Perform tests in the workplace, such as air sampling tests, as per OSHA standards
- Provide hearing exams or other medical tests required by OSHA standards
- Post OSHA citations, injury, and illness data in a suitable place accessible to the workers
- Notify OSHA within 8 h of a workplace fatality or within 24 h of any work-related inpatient hospitalization, amputation, loss of an eye, etc.
- Refrain from retaliating against workers for using their rights under the law, including their right to report a work-related injury or illness

OSHA strives to make sure that every worker goes home unharmed and in good health, at the end of any working day (Workers' rights n.d.).

Clean Water Act

In the United States, the Clean Water Act (CWA) is established to regulate discharges of pollutants into the water bodies and to regulate water quality standards for surface waters (i.e., stream, river, lake, wetland, or ocean). The basis of the CWA enacted in 1948 was called the Federal Water Pollution Control Act (FWPCA). Later, the act was significantly reorganized and expanded in 1972. "Clean Water Act" became the common name with amendments done in 1972 (Laws & Regulations n.d.).

Under the CWA, US EPA employed pollution control programs such as setting wastewater standards for industry and developing national water quality criteria and recommendations for pollutants in surface waters. The CWA made it unlawful to discharge any pollutant into navigable waters. Industrial facilities, municipal facilities, and other facilities must obtain permits if their discharges go directly into surface waters. EPA established water quality criteria, which are based on specific pollutant levels that would make the water harmful if used for drinking, swimming, farming, fish farming, or recycling to industrial processes. The states have developed water quality standards based on the federal water quality criteria to maintain the existing activities of fishing, swimming, boating, etc. Similarly, ocean discharge regulations prohibit the release of pollutants into marine waters, whereas pretreatment standards limit pollutants discharge into publicly owned treatment works (POTWs), and dredge and fill standards regulate the discharges of dredge (excavation materials) into waters.

Safe Drinking Water Act

The Safe Drinking Water Act (SDWA) was passed in 1974 to protect the public health by regulating the drinking water supply. The law was amended twice in 1986 and 1996, and it involves many actions to protect drinking water and its sources such as rivers, lakes, reservoirs, springs, groundwater wells, etc. SDWA authorizes the US EPA to set health-based standards for drinking water to protect living beings against both naturally occurring and man-made contaminants that may be found in the drinking water. The 1986 amendments stated the establishment of drinking water standards for 83 specific contaminants, including toxic chemicals and viruses (Laws and Regulations n.d.; LaGrega et al. 2001).

Clean Air Act

The Clean Air Act (CAA) is the comprehensive federal law that regulates air emissions from stationary sources, i.e., air emissions from factories, refineries, boilers, and power plants, and mobile sources, i.e., motor vehicles, airplanes, and locomotives. CAA authorizes EPA to establish National Ambient Air Quality Standards (NAAQS) to protect the public health and welfare and also to regulate emissions of hazardous air pollutants (HAPs). The NAAQS set maximum concentration levels of pollutants (or "threshold levels") in the ambient air, and in case of exceeding these levels, the humans and the environment will witness adverse effects. NAAQS regulates six "criteria" pollutants in outdoor air. These criteria pollutants are carbon monoxide, lead, ground-level ozone, nitrogen dioxide, particulate matter (PM), and sulfur dioxide. Some of these pollutants are "primary" (directly emitted; i.e., lead, PM), whereas others are secondary, which are formed by undergoing chemical reactions in the atmosphere (i.e., ozone, NO_2). Because of CAA, most of the states in the United States are substantially in compliance with the NAAQS for all the criteria pollutants, except for ozone and carbon monoxide.

In addition to the control of ambient air pollutants, CAA ensures that "best available pollution control technologies (BACT)" are employed in industrial facilities, in order to control hazardous air pollutant (HAP) emissions, from both existing and new emission sources. HAPs, also known as air toxics, cause cancer or other serious health effects, reproductive effects, birth problems, adverse environmental effects, etc. Examples of HAPs include benzene (found in gasoline), perchloroethylene (emitted from dry cleaning facilities), and methylene chloride (used as a solvent and paint stripper by a number of industries). Currently, 187 HAPs are regulated (HAPs 2021; Laws and Regulations n.d.).

Basel Convention-Hazardous Wastes Transport Between Countries

The awakening of environmental awareness in the early 1970s and the reciprocating tightening of environmental regulations had led to public resistance against the dumping of hazardous wastes in their backyards. This created waste disposal problems for industries; hence the industries followed the "not in my back yard" (or NIMBY) syndrome and sought disposal of hazardous wastes at lower costs in poor and developing counties where environmental awareness was not greatly established at that time and regulations or enforcement mechanisms were missing.

There has been a public outcry in the 1980s, following the discovery of hazardous waste deposits in Africa and other parts of the developing world, due to the export of hazardous wastes from wealthy nations. This "toxic trade" was terminated through "Basel Convention." Basel Convention of 1989 is an international treaty adopted by the United Nation Environment Program (UNEP) to control the movements of hazardous wastes and their disposal between the countries, more specifically, to prevent the transfer of hazardous waste from developed to less developed countries. In this convention, a hazardous waste list was adopted by 116 countries of UNEP (LaGrega et al. 2001; Basel Convention 2021). Categories of the wastes controlled by Basel Convention is listed in Table 1.4.

1.4 Hazardous Waste Management Methods

1.4.1 Pollution Prevention

The main purpose of hazardous waste management and control is to reduce the generation of hazardous wastes, while lessening the long-term costs and liabilities associated with the wastes. One of the main methods for hazardous waste management is through pollution prevention (P2) or source reduction activities. P2 activities include waste minimization, waste recycling, waste reuse, waste reduction, and source reduction. P2 can be achieved through simple commonsense waste reduction methods such as segregating hazardous wastes, sweeping floors prior to washing, or training employees, or it can be achieved through waste minimization audit (discussed below) or through research and development (R&D) on any of the following: new process chemistry, equipment changes, changes in product specification, changes in process conditions, etc. (LaGrega et al. 2001). Figure 1.3 illustrates the order of preference in hazardous waste management (Facility Management 2021).

Table 1.4 Categories of wastes controlled by Basel Convention (Defining Hazardous Waste 2021)

Category	Description of the waste
Y1	Clinical wastes from medical care in hospitals, medical centers, and clinics
Y2	Wastes from the production and preparation of pharmaceutical products
Y3	Waste from pharmaceuticals, drugs, and medicines
Y4	Wastes from the production, formulation, and use of biocides and phyto-pharmaceuticals
Y5	Wastes from manufacture, formulation, and use of wood-preserving chemicals
Y6	Wastes from the production, formulation, and use of organic solvents
Y7	Wastes from heat treatment and tempering operations containing cyanides
Y8	Waste mineral oils unfit for their original intended use
Y9	Waste oils/water, hydrocarbons/water mixtures, emulsions
Y10	Waste substances and articles containing or those contaminated with polychlorinated biphenyls (PCBs) and/or polychlorinated terphenyls (PCTs) and/or polybrominated biphenyls (PBBs)

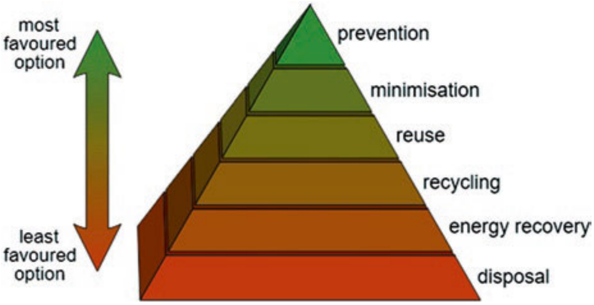

Fig. 1.3 Hazardous waste management hierarchy – from the highest preference to the lowest (Waste hierarchy n.d.)

P2's objective is to reduce, eliminate, or prevent the generation of pollution from its source. Thus, P2 is also known as "source reduction." Reduction in the volume or mass of hazardous waste means less waste to control, treat, and dispose (Pollution Prevention (P2) n.d.). Before the 1980s, P2's activities were not widely practiced, and the Environmental Health and Safety (EHS) function within the industries were independent. Industries opted for pollution control methods instead of P2 activities. However, now the EHS function is integrated throughout the corporations from top-down levels (LaGrega et al. 2001).

Implementing P2 programs in industry has many benefits including enhanced economic incentives, meeting legal requirements and public demands. The economic benefits are one of the most rewarding benefits, when compared to the rest, because reduction in the waste generation is equivalent to saving up on raw materials, reducing the expenditure for waste transport, and treating and managing the waste. Furthermore, by implementing the P2 program, any potential future liability issues related to hazardous wastes can be avoided. The public no longer tolerates the continued production of hazardous wastes. The intolerance by the public manifests itself in many forms, including new legislation and consumer boycotting of products from industries which are not environmentally responsible for proper management of hazardous wastes (LaGrega et al. 2001). Thus, P2 programs also help to improve the corporate image and meet public demands related to efficient management of wastes. Currently, P2 is no longer optional, and it has become mandatory and regulated by environmental laws in the United States and in many developed countries.

EPA suggests the following steps in implementing P2 programs: (a) planning; (b) characterizing wastes; (c) developing P2 options; (d) performing technical, regulatory, and economic feasibility studies; (e) implementing P2 options; (f) monitoring; and (g) continuing until P2 targets are met. Since pollution prevention is one of the most important aspect of hazardous waste management, a separate chapter is included in the book to elaborate further on this topic.

1.4.2 Environmental Audit

Environmental auditing is a standard waste management practice in most corporations. Similar to financial auditing, environmental auditing is an independent, systematic method used for verifying environmental regulations, internal policies, and operating practices, as well as ensuring that they are being followed. There are several types of environmental audits performed in the industry depending on its objectives such as meeting regulatory requirements, minimizing waste generation at the facility, obtaining insurance for hazardous materials storage, etc. Different types of environmental audits are briefly explained below.

Compliance Audit

Compliance checks and verification of meeting environmental regulations were the driving force behind the initial development of environmental auditing. The audit, with this objective, is termed as the compliance audit. The major goals of compliance auditing are to (1) determine the specific regulatory requirements, (2) to find out whether the operation complies with the requirements, and (3) to pinpoint any possible violations in time, so that facilities can take proactive measures to meet compliance.

Management Audit

Another type of environmental audit is known as the management audit. The management audit is used to evaluate the industry’s adherence to either internal or external environmental management system requirements that aim to develop, implement, maintain, and review existing environmental policies. An example of this type of audit is done to evaluate adherence to ISO 14000 series specifications and guidelines. ISO 14000 standards are based on the environmental management methods that help industries to minimize their negative effects on the environment, to comply with the applicable environmental laws and regulations, to meet other environmentally focused requirements, and to continually improve the environmental performance of their facilities (ISO 14,000 n.d.).

Waste Minimization Audit

The waste minimization audit is done at industrial facilities to minimize hazardous waste generation. The waste minimization audit consists of planning and characterizing of all the wastes generated in every process stream. In planning for waste minimization, the following steps are generally followed: (a) obtaining management support to allocate financial and human resources for auditing, (b) setting up goals for either the entire operation or parts of the operation, (c) designating a person to lead the waste minimization audit, and (d) preparing schedules, worksheets, and other necessary documents needed for waste minimization audit.

In characterizing wastes, a thorough survey is done to obtain the following data for each hazardous waste stream:

1. Specific sources that generate hazardous wastes
2. Physical and chemical characteristics of each waste stream
3. Production rate and operations that generate the hazardous waste
4. Current management methods used with the generation and disposal activities and
5. Cost of each management method

The information needed for characterizing the wastes can also be obtained from several other sources including existing process flow diagrams, material and heat balance data of the process, information from operating and process description manuals, equipment lists, equipment specification piping and instrument diagrams, Material Safety Data Sheets (MSDS), material purchase records, raw material inventory records, production records, operator data logs, and maintenance records. Once the characterization data are obtained, several options for waste minimization are evaluated. Before implementation, each selected waste minimization option must be evaluated for its technical, regulatory, and economic feasibility.

Liability Definition Audit

Another type of environmental auditing is the liability definition audit, which is typically done for potential buyers or proposed mergers and acquisitions of real estates. Liability definition audit identifies environmental problems that could reduce the value of a property or expose the buyers to liability. This type of audit helps to establish due diligence to gather facts and information in a careful manner. The transactions involving mergers and acquisitions of real estates can convey the liabilities associated with contaminations present in the properties of interest (LaGrega et al. 2001).

Waste Contractor Audit

A significant amount of nonhazardous and hazardous waste is treated off-site. For off-site treatment and disposal of hazardous wastes, waste generators contract private waste management companies. Due to the nature of transportation and disposal issues, the potential for making damages (i.e., vehicle accidents, spillage of the hazardous wastes, etc.) and liabilities to third parties is higher for the contracted waste management companies. Thus, this type of audit uses features from both a compliance audit and a liability definition audit, discussed previously (LaGrega et al. 2001).

Risk Definition Audit

The risk definition audit is done to obtain insurance coverage for facilities that handle hazardous materials and substances. Such insurance coverage is required by some governments as part of the catastrophe prevention planning (LaGrega et al. 2001).

1.4.3 Product Life Cycle

Another waste management practice is to apply product life cycle analysis (LCA) which is defined as a systematic approach for identifying and evaluating opportunities to improve the environmental performance of industrial activity in all stages of a product (LaGrega et al. 2001). Life cycle stages of a product, from cradle to grave, as shown in Fig. 1.4 include the raw material selection stage, manufacturing process stage, usage stage (distribution, marketing, packaging stage, and human consumption), and final disposal stage. In each stage of a product's life, the waste generated, its impact on the environment and the human health, and the potential improvements in the reduction of wastes are investigated. The design for disassembly is one of the many life cycle examples used by the automobile industry and various other industries. For example, in automobile industries, plastic parts are stamped by the type used during fabrication so that they can be sorted quickly and accurately; thus, the cars are designed for disassembly. Another example for LCA is related to various packaging alternatives for a liquid fabric softener. Of the four possible alternatives examined for packaging, the use of concentrated product in a paper carton to refill high-density polyethylene (HDPE) bottle showed the highest percent decrease,

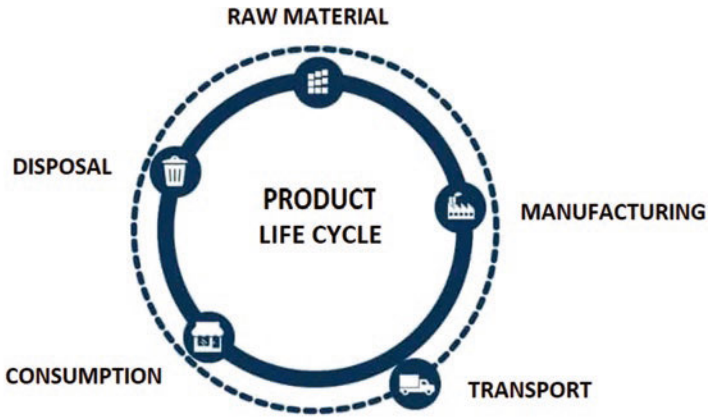

Fig. 1.4 Product life cycle (Life Cycle Assessment n.d.)

for each of the energy and waste emission categories as compared to other packaging materials considered (LaGrega et al. 2001).

In LCA analysis, several questions are asked: (a) What type and quality of raw materials were used? (b) Where did the raw materials come from? (c) How were the final products made? (d) How much is the consumption of water, energy, etc. in each stage? And (e) how were the products transported, consumed, disposed, etc.? After careful evaluations, the environmental impacts are minimized in each stage of the process. By incorporating LCA methods, industries reduce the environmental impacts, while maintaining and gaining competitive advantages (Life Cycle Assessment n.d.; LaGrega et al. 2001).

1.5 Hazardous Waste Treatment Technologies

1.5.1 Physical and Chemical Methods

The treatment of hazardous wastes includes physical, chemical, thermal, and biological methods. The physical treatment method concentrates, solidifies, and reduces the volume of the waste through various processes such as evaporation, sedimentation, flotation, and filtration. Solidification is done by capturing the waste in concrete, asphalt, or plastic. This process produces a solid mass that is resistant to leaching. The physical waste treatment method relies on the physical characteristics of the waste materials in order to separate the hazardous constituents in a waste stream, wherein residues are further treated and ultimately sent for disposal (Shukla et al. 2020). Other physical treatment processes include aeration, air stripping, ammonia stripping, carbon absorption, centrifugation, dialysis, distillation, electrodialysis, encapsulation, flocculation, ion exchange, reverse osmosis, steam stripping, thickening process, and vapor scrubbing process (Shukla et al. 2020).

Ion exchange, precipitation, oxidation and reduction, and neutralization are some of the common chemical treatment methods. The basic principle behind the chemical treatment method relies on changing the chemical structure of the constituents, which produces residues that are less hazardous than the original waste generated (Shukla et al. 2020). Other chemical treatment processes include alkali metal dechlorination, calcination, solvent extraction, sorption, and ozonation (Shukla et al. 2020).

1.5.2 Thermal Methods

Thermal treatment is generally applicable to all types of wastes as compared with other treatment methods (i.e., physical, biological, etc.). High-temperature incineration reduces the volume and toxicity of the wastes, significantly. Different types of incinerators such as fluidized-bed incinerators, multiple-hearth furnaces, rotary kiln incinerators, liquid-injection incinerators, etc. are used to combust gaseous, liquid, or solid hazardous wastes (Treatment-storage-and-disposal n.d.). Air pollution control must be in place during hazardous waste incineration to avoid any release of harmful hazardous air pollutants (HAPs). Other thermal treatment methods include pyrolysis, wet air oxidation, molten salt destruction, and plasma torch. In pyrolysis process, the waste is chemically decomposed by heating the material under anaerobic conditions. Wet oxidation method is used when organic wastes are too dilute to be incinerated economically. In molten salt destruction, organic waste is simultaneously burned while sorbing the objectionable by-products from the effluent stream, and this is accomplished through mixing the wastes with air in a pool of sodium carbonate. This method is used in the treatment of wastes with low ash or high chlorine content. In the application of plasma torch, the waste is brought into contact with a gas and consequently energized to its plasma state by the help of an electrical discharge to destroy hazardous wastes (Shukla et al. 2020).

1.5.3 Biological Methods

Many of the organic hazardous wastes can be biologically treated. Biological degradation of hazardous materials is one of the most practical and feasible option in waste treatment. In this process, microorganisms degrade or detoxify the hazardous waste components present, to less harmful products, through metabolic processes that can occur in water, soil, or air phases. For example, in land farming, which is considered as one of the many biological methods used, the waste is carefully mixed with soil which contains naturally occurring microbes and nutrients. In some cases, a genetically modified bacterium, suitable for the degradation of wastes, can be used. Thus, contaminated sites due to past malpractices can be bioremediated (Treatment-storage-and-disposal n.d.). In many industries biological treatment units and systems such as aerobic treatment units, activated sludge reactor systems, rotating biological units, membrane biological systems, bio-reclamation methods, air phase biological reactors (i.e., biofilter, bio-scrubber, bio-trickling filter), anaerobic digestion systems, etc. are employed to treat hazardous wastes biologically. Details on different hazardous waste treatment methods are discussed in the chapters that follow.

1.6 Summary

In this chapter, the definition of hazardous wastes, waste characteristics, hazardous waste symbols, EPA listed wastes (F, K, U, P), hazardous waste identification methods, types of waste generators, waste sites from past malpractices, etc. are introduced. The importance of environmental chemistry, physical-chemical properties of hazardous wastes, fate, transport of hazardous wastes, and consequences of improper management of hazardous wastes, based on past and a few recent incidents, are emphasized. Important environmental laws including Resource Conservation and Recovery Act (RCRA); Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA); Hazardous and Solid Waste Amendments (HSWA); Emergency Planning and Community Right-to-Know Act (EPCRA); Toxic Substances Control Act (TSCA); Occupational Safety and Health Act (OSHA); Clean Water Act (CWA); Safe Drinking Water Act (SDWA); Clean Air Act (CAA); and Basel Convention-Hazardous Wastes Transport between Countries are discussed. Hazardous waste management techniques, such as pollution prevention (P2), environmental auditing, and product life cycle analysis (LCA), are introduced. Finally, different physical, chemical, thermal, and biological treatment techniques are presented. The management and control of hazardous wastes is not limited to technical issues, but it is also related to legal, social, political, and ethical concerns. Laws and regulations continue to increase and will become more stringent with time. Therefore, industries must always be prepared to comply with the current regulations, as well as to meet future challenges related to technical, management, and legal issues that may be expected in the course of hazardous waste management and control. This chapter is only introductory, and the details on all aspects of hazardous wastes are covered in the subsequent chapters.

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Chapter 2
Hazardous Waste Accidents: From the Past to the Present

Zarook Shareefdeen and Janak Bhojwani

2.1 Introduction

Thousands of chemical plants across the world produce a vast number of toxic chemicals and hazardous wastes in the form of by-products, and these undergo physical and chemical changes (The American Chemistry Council 2020). As a result, generated hazardous wastes must be properly managed, transported, processed and disposed with due diligence that meets the local and international environmental regulations. The objective of this chapter is to highlight and summarize several case studies related to improper management of these hazardous waste substances generated from various parts of the globe. Each of the 15 case studies identifies the time, location, management, contaminant(s), causes and consequences of each of these disasters. Readers of this chapter will be able to develop clear ideas on the tragic causes and consequences (such as loss of biotic lives, damage to the environment, global-scale pollution, financial losses, liabilities, etc.), which occurred as a result of the mismanagement of hazardous waste materials.

2.2 Industrial Case Studies

2.2.1 *Minamata Methylmercury Poisoning*

Date: July 1959 (methylmercury poisoning was revealed as the cause of the disaster)

Contaminant: Methylmercury. Methylmercury is a very toxic organometallic substance that is formed by the activity of bacteria on mercury. It is used in

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fluorescent lights, polyvinyl chloride (PVC) and batteries. Methylmercury is extremely detrimental to human health. Exposure to methylmercury can cause blindness, deafness, cerebral palsy and mental retardation (Methylmercury Poisoning 2019).

Geographical significance: Minamata is a city situated in the Kumamoto Prefecture in Kyushu, Japan (Britannica 2016). Minamata was an important fishing hub in Japan but is now primarily known for the manufacture of chemical fertilizer and vinyl chloride. It has an approximate population of 27,000 people. Minamata is popular for being the origin of the Minamata disease (Britannica 2016).

Involved company: Nippon Chisso Hiryo Corporation. The Nippon Chisso Hiryo Corporation is a Japanese chemicals company that was involved in the production of chemical fertilizer, vinyl chloride and carbide (Britannica 2016). In 2011, the company was restructured as Japan New Chisso (JNC) and is now involved in the manufacture of liquid crystals, cosmetics, electronic elements and other chemical products (JNC n.d.).

Event: From 1932 to 1968, the Nippon Chisso Hiryo Corporation was involved in the production of acetaldehyde in Minamata (Yorifuji and Tsuda 2014). A major by-product of this chemical process was mercury. The company continually dumped the mercury waste into the Minamata Bay where it was subject to biotransformation by the bacteria in the water to create toxic methylmercury (Mercury 2019). Approximately 27 tonnes of mercury was dumped by the company into the Minamata Bay (Kugler 2019). Since Minamata was a fishing hub, methylmercury entered the food chain through ingestion of fish; hence it found its way into Minamata's residents (Kugler 2019).

Causes

1. Improper handling and lack of recognition of toxic by-product wastes resulting from the chemical reactions being run at the plant. The Nippon Chisso Hiryo Corporation was unable to evaluate the safest method of disposal of mercury waste and displayed no regard towards the consequences of releasing the chemical into the environment.
2. Hindrance of clean-up programmes due to deflection of blame. In July 1959, research conducted at Kumamoto University discovered that mercury poisoning was responsible for the rising incidences of health issues that were reported in Minamata (Kugler 2019). Upon interrogation, the Nippon Chisso Hiryo Corporation denied the claims addressed to them regarding the adverse health effects that were shown on living species due to their exposure to the plant's generated mercury waste. In fact, the company refused to change or evaluate the process being used to produce acetaldehyde and continued operating until 1968 (Kugler 2019).
3. Negligence and lack of accountability on the part of the Japanese government was noted. Upon the discovery of the contamination in 1959, the government did not take appropriate remediation action or regulatory steps (Kugler 2019).

Aftermath

1. Cats in Minamata that consumed the contaminated fish began to die (Kugler 2019). Several residents then began to suffer from tremors, numbness, deafness, blindness and brain damage. Cases of damage to the central nervous system in the form of sensory disturbances, lesions of the brain and mental retardation were seen in many victims of the accident (Harada 1995). Many foetuses and children born to mothers who were exposed to methylmercury, as a result of their ingestion of contaminated fish, displayed prospective mental retardation, poor reflexes and limb deformities (Yorifuji and Tsuda 2014).
2. The ‘Minamata disease’ refers to the effect of methylmercury poisoning on the central nervous system and was named after the incident that took place in Minamata (Yorifuji and Tsuda 2014). The Minamata disease is a neurological disorder that is caused by mercury poisoning.
3. According to the Japanese government, 2955 people were afflicted with the Minamata disease, and 1784 people died as a result (Kugler 2019).
4. In 2001, the Osaka High Court instructed the Nippon Chisso Hiryo Corporation to pay $2.18 million to the plaintiffs who filed lawsuits against the company (Kugler 2019). In 2004, the Supreme Court of Japan ordered the Japanese government to pay $703,000 in compensations to the victims of the incident (Yorifuji and Tsuda 2014).

2.2.2 Seveso Disaster

Date: July 10th, 1976

Contaminant: 2,3,7 and 8 tetrachlorodibenzoparadioxin (TCDD). This chemical is heralded as one of the most toxic, artificially made substances known to mankind (Phillips et al. 2007). TCDD is a chemically stable compound; hence it is able to reside in the bodies of organisms for a very long time. It is one of the chemicals that fall under the ‘dirty dozen’, a term for highly toxic and detrimental chemicals, identified as persistent organic pollutants (POPs) (Dioxins 2016). Chronic effects of TCDD include cancer and failure of the human immune, endocrine and reproductive systems. Consequences of acute exposure are darkening of the skin and liver failure (Dioxins 2016).

Geographical significance: Seveso is a town located in the Region of Lombardy, Northern Italy (What n.d.). Seveso has an approximate population of 23,400 people (Seveso n.d.). It is known for the TCDD disaster that occurred during 1976 (What n.d.).

Involved company: Industrie Chimiche Meda Società Azionaria (ICMESA). Industrie Chimiche Meda Società Azionaria was a chemical company that was owned by a Swiss corporation, Givaudan. Givaudan, in turn, is a subsidiary of the Swiss diagnostics and pharmaceuticals company, Hoffman-La Roche (Lonigro 2015).

Event: ICMESA was involved in the production of 2,4,5-trichlorophenol, a compound that was required for the manufacture of cosmetic and pharmaceutical products (Centemeri 2015). On July 10th, 1976, a runaway chemical reaction, triggered by the failure of a ventilation system, led to the release of 15–30 kg of TCDD along with sodium hydroxide, ethylene glycol and sodium trichlorophenate over an area of 18 km^2 in Seveso (Centemeri 2015).

Causes

1. Failure to follow safe operating procedures. No appropriate methods, devices or measures of disposal were in place to capture the toxic pollutants that were released as by-products from the chemical reactions (Icmesa n.d.). Furthermore, when the production cycle was inadvertently disrupted, failure of the cooling mechanisms allowed the runaway reaction to take place (Icmesa n.d.).
2. Improper design and maintenance of control systems. The control systems employed in the production process did not have appropriate cooling (Icmesa n.d.). Additionally, the threshold pressure for the relief systems, at which venting would begin, was too high. Had a lower threshold pressure been set, venting would have occurred at a much lower temperature—this may have avoided the runaway reaction from taking place (Icmesa n.d.).
3. Unawareness of the nature of possible toxic releases. The operating staff at the plant was not well-versed with the nature of the toxic waste products that were released and was unaware of possible runaway reactions (Icmesa n.d.).
4. Withholding of relevant information and poor communication. ICMESA initially refused to admit that TCDD was released into the environment as a result of the accident (Icmesa n.d.). Subsequently, the company did not provide any information about the nature of the toxicants that were released. This hindered local authorities as they were unable to plan, control and contain the TCDD released and evacuate the plant after the disaster (Icmesa n.d.).

Aftermath

1. Residents of the area experienced several health concerns. Some victims exhibited nausea, headaches and eye irritation (Eskenazi et al. 2018). Approximately 200 victims also reported chloracne as a direct result of exposure to the chemical. Nineteen children with skin burns were admitted to hospitals in the area. Exposure to TCDD greatly reduced male and female fertility (Eskenazi et al. 2018). Epidemiological studies in the area also linked the exposure of TCDD to spread of cancer, cardiovascular disease and neurological disorders among residents of nearby areas. Twenty-six pregnant women decided to have abortions due to exposure to TCDD (Eskenazi et al. 2018). Two weeks after the release, over 500 citizens were evacuated from their homes (Scars 2001).
2. Thousands of florae and fauna were killed by the accident, and several thousand more were killed or slaughtered to contain the chemical and avoid biomagnification (Icmesa n.d.).
3. Parent company of ICMESA, Hoffman-La Roche, paid approximately $168 million as a result of damages and to compensate for the clean-up programmes that

were directed to contain the release (Scars 2001). The company also compensated the victims of the accident (Scars 2001).

4. The 'Seveso Directive' of 1982 was implemented by the European Union to control the release of chemical hazardous pollutants into the environment and to avoid similar chemical accidents (Centemeri 2015).

2.2.3 Love Canal Disaster

Date: August 7th, 1978 (federal emergency declared at Love Canal)

Contaminant: Two hundred chemical compounds and at least 12 chemical carcinogens. One of the major contaminants was TCDD. This chemical is heralded as one of the most toxic, artificially made substances known to mankind (Phillips et al. 2007). TCDD is a chemically stable compound; hence it is able to reside in the bodies of organisms for a very long time. It is one of the chemicals that fall under the 'dirty dozen', a term for highly toxic and detrimental chemicals identified as persistent organic pollutants (POPs) (Dioxins 2016). Chronic effects of TCDD include cancer and failure of the humans' immune, endocrine and reproductive systems. Consequences of acute exposure include darkening of the skin and liver failure (Dioxins 2016).

Geographical significance: The land that used to be called the Love Canal landfill is a rectangular, 16 acre land that is located in Niagara Falls, New York (Phillips et al. 2007). It was originally sanctioned for the construction of a canal, but the project was quickly abandoned (Dabkowski 2018). Eventually, it was used as a landfill for the disposal of municipal and industrial waste (U.S. V. Occidental 2015). The land covered an approximate area of 3000 ft long by 100 ft wide (Phillips et al. 2007).

Involved company: Hooker Chemical Company. Hooker Chemical Company, which was later known as Hooker Electrochemical Company, was a large-scale chemical corporation that was involved in the production of dyes, caustic soda and bleaches (Hooker Chemical n.d.). The predecessor of the company, the Development and Funding Company, was founded in 1903 (Murray 1957). In 1968, Hooker Electrochemical Company and all of its subsidiaries were acquired by Occidental Petroleum Corporation (OCC) (U.S. V. Occidental 2015).

Event: In August 1978, the neighbourhood adjacent to Love Canal was declared as the target of a federal emergency, and this was issued by President Jimmy Carter after discovering that the landfill contents were leaching, which caused an imminent threat of exposure to these chemicals (Fowlkes and Miller 1987). It was uncovered that between 1942 and 1953, Hooker Chemical Company was utilizing the landfill (which belonged to them at the time) to dispose nearly 22,000 tonnes of industrial waste; this waste leached to the surface and contained several hazardous chemicals and pollutants (Phillips et al. 2007). The people that resided directly adjacent to the landfill were also informed that some of the contaminants could have leaked laterally and seeped into their properties (Fowlkes and Miller 1987).

Causes

1. Improper disposal of industrial waste in an unmonitored landfill adjacent to residential areas (Phillips et al. 2007).
2. Absence of government regulation of industrial waste disposal sites (Phillips et al. 2007).
3. No installation of a lining to prevent the leaching of chemicals and hazardous waste (Phillips et al. 2007).
4. Delayed action of state and central government, even after the declaration of emergency (Fowlkes and Miller 1987).

Aftermath

1. The entire community, of around 700 families that inhabited areas near Love Canal, was evacuated (Love Canal n.d.).
2. Immediately after the incident, it was uncovered that there was a significant increase in miscarriages, stillbirths, epilepsy, urinary tract disorders and cancer among the residents of communities surrounding Love Canal (Love Canal n.d.). Fifty-six percent of children were born with birth defects and the occurrence of miscarriages was tripled in neighbourhoods surrounding Love Canal from 1974 to 1978 (Love Canal n.d.).
3. OCC paid New York \$20 million and settled the federal case against them for \$129 million (Phillips et al. 2007). As a result, around 900 former residents of the area received a compensation fee ranging between \$63 and \$133,000 for the damages (Dabkowski 2018).
4. The disaster at Love Canal led to the enactment of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) in 1980 (unofficially known as the US Federal Superfund law) (U.S.V. Occidental 2015). The act established a tax and several rules for the proper disposal of hazardous chemical waste from industries, in the interest of inhabitants residing nearby (Superfund n.d.).

2.2.4 Sydney Tar Ponds

Date: 1980 (the first of the clean-up programmes was initiated)

Contaminant: Coal tar. Coal tar is usually a by-product of industrial processes, including the steel manufacturing and other coal-related processes (Coal Tar 2017). Coal tar contains a wide range of toxic heavy metals that can impact life, property and the environment negatively (Sydney n.d.). Coal tar has been reported to display adverse effects on human health in the form of skin reactions, genetic disorders, cancer and infertility (Coal Tar 2017). Coal tar also has chronic effects on aquatic life if introduced into a marine ecosystem (Coal Tar 2017).

Geographical significance: Cape Breton Island is an island in the north-eastern segment of Nova Scotia, Canada (Britannica 2021). The most common economic activities in Cape Breton Island include coal mining, lumbering and fishing (Britannica 2021). The approximate population of Cape Breton Island is 94,285 (Nova Scotia Population n.d.).

Involved company: Sydney Steel Corporation (SYSCO). SYSCO was a corporation based in Sydney, Nova Scotia (Peacey 2015). It operated a steel mill in Sydney that was eventually taken over by the Nova Scotian and Canadian governments in 1967. SYSCO operated the steel mill from 1900 to 1967 (Peacey 2015).

Event: An important aspect of the production of steel is the conversion of coal to coke. In the 1900s, SYSCO employed coke-oven technology to carry out this conversion (MacAulay 2002). This process resulted in the accumulation of several toxic waste by-products like mercury and other heavy metals in the form of coal tar sludge ponds (Sydney n.d.). Approximately 750,000 tonnes of chemical toxicants were released in nearby areas, as a result of this accumulation (Trudell n.d.). This toxic waste was drained into a nearby estuary, Muggah Creek (MacAulay 2002). The region that was affected by this accident was approximately 274.1 acres (Sydney n.d.).

Causes

1. The major cause of this accident was the dependence of all three involved sides, i.e. SYSCO, the Nova Scotian government and the Canadian government, on antiquated coke-oven technology to manufacture steel. The authorities of the steel mill did not improve this technology, due to negligence, until the accident occurred (MacAulay 2002).
2. Improper handling and disposal of toxic by-products. The companies and authorities involved did not handle the disposal of coal tar on time; furthermore, they drained the waste by-products into Muggah Creek without accounting for possible consequences on life, property or the environment (Trudell n.d.).
3. Inefficient remediation efforts were undertaken upon discovery of the accident (Trudell n.d.). Several political controversies obstructed the operation of a successful and immediate clean-up drive. An incinerator was also employed to burn off the toxicants in the developed sludge ponds but failed due to ineffective piping (Trudell n.d.).

Aftermath

1. Approximately 25,000 local residents of Cape Breton Island reported experiencing several health effects as a result of the contamination. There were higher reported cases of cancer, Alzheimer's disease, respiratory disorders and birth defects (Weber 2019).
2. The Sydney Tar Ponds Agency was established in order to repair the environmental, property and health ramifications and damages due to the contamination (Sydney Tar Ponds n.d.).
3. The Sydney Tar Ponds Agency generated a fund of $393 million towards a project which aimed to remediate the affected areas (Sydney n.d.). The funds led to the clean-up of the waste, and the construction of Open Hearth Park in the area (Weber 2019).

2.2.5 Times Beach Evacuation

Date: December 1982

Contaminant: 2,3,7 and 8 tetrachlorodibenzoparadioxin (TCDD). Please refer to Sect. 2.2.3.

Geographical significance: Times Beach was a resort town located in St. Louis County, Missouri (Wills n.d.). It was founded in 1925 and had a population of approximately 2000 people (Weiser 2019). Times Beach was a popular destination and stop for tourists and residents along the United States's famous Route 66. Times Beach was initially founded as a tourist attraction and summer leisure destination but soon became a permanent residence for its inhabitants (Weiser 2019). Now, Times Beach is a ghost town and home to the Route 66 State Park.

Involved company: The Bliss Waste Oil Company. The Bliss Waste Oil Company was owned by Russell Bliss in the 1960s and 1970s (Weiser 2019). The company was involved in the transport, storage and disposal of industrial, chemical and process wastes and was particularly involved in the disposal of waste oil products. The company usually disposed these products in pits and drums or dumped them in designated areas (Weiser 2019).

Event: In the 1970s, the Northeastern Pharmaceuticals and Chemicals Company (NEPACCO) was involved in the production of Agent Orange and hexachlorophene; the former was a defoliant used by the United States in the Vietnam War, while the latter was a chemical commonly used in the production of disinfectants (McIntyre n.d.). A by-product of the manufacture of these chemicals was TCDD (Weiser 2019). In order to dispose the TCDD in the waste sludge, NEPACCO employed the Independent Petrochemical Corporation (IPC). However, IPC was not aware of how to dispose the TCDD; hence it sub-contracted the job to Bliss Waste Oil Company. Russell Bliss mixed the chemical waste with motor oil, to be used as a chemical dust suppressant (McIntyre n.d.). He was then hired by the city of Times Beach to control the widespread dust problem on its streets. Bliss used the motor oil mixture laced with TCDD as a dust suppressant and sprayed it on 23 miles of unpaved streets in Times Beach (McIntyre n.d.).

Causes

1. Failure of NEPACCO and IPC to effectively employ authorized waste disposal companies for the treatment of toxic waste. IPC was not qualified to treat the dangerous TCDD and further sub-contracted the job to Bliss Waste Oil Company. Neither of the companies followed up on the treatment process (McIntyre n.d.).
2. Improper identification of toxic pollutants and contaminants by Bliss Waste Oil Company. In order to cut down on the costs, Bliss Waste Oil Company mixed motor oil with the toxic TCDD, without realizing the potential ramifications of its actions (McIntyre n.d.).
3. Withholding important information regarding the contents of the toxic sludge and the motor oil mixture. NEPACCO did not admit to the presence of TCDD in

its waste sludge, until an employee of the company admitted to it (McIntyre n.d.). Initially, Bliss did not admit to the use of TCDD in his motor oil mixture, even after his customers filed complaints. This suppression of important information delayed the reaction to the incident and hindered the subsequent clean-up process (McIntyre n.d.).

Aftermath

1. In 1983, Times Beach was bought by the federal government and the US Environmental Protection Agency (EPA) for $32 million (McIntyre n.d.). Times Beach was declared a Superfund site, and the town was completely evacuated (Weiser 2019).
2. There were many reported deaths of horses and birds in Times Beach at the time of the incident. The residents of Times Beach experienced nose bleeds, gastrointestinal problems and skin rashes (McIntyre n.d.). Several children were also severely affected due to exposure to TCDD (Little n.d.). The chronic effects of the exposure of the residents of Times Beach to TCDD is still unknown.
3. Due to the Superfund activity, the government and EPA were able to launch a clean-up drive that remediated 265,00 tonnes of contaminated soil in the Times Beach area. The clean-up programme costed nearly $110 million (Weiser 2019).
4. Several lawsuits were filed against NEPACCO, IPC and Bliss Waste Oil Company (Weiser 2019). While Russell Bliss was condemned for his actions, he was never sentenced or imprisoned for his crime.

2.2.6 Bhopal Gas Tragedy

Date: December 3rd, 1984

Contaminant: Gaseous methyl isocyanate (C_2H_3NO) (Broughton 2005). Methyl isocyanate is a substance commonly used as an intermediate compound in the manufacture of pesticides and herbicides (EPA 2000). Methyl isocyanate is extremely toxic and caused adverse acute health effects on humans. It can cause severe respiratory infections, damage to the eyes, blindness and nausea (EPA 2000). There is no information about the chronic effects of methyl isocyanate (EPA 2000).

Geographical significance: Bhopal is a central city in the India state of Madhya Pradesh. Bhopal is known as the ‘city of lakes’ as it is home to the Upper Bhopal Lake and the Lower Bhopal Lake. These lakes are used to supply drinking water and is used for other recreational and agricultural purposes (Britannica 2019). Bhopal has a population of 1,798,218 people (Bhopal City n.d.).

Involved company: Union Carbide Corporation (UCC). The American company Union Carbide Corporation is a subsidiary of The Dow Chemical Company. UCC produces chemicals and polymers that are used for various purposes including agriculture, paints and pharmaceuticals (Union Carbide n.d.). Due to the progress of international relations in the 1970s, a subsidiary of the UCC, Union Carbide India Limited (UCIL), built a chemical processing plant to facilitate the manufacture of a commonly used pesticide, carbaryl (Broughton 2005). The plant was opened in the Indian city of Bhopal, owing to its geographic centrality.

Event: In the early hours of December 3rd, 1984, 41 tonnes of methyl isocyanate leaked from a storage tank of the UCC plant in Bhopal and spread to the densely populated region (Bisarya and Puri 2005). The gas leaked as a result of an exothermic reaction in the storage tank that was caused by the unsafe introduction of water into the tank. The highly explosive reaction caused a pressure build-up inside the storage tank. Consequently, the safety valve ruptured, and the gas escaped to the atmosphere (Bisarya and Puri 2005).

Causes

1. Incomplete and unmaintained safety precautions and improper storage of hazardous chemicals.
2. Dismissive consideration of the handling of such dangerous chemicals and absence of installation of efficient valves as a safety precaution.
3. Inadequate coordination between the facility and the rescue services (Bisarya and Puri 2005).
4. Ineffectiveness of absence of mock drills, control systems and warning systems (Bisarya and Puri 2005).
5. Lack of concern and the absence of vital staff and experienced engineers at the time of the incident (Bisarya and Puri 2005).

Aftermath

1. At least 3000 people died, and 102,000 people suffered chronic illnesses and/or injuries (Broughton 2005).
2. The effects of the gas leak are still seen today; deformed foetuses are still born to date in Bhopal, and there is still a large number of cancer and mental retardation cases prevalent in the state that directly link to the incident (Bisarya and Puri 2005).
3. Numerous people in Bhopal are critically diagnosed with pulmonary fibrosis and chemical asthma to date because of the chemical tragedy (Broughton 2005). There is still an outflow of hazardous substances from the chemical facility which are impacting nearby water bodies and are finding their way into the bodies of humans and animals (Broughton 2005).
4. The Indian government established the Bhopal Gas Leak Disaster Act (BGLDA) to deal with the population affected by the incident effectively and swiftly (Broughton 2005).
5. After a long dispute, UCC agreed to pay a mere $470 million to the Indian government to aid the survivors and the suffering victims (Broughton 2005).

2.2.7 Hinkley Groundwater Contamination

Date: December 7th, 1987 (PG&E informed the local water board about the incident)

Contaminant: Hexavalent chromium (Cr^{6+}). Hexavalent chromium is used for chrome plating; and dyes, paint, pigment and printer toner manufacturing; and leather and wood preservation (Health Effects n.d.). Hexavalent chromium is highly toxic and has severe effects on the respiratory system. Acute exposure to it leads to shortness of breath and coughing, whereas chronic exposure leads to bronchitis, pneumonia and pulmonary failure (Health Effects n.d.).

Geographical significance: Hinkley is a farming community located in Mojave Desert in San Bernardino, California, USA. Hinkley has a very low population, and the area relies mostly on agriculture and rural development (Public Health 2000). The residents derive their water needs from the Mojave River groundwater basin which encompasses the Hinkley Valley. In the 1960s, groundwater flowing from Hinkley valley originated from recharge areas that ran beside the Mojave River.

Involved company: Pacific Gas and Electric Company (PG&E). Pacific Gas and Electric Company (PG&E) is a holding company based in Central and Northern California. The company focuses on selling and supplying electricity and natural gas (Thomson Reuters n.d.). In 1952, the company established a compressor station in San Bernardino County, California, near the small town of Hinkley. The compressor station was lodged as a part of a larger gas pipeline that linked the states of California and Texas.

Event: From the establishment of the Hinkley compressor station in 1952 to 1964, PG&E utilized highly toxic hexavalent chromium to prevent corrosion in the station's cooling system (Izbicki n.d.). Wastewater released from the station was contaminated with this compound. This contaminated water was released without any treatment into Hinkley Valley, where residents obtained most of their water requirements. Additionally, this contaminated water formed a plume of width 1.5 mi in the groundwater basin, and it continued to spread and contaminate the nearby soil (Public Health 2000).

Causes

1. Failure to follow guidelines as set by the EPA. Hexavalent chromium levels detected in the groundwater were equivalent to 0.57 mg/L. EPA drinking water standard allows for a maximum contaminant level of only 0.05 mg/L (Public Health 2000).
2. Plume of hexavalent chromium spread beyond the boundary set by PG&E. The substance was later discovered in a lower part of the basin which PG&E ignored; they assumed that the lower part of the basin was covered with a thick layer of clay (Sahagun 2010).

Aftermath

1. Effects of contamination were tested among 12 families who consumed the contaminated drinking water. All of them experienced varying diseases including gastrointestinal problems, skin problems, headaches and mouth/throat problems (Groundwater Contamination 2019).
2. PG&E started to buy property impacted by the pollution to avoid remediation. Erin Brockovich, a law firm clerk, helped Hinkley residents by investigating the case and persuading residents to take legal action (Groundwater Contamination 2019).
3. After a tedious legal battle, PG&E paid a total of $33 million as settlement to the affected parties (Groundwater Contamination 2019).
4. Official remediation of the site began in 1992. Remediation focussed on cleaning and prevention of groundwater plume from moving northwards. By fall 1992, remediation activities removed 500 mg/kg of hexavalent chromium (Public Health 2000).
5. Although remediation was in progress, the plume continued to grow in size. To tackle this, PG&E resorted to buying the affected areas and homes (Groundwater Contamination 2019).

2.2.8 Exxon Valdez Oil Spill

Date: March 23rd, 1989

Contaminant: Crude oil. Crude oil is used to manufacture petroleum products that are used as fuel for a wide range of industrial processes (Oil and Petroleum Products Explained 2020). Crude oil is extremely flammable and can cause irritation to the eyes, skin and lungs. It may result in a number of respiratory and gastrointestinal illnesses and causes nausea, headache and dizziness. Chronic effects of exposure to it include leukaemia and neurotoxicity (Crude Oil 2008). Exposure to crude oil can also impact marine life, negatively and permanently, and can damage its ecosystems.

Geographical significance: Prince William Sound (PWS) is a place in the northern Gulf of Alaska (GOA) in the Pacific Ocean (Wiens 2013). PWS is popular for its remarkable, mountainous beauty and diverse ecosystem (Wiens 2013). It is home to one of the world's largest fisheries. PWS's largest port is the city of Valdez in Alaska.

Involved company: Exxon. Exxon, more commonly known as ExxonMobil, is one of the world's largest petroleum and chemical manufacturing companies (Exxon Mobil n.d.). The company is primarily involved in the production, transportation, storage and sale of crude oil and natural gas (Exxon Mobil n.d.). It is also involved in the manufacture of petrochemicals and a wide range of plastics. The company was founded in 1882 and is headquartered in Irving, Texas, USA.

Event: On March 23rd, 1989, Exxon Valdez, an oil tanker owned by Exxon, departed from the Valdez dock for Long Island, California, and it was loaded with approximately 53 million gallons of crude oil (Wiens 2013). Approximately 3 h after its departure, Exxon Valdez was involved in a major collision with the Bligh Reef in Prince William Sound. Soon after the collision, approximately 11 million gallons of the crude oil spilled into PWS (Wiens 2013). Approximately 40% of the spilled crude oil was trapped on the PWS and GOA shoreline, while the rest either evaporated or was carried into the GOA (Wiens 2013).

Causes

1. Due to previous successes of the tanker, there was a lack of attention displayed by the crew and company towards the operation of the tanker (Exxon Valdez Oil Spill Trustee Council 1990). The captain of the tanker, Captain Joseph Hazelwood, was reportedly not at the helm of Exxon Valdez at the time of its impact (Mambra 2020).
2. Lack of professionalism displayed by the crew of the tanker; many of the tanker's crewmates were underprepared, untrained and underqualified (Mambra 2020).
3. The company did not install appropriate iceberg monitoring equipment despite it being a precautionary regulatory measure required by authorities (Mambra 2020).
4. The tanker deviated from its shipping lane prior to the accident due to a broken radar that was not repaired by the company, for more than a year, in order to prevent expenditure (Mambra 2020).

Aftermath

1. The US Coast Guard (USCG) and Exxon initiated a large-scale clean-up programme. While no deaths were reported as a result of the collision, four workers involved in the clean-up operation died due to the exposure to the crude oil (Exxon Valdez Oil Spill Trustee Council 1990).
2. The marine ecosystem of PWS was severely impacted by the spillage. Approximately 250,000 seabirds, 2800 sea otters, 300 harbour seals, 250 bald eagles and 22 killer whales died as a direct result of the collision (Exxon Valdez Oil Spill Trustee Council 1990). Consequently, fisheries in the PWS area were immediately closed. This impacted the livelihoods of several fishermen and resulted in a loss of approximately $580 million (Exxon Valdez Oil Spill Trustee Council 1990).
3. Exxon paid $100 million as compensation for environmental damages and a fine of $150 million (Wiens 2013). Exxon was also required to pay $5 billion in punitive damages, but the amount was reduced to $507.5 million by the US Supreme Court (Wiens 2013).
4. In order to prevent similar accidents from occurring, the US Congress developed the Oil Pollution Act of 1990. This required all new oil tankers being operated between ports in the United States to have a fully functional double hull (Oil and Petroleum Products Explained 2020).

2.2.9 DuPont C8 Lawsuit

Date: December 1999 (First lawsuit filed against the company)

Contaminant: Perfluorooctanoic acid (PFOA) or C8. This chemical does not exist naturally; it is usually formed as a by-product of manufacturing processes (Technical Fact Sheet 2017). PFOA is primarily used to produce Teflon, fast food wrappers, waterproof clothing, cosmetics and many other daily-use products. PFOA is a very toxic compound, and it reported to be a carcinogen (Technical Fact Sheet 2017). Animal testing has shown that PFOA causes high cholesterol, decrease in immunity response, weakness in liver function and thyroid disorders (Technical Fact Sheet 2017).

Geographical significance: The DuPont Washington Works facility is located in Parkersburg, West Virginia, USA. The nearest water connecting districts to the facility are in the states of Ohio and West Virginia. In Ohio, these water districts include the Little Hocking Water Association, the City of Belpre, Tuppers Plains-Chester Water District and the Village of Pomeroy. In West Virginia, the water districts are the Lubeck Public Services District and the Mason County Public Service District (DuPont n.d.).

Involved company: DuPont. DuPont De Nemours Inc. is a holding company established in 1986. It is specialized in producing chemicals, agricultural products and other technology-based material to provide solutions to industrial problems around the world (Dupont De Nemours n.d.). The DuPont headquarters is located in Wilmington, North Carolina. DuPont handles products for a wide range of sectors such as electronics, nutrition, transportation and safety (Dupont De Nemours n.d.).

Event: The DuPont Washington Works facility was opened in 1948 in Washington, West Virginia, USA. The facility produces a variety of polymer products including Teflon (DuPont n.d.). PFOA is an important chemical compound that is utilized in the production of these polymer products. Thus, the discharged wastewater from the plant contains substantial amounts of PFOA. This discharge was removed from the plant by flushing it into surface water from 1961 to 2002 (DuPont n.d.). Over the course of the operation of the facility, several million pounds of PFOA or C8 were released into the Ohio River, as well as other major water public supply systems in West Virginia and other nearby private water wells. All these zones were important areas from which drinking water and water for residential needs were derived (DuPont n.d.).

Causes

1. In 1961, an internal toxicology study conducted by DuPont chief of toxicology confirmed that PFOA is a toxic chemical. This report was not disclosed to the government and the general public (DuPont n.d.).
2. In 1984, DuPont conducted a study that showed high concentrations of PFOA in the water consumed by the residents of cities near the Washington Works facility (DuPont n.d.). Yet, the facility continued to dump the toxic chemical into surface water without treatment.

3. DuPont failed to apply any occupational safety measures, in order to avoid exposure of PFOA to its employees.
4. The company waited to face legal action and to be held liable before taking steps towards remediation. There were no attempts at taking preventive measures (DuPont n.d.).

Aftermath

1. Employees of the Washington Works facility showed abnormal rates of liver function upon conducting medical tests (DuPont n.d.). Soon after, female employees working in the Teflon division of the facility gave birth to children with birth defects (Steenland et al. 2010). Studies show that the exposure of inhabitants to the discharged PFOA was directly linked to renal and testicular cancer, pregnancy issues, hypertension and ulcerative colitis (Frisbee et al. 2009).
2. A study released in 2004 concluded that a total of 1.7 million pounds of PFOA was dumped into surface water by the Washington Works plant (DuPont lawsuits n.d.).
3. In 2001, lawyer Rob Bilott was hired by a West Virginia farmer to sue DuPont for the sudden death of his cattle (DuPont lawsuits n.d.). This case triggered 80,000 more residents living near the facility to file for class action lawsuits, all led by attorney Bilott. These lawsuits were settled in 2005 with DuPont paying $235 million as a compensation (DuPont lawsuits n.d.).
4. In 2017, DuPont provided $671 million as compensation for 3550 pending legal cases but continued to deny any misconduct (DuPont lawsuits n.d.). However, they paid $16.5 million to the EPA for failing to disclose evidence about the toxicity of PFOA (DuPont n.d.).
5. In 2019, EPA released the PFOS Action Plan, dedicated to addressing PFOA concentration in drinking water in the United States (EPA PFAS 2020).

2.2.10 Ivory Coast Toxic Waste Dump

Date: August 19th, 2006

Contaminant: Spent caustic. Spent caustic refers to a general toxic waste product that is a result of a chemical process known as caustic washing (Trafigura n.d.). Exposure to spent caustic can result in adverse health effects on the human eyes, skin, gastrointestinal tract and respiratory system (Spent Caustic 2017). In high concentrations, spent caustic can cause irritation and burns to the lips, oesophagus and mucous membrane of the lungs (Spent Caustic 2017).

Geographical significance: Abidjan is the chief port and the largest city of the Ivory Coast (Britannica 2015). It is also known as the effective or de facto capital of the Ivory Coast. It is home to an international airport and several tourist attractions like Hôtel Ivoire and St. Paul's Cathedral (Britannica 2015). It is also one of the most important communication centres of the Ivory Coast. Abidjan is known for exporting coffee, cocoa, timber, bananas and pineapples, in the Ivory Coast. Abidjan has an approximate population of 4,700,000 (Britannica 2015).

Involved company: Trafigura. Trafigura is a Singaporean-Swiss multinational commodities trading and logistics company (Trafigura Group n.d.). The company is primarily involved in the oil and gas industry. Trafigura sells and deals with the transport and trading of gasoline, crude oil, biodiesels and refined metals across the world (Trafigura Group n.d.). Trafigura was founded in 1993, under parent company Trafigura Beheer BV (Trafigura Beheer n.d.).

Event: In 2006, Trafigura was interested in the production of petrol by mixing gasoline with clean coker naphtha (Trafigura n.d.). Coker naphtha is originally a sulphurous cheap petroleum product. In order to clean the coker naphtha, Trafigura deployed the process of caustic washing, upon cargo ship Probo Koala. This process generated spent caustic as a toxic by-product waste (Trafigura n.d.). Consequently, the toxic spent caustic had to be offloaded from Probo Koala and disposed of safely. Instead, on August 19th, 2006, Trafigura chose to dump the toxic waste (in a quantity of approximately 500 tonnes) illegally, in at least 18 locations in the city of Abidjan, Ivory Coast (Trafigura n.d.).

Causes

1. Failure of predicting and planning safe disposal of toxic waste produced by chemical processes. Trafigura did not have an adequate plan to deal with the toxic waste produced from caustic washing, before proceeding with the operation on Probo Koala (Trafigura n.d.).
2. Decision to reduce expenditure at the cost of safety. Trafigura was denied permission to dump the waste in five countries: Malta, Italy, Gibraltar, the Netherlands and Nigeria (Trafigura n.d.).
3. Withholding important information about the contents of the released toxic waste. Trafigura tried to mislead a waste disposal company in Amsterdam by trying to mask the contents of the waste as less hazardous; upon discovery of this, the company raised its price of disposal to approximately $620,000 (Trafigura n.d.). To avoid paying the higher price, Trafigura dumped the waste in Abidjan after employing a local waste disposal company, Compagnie Tommy, for just $17,000 (Trafigura n.d.).

Aftermath

1. Fifteen people died, 69 people were hospitalized and at least 108,000 people requested medical treatment as a direct result of the incident in Abidjan (Ten years on 2016). The victims were diagnosed with respiratory illnesses, gastrointestinal conditions and digestive problems (Trafigura n.d.).
2. A clean-up programme was launched in September 2006 to bolster remediation of the area impacted by the incident (UN Environment 2018).
3. Trafigura continued to conceal information about the exact contents of the toxic waste, which hindered the clean-up process and caused difficulty in the prediction of possible chronic effects on residents of the surrounding area (Trafigura n.d.).

4. The incident caused several environmental issues such as air pollution, floods, contamination of soil, waste overflow and groundwater pollution (Moloo and Stoisser 2020).
5. In 2007, Trafigura paid the Ivory Coast government $200 million as a fine to avoid any further legal prosecution (Trafigura n.d.).

2.2.11 Kingston Fossil Plant Fly Ash Spill

Date: December 22nd, 2008

Contaminant: Fly ash particles. Fly ash particles are components of coal ash. Coal ash is a by-product of coal combustion (Evans 2014). Fly ash particles can cause major respiratory problems in the human body. They can also cause asthma and inflammation of the lungs. In high concentrations, fly ash particles are linked to heart diseases, cancer, strokes and even death (Evans 2014).

Geographical significance: Emory River is a river that starts in Cumberland County, Tennessee, and flows through Morgan County and Roane County, before draining into Clinch River (G.P.O. 1892). By the residents and tourists, Emory River is well-known for fishing, paddling, kayaking and rafting (Tennessee n.d.).

Involved company: Tennessee Valley Authority (TVA). Tennessee Valley Authority is a US governmental agency that was founded in 1933 (Britannica 2020). Its primary goal is the maintenance and control of the Tennessee River. It is involved in the construction of dams, control of floods and production of electrical power in the form of hydroelectric energy (along the Tennessee River) (Britannica 2020). The board of the TVA is directly selected by the president of the United States and approved by the US Senate (Britannica 2020).

Event: On December 22nd, 2008, a dike, comprised roughly 20 million cubic yards of coal ash, at the TVA-owned hydroelectric plant, on Emory River in Roane County, failed (TVA n.d.). As a result, about 5.4 million cubic yards of fly ash particles were released from the plant. Upon mixing with the water, the fly ash particles generated a very large wave of sludge that clogged the river, damaged a railway, broke a natural gas pipeline and interrupted the distribution of electric power in the area (TVA n.d.).

Causes

1. The foundational layer of coal ash sludge was reportedly unstable. TVA was unable to detect this instability in any of its analyses of the plant (Bourne 2019).
2. Improper handling, control, storage and monitoring of toxic waste pollutants like coal ash and its components (Bourne 2019).

Aftermath

1. Due to improper preparation and lack of protective gear provision by the TVA, 36 workers who participated in the clean-up of Emory River died from brain cancer, lung cancer, leukaemia and other diseases that were a direct result of

exposure to high concentrations of fly ash particles (Bourne 2019). Hundreds of workers were also diagnosed with respiratory illnesses, cancer, neurological disorders and other health conditions due to exposure to fly ash particles without proper protection (Gaffney 2020). As a result, 200 workers have been involved in a lawsuit against the TVA, demanding compensation for its negligence (Bourne 2019).

2. New dikes and weirs were constructed in order to contain the toxic sludge (TVA n.d.).
3. A three-phase clean-up plan was initiated by the TVA under directions from the US Environmental Protection Agency (EPA) (TVA n.d.).
4. The Tennessee Department of Environment and Conservation levied a fine of $11.5 million on TVA for environmental and civil damages (Gang 2013).

2.2.12 Mayapuri Radiological Accident

Date: April 8th, 2010

Contaminant: Cobalt-60 (Co-60). Cobalt-60 is a metallic radioisotope that is primarily used in the medical industry for radiation therapy (Radioisotope 2018). It is also used in several industries to detect structural flaws in gauges and other mechanical units. Furthermore, Cobalt-60 is used in irradiation and sterilization processes. Cobalt-60 decays by gamma radiation; thus, it can have adverse effects on human health. Exposure to Cobalt-60 can result in skin burns, acute radiation sickness and even death (Radioisotope 2018).

Geographical significance: Mayapuri is an industrial area in New Delhi, India. It is often referred to as the ‘junk metal capital of India’ (Jha 2011). Scrap metal is imported from the rest of the world to Mayapuri in large quantities, to be sold to scrap dealers. Since the radiological accident, government sanctions have reduced and monitored the import of scrap metals into Mayapuri (Jha 2011).

Involved company: Delhi University (DU). Delhi University is one of India’s most prestigious universities (About 2021). It was established in 1922 and offers 500 programmes for higher education. DU has grown into one of the largest universities in India. The chemistry, geology, zoology, sociology and history departments of DU have been conferred the position of the centres of advanced studies for their respective fields in India. DU is involved in teaching, research and community outreach (Delhi University 2021).

Event: Gamma irradiators are process units that are used for sterilization and irradiation. Gamma irradiators operate by exposing the product, to be sterilized, to gamma radiation; one of the most commonly used sources of this gamma radiation is Cobalt-60. A gamma irradiator was purchased from Canada and brought to India in 1968. This was not used after 1985 and was in possession of Delhi University’s chemical department at the time of the incident (NDTV Correspondent 2011). In February 2010, DU’s chemical department auctioned the irradiator off to a scrap dealer in Mayapuri. The scrap dealer, unaware of the radioactive nature of the

Cobalt-60 pencils in the irradiator, disassembled the irradiator inadvertently, stripping the protective lead off the machinery. He then sold the pieces of the irradiator to other people who were all affected by the radioactive nature of the Cobalt-60, as they came in contact with it (NDTV Correspondent 2011).

Causes

1. Lack of monitoring the industrial sectors in the affected area. Had the concerned organizations monitored the sale of metal in the Mayapuri region, this accident could have been easily avoided.
2. Exposure of unprotected and unaware people to radioactive machinery. Delhi University and its chemistry department did not assess or monitor the potential ramifications of the sale of a radioactive piece of machinery to the general population.

Aftermath

1. After exposure to the radioactive Cobalt-60, one person died due to acute radiation sickness, and six others were hospitalized. Some of the victims displayed severe radiation burns. The surviving victims had to undergo comprehensive and expensive treatment, to recover from the effects of radioactive exposure (NDTV Correspondent 2011). Fragments of the stomach, thighs and legs of one of the victims had to be peeled off (NDTV Correspondent 2011).
2. In 2011, six professors of DU's chemistry department were charged for causing injuries and death and for endangering lives due to ignorance and negligence (NDTV Correspondent 2011).
3. The Atomic Energy Regulatory Board (AERB) of India and associated authorities took drastic measures to monitor the handling of radioactive substances and to prevent unapproved research organizations and institutions from handling them to prevent such accidents from happening again (Remesh and Vinod 2010).

2.2.13 Deepwater Horizon Oil Spill

Date: April 20th, 2010

Contaminant: Crude oil. Refer to Sect. 2.2.8.

Geographical significance: The Gulf of Mexico is a body of water that is partially surrounded by North America (Geyer et al. 2020). The Gulf of Mexico is known for its biological diversity, exemplified by the presence of different species of fish and birds. It is known to have substantial deposits of petroleum and natural gas and is famous for many recreational activities including boating, swimming and fishing (Geyer et al. 2020).

Involved company: Beyond Petroleum (BP). Beyond Petroleum, formerly known as British Petroleum, is a British multinational oil and gas company that was founded in 1909 (Sönnichsen 2021). BP is involved in the upstream and downstream processes of petroleum operations. BP conducts exploration, production, processing and distribution of petrochemicals across the world (Sönnichsen 2021).

Event: On April 20th, 2010, one of Beyond Petroleum's offshore oil drilling rigs, Deepwater Horizon, exploded, burned and eventually sank in the Gulf of Mexico (Deepwater n.d.). The incident occurred when the crew on board was attempting to close an exploratory well in the Gulf of Mexico (Borunda 2020). A surge of gas damaged the drill pipe. The emergency blowout protector failed; thus, the gas leaked onto the oil rig. This triggered an explosion after which approximately 134 million gallons of oil spilled into the Gulf of Mexico, over three subsequent months (Summerhayes 2011). Figure 2.1 illustrates an explosion on BP's oil rig (Pallardy 2021).

Causes

1. Improper maintenance of safety protocol by the company. Beyond Petroleum did not verify the operation of the emergency blowout protector (a valve designed to prevent explosions on an oil rig) (Borunda 2020). Several other safety protocols were also overlooked by BP through the entire drilling process (Summerhayes 2011).
2. Lack of training, combined with unawareness and unpreparedness of the crew on board on the oil rig, which was a cause of accident (Summerhayes 2011). The crew missed several signs of a potential explosion before the blowout occurred.

Fig. 2.1 The BP oil rig explosion (BP oil rig explosion n.d.)

The crew could have prevented or diminished the impact of the explosion, had it been able to detect these signs and respond to them (Summerhayes 2011).

Aftermath

1. The explosion of Deepwater Horizon resulted in the death of 11 crewmembers (Borunda 2020).
2. The incident was recorded as the largest oil spill in the history of the United States. The quantity of oil spilled was approximately 12 times that of the Exxon Valdez disaster (Borunda 2020).
3. While the extent and impact of the oil spill has still not been fully evaluated, the incident has had disastrous consequences on the marine ecosystem in the Gulf of Mexico in the form of sediment contamination and the death of several aquatic animals (Borunda 2020).
4. As a result of this disaster, the Bureau of Safety and Environmental Enforcement (BSEE) was created to monitor and regulate offshore oil drilling and impose appropriate safety protocol (Borunda 2020).
5. Beyond Petroleum was required to pay around $13 billion for remediation, reparation and damage of natural resources. BP was also instructed to pay an estimated $20 billion in fines and compensations (Borunda 2020).

2.2.14 Ajka Alumina Plant Accident

Date: October 4th, 2010

Contaminant: Red mud mixed with spent caustic.

Geographical significance: Ajka is a city in Hungary that is located on the hills of Bakony. Ajka has a population of approximately 35,000 and is known for the Ajka alumina plant accident (Ajka n.d.).

Involved company: MAL Hungarian Aluminium. MAL Hungarian Aluminium was a Hungarian company that was involved in the production of aluminium and aluminium-related products (MAL n.d.). It was founded in 1995 and its biggest asset was the Bakony bauxite mine, as a part of an alumina factory in Ajka. In 2013, the company was liquidated, and all its properties and assets were sold to inorganic chemical manufacturing company, IC Profil Limited (MAL n.d.).

Event: MAL Hungarian Aluminium was involved in the production of aluminium. The refinement of bauxite is an important step in the aluminium production process. A major by-product of the bauxite refining process is spent caustic mixed with red mud, which is a highly alkaline red sludge (Accident n.d.). On October fourth, 2010, the retaining wall of a sludge reservoir at the Bakony bauxite mine was breached, leading to the spillage of approximately 1,000,000 m^3 of red sludge (Taylor 2011). This caused a wave of red sludge to flood nearby villages and rivers in Ajka (Taylor 2011). Figure 2.2 illustrates red sludge release from an alumina plant accident.

Fig. 2.2 Red sludge from alumina plant accident (Red sludge n.d.)

Causes

1. Improper disposal of toxic chemical waste in a poorly designed reservoir, located adjacent to residential areas (Taylor 2011).
2. Improper maintenance of the sludge reservoir tank and ignorance of faulty signs at the site (Pangalos 2019). The operators of the plant reportedly ignored signs of concern in the sludge reservoir and continued to operate without implementing appropriate chemical safety protocols (Pangalos 2019).
3. Misleading the general population regarding the actual quantity and alkalinity of the sludge released (Pangalos 2019).
4. Inappropriate storage, maintenance and processing of toxic waste produced by the Bakony bauxite mine (Pangalos 2019).

Aftermath

1. Ten people died, including a 14-month-old baby, as a result of the accident (Pangalos 2019). At least 120 others were injured and suffered from severe chemical burns (Taylor 2011). The marine ecosystems of nearby rivers were also negatively impacted; nearly all marine life in the adjacent rivers came to an end (Taylor 2011). The flood of red sludge also damaged numerous homes and submerged several cars at the time of the incident (France-Presse 2016).
2. At the time of the accident, the Hungarian government declared a national emergency and evacuated 8000 people from nearby areas (France-Presse 2016).
3. In 2015, Budapest established a compensation fund for the victims of the accident in Ajka (France-Presse 2016).

4. A clean-up drive was implemented to remediate the area affected by the accident, and authorities levied a fine of approximately $647 million on MAL Hungarian Aluminium for environmental reparations (Taylor 2011).
5. In 2019, the criminal negligence case, filed against 15 people, involved in the operation of the plant resulted in the conviction of 10 due to disregarding adequate safety protocol and maintenance of the Bakony bauxite mine (Pangalos 2019).

2.2.15 X-Press Pearl Disaster

Date: May 20th, 2021.

Contaminant: Nurdles, nitric acid (HNO_3), sodium hydroxide (NaOH) and several other potential chemical toxicants (Ellis-Petersen 2021). Nurdles are tiny, plastic balls (pellets) that are used for making several plastic products (The Problem n.d.). Nurdles are possibly toxic if they make their way into the food chain. Marine animals can mistake nurdles for food and consume them; eventually, due to bioaccumulation, it could make its way into the human body (The Problem n.d.). Nitric acid is used in the manufacture of fertilizers, polymers and dyes (Nitric Acid 2018). It is a highly corrosive chemical and can cause several medical issues such as bronchitis and pneumonitis (Nitric Acid 2018). Sodium hydroxide is used in the manufacture of dyes, paper and soaps (Sodium Hydroxide 2019). It is a highly corrosive chemical and can cause allergic reactions and irritation to the eyes and skin (Sodium Hydroxide 2019).

Geographical significance: Negombo is a city that is located on the west coast of Sri Lanka (Negombo n.d.). Negombo is one of Sri Lanka's most popular resort cities and is often regarded as one of Sri Lanka's major transportation centres (Negombo n.d.). Negombo has several attractive beaches and has a population of approximately 130,000 people (Negombo n.d.).

Involved company: EOS RO PTE. Ltd. is a Singaporean company that began operation in late 2020. EOS RO PTE. Ltd. is primarily involved in the scheduled shipping lines industry (EOS RO n.d.).

Event: On May 20th, 2021, X-Press Pearl, a cargo ship owned by EOS RO PTE. Ltd., caught fire off coast of Sri Lanka (Sirilal and Illmer 2021). The fire was caused by a nitric acid leak from some containers; the leak was detected by the crew, but it was not handled efficiently (Sirilal and Illmer 2021). Upon detection of the leak, the captain of the ship tried to offload the compromised containers in two neighbouring countries; but permission to offload was denied (Chambers 2021). The ship was carrying more than 1400 containers of chemicals. Many of these chemicals are potentially dangerous and, at the time of this writing, could have leaked into the sea due to the fire and subsequent explosions (Satellite 2021). This disaster is being reported as one of the worst environmental disasters in Sri Lankan history (Ellis-Petersen 2021).

Causes

1. Improper storage of potentially hazardous chemicals and inability to deal with a potential leak.
2. Poor containment of the hazardous chemicals being transported (Chambers 2021).
3. Lack of concern and delay in taking appropriate measures at the time of discovering the leak (Sirilal and Illmer 2021).

Aftermath

1. The fear of the catastrophic effects on marine life, as a result of hundreds of tonnes of ship fuel spilling into the sea, is still imminent as of this writing (Sirilal and Illmer 2021).
2. It is feared that several tonnes of nitric acid, sodium hydroxide and other toxic chemicals have already leaked into the sea. This could environmentally devastate Sri Lanka for decades (Sirilal and Illmer 2021).
3. Nurdles have already washed up on the shores of the Negombo beaches. Fish, dolphins and turtles have been found dead at the beaches as a result of ingesting these nurdles. Consequently, fishing has been banned within a 50 mile radius of the incident, which has negatively impacted the livelihoods of several fishermen in Sri Lanka (Ellis-Petersen 2021).
4. At the time of this writing, the crew of the ship has been intensely interrogated by the Sri Lankan police to identify the culprit of this disaster (Sirilal and Illmer 2021).
5. Several navy personnel and specialists have been employed to clean up the hazardous wastes that have already washed up on the Sri Lankan shore (Ellis-Petersen 2021).

2.3 Summary

The case studies discussed in this chapter are summarized in Table 2.1. This chapter discussed 15 hazardous waste mismanagement incidents that took place worldwide, from the past to the present. Each incident described highlights the companies involved, contaminant properties, geographical significance of the affected areas, causes of contamination and the aftermath. The causes of each disaster can be attributed to mismanagement of hazardous wastes, human error, negligence, ignorance of protocol and prioritizing economic gain over safety. The catastrophic repercussions of these incidents affected the lives of not only the employees working for each of these companies but also innocent people who inhabited the surrounding areas. Most of the companies involved were forced to work with local and international organizations to remediate contaminated sites and to pay fines and monetary compensations for the damages caused to human and animal lives, properties and ecosystems as a whole.

Table 2.1 Summary of all case studies with relevant information

Case study	Year	Contaminant	Involved company	Major consequence
Minamata methylmercury poisoning	1959	Methylmercury	Nippon Chisso Hiryo Corporation	2955 people were affected, of which 1784 died
Seveso disaster	1976	2,3,7 and 8 tetrachlorodibenzoparadioxin (TCDD)	Industrie Chimiche Meda Società Azionaria (ICMESA)	219 people were affected
Love Canal disaster	1978	2,3,7 and 8 tetrachlorodibenzoparadioxin (TCDD) and 200 other contaminants	Hooker chemical company	700 families were evacuated
Sydney tar ponds	1980	Coal tar	Sydney steel Corporation (SYSCO)	25,000 people were affected
Times Beach evacuation	1982	2,3,7, and 8 tetrachlorodibenzoparadioxin (TCDD)	The bliss waste Oil company	The town was completely evacuated
Bhopal gas tragedy	1984	Gaseous methyl isocyanate (C_2H_3NO)	Union carbide Corporation (UCC)	105,000 people were affected, of which 3000 died
Hinkley groundwater contamination	1987	Hexavalent chromium (Cr^{6+})	Pacific gas and electric company (PG&E)	12 families exhibited effects of contamination
Exxon Valdez oil spill	1989	Crude oil	Exxon	4 workers died as a result of clean-up operations
DuPont C8 lawsuit	1999	Perfluorooctanoic acid (PFOA)	DuPont	80,000 residents and several employees were affected
Ivory Coast toxic waste dump	2006	Spent caustic	Trafigura	108,000 people were affected, of which 15 died
Kingston fossil plant fly ash spill	2008	Fly ash particles	Tennessee Valley authority (TVA)	236 workers involved in clean-up operations were affected, of which 36 died
Mayapuri radiological accident	2010	Cobalt-60 (co-60)	Delhi University (DU)	7 people were affected, of which 1 died
Deepwater Horizon oil spill	2010	Crude oil	Beyond petroleum (BP)	11 crewmembers died

(continued)

Table 2.1 (continued)

Case study	Year	Contaminant	Involved company	Major consequence
Ajka alumina plant accident	2010	Red mud mixed with spent caustic	MAL Hungarian Aluminium	130 people were affected, of which 10 died
X-press pearl disaster	2021	Nurdles, nitric acid (HNO_3) and sodium hydroxide (NaOH)	EOS RO PTE. Ltd.	No information available at the time of this writing

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Chapter 3
Conventional and Emerging Practices in Hazardous Waste Management

Zaeem Bin Babar, Rizwan Haider, and Hamed Sattar

3.1 Introduction to Solid Waste

Solid waste includes garbage (i.e., useless food waste and containers), refuse (i.e., metal scraps), sludges and industrial wastes from wastewater treatment plants, air pollution control facilities and manufacturing industries, and other unwanted solid, semi-solid, liquid, and gaseous materials (RCRA 2014).

In 2016, the world generated approximately 2.01 billion tons of solid waste and roughly 33% of which was not properly managed in an environmentally friendly and economical way. The solid waste generation in 2016 and the projected solid waste generation for years 2030 and 2050 in various regions of the world are presented in Fig. 3.1. In 2016, the top contributor in global waste generation was the region of East Asia and Pacific which generated 468 million tons of solid waste followed by Europe and Central Asia which generated approximately 392 tons of solid waste in the same year. Additionally, Middle East and North Africa made least contribution of approximately 129 million tons to the worldwide solid waste generation (Kaza et al. 2018).

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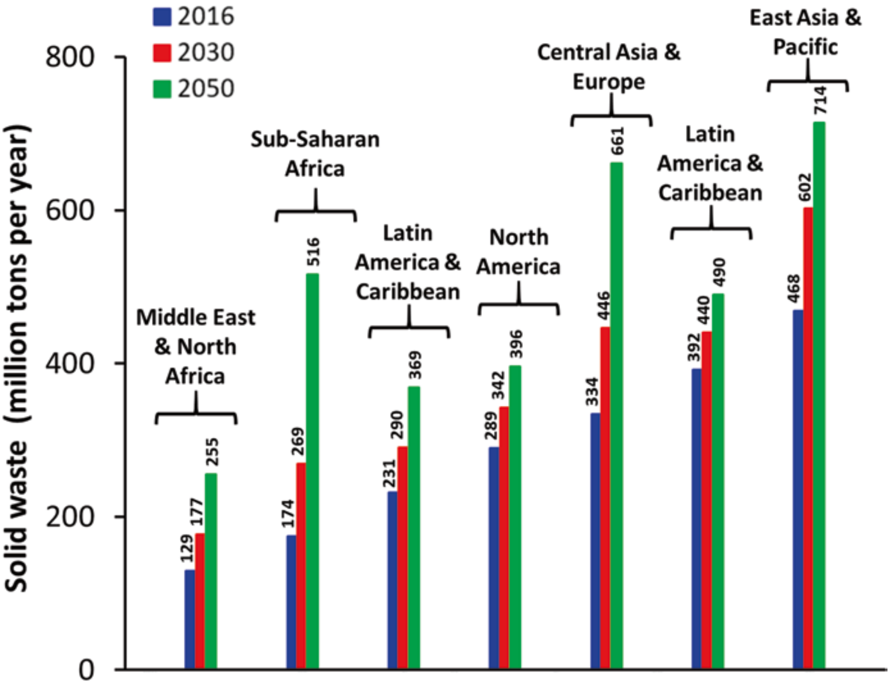

Fig. 3.1 Estimated solid waste generation in 2016 and the projected solid waste generation for the years of 2030 and 2050 in various regions of world (Kaza et al. 2018)

It is estimated that by year 2050, global solid waste generation will increase by 69% to nearly 3.4 billion tons yearly. Worldwide, the daily average waste generation per capita is about 0.74 kg and typically ranges between 0.11 kg and 4.54 kg. The regions of sub-Saharan Africa, Middle East and North Africa, and South Asia are the fastest in contributing to the global solid waste generation by year 2050. For instance, it is evident from Fig. 3.1 that for the region of sub-Saharan Africa, the waste generation in year 2016 was 174 million tons which is expected to increase by approximately 197% to 516 million tons in year 2050. Similarly, waste generation by Middle East and North Africa and South Asia will be increased by 98% in year 2050. However, these countries do not have appropriate waste collection, treatment, and disposal facilities. In fact, it is reported that nearly half of the waste is dumped openly, and considering the waste generation projections of these regions for year 2050, the generated waste will have a significant impact on human health and the environment (Kaza et al. 2018).

3.2 Types of Solid Waste

Solid waste is typically characterized into two major types: nonhazardous solid waste and hazardous solid waste (Bulucea et al. 2010).

3.2.1 Nonhazardous Waste

Any waste material that does not pose detrimental effects on human health and the environment (RCRA 2014; Kanagamani et al. 2020) is known as nonhazardous waste. Typical examples of nonhazardous waste include discarded food, paper, cardboard, plastics, leather, yard wastes, wood, glass, metals, etc. from residential, commercial, industrial, and institutional sources (Tadesse 2004; RCRA 2014).

3.3 Hazardous Waste

Hazardous waste is any waste that has inherent physicochemical properties or infectious characteristics that may cause harmful effects on human health and the environment when managed in an improper way (US EPA 2005; RCRA 2014).

3.3.1 Hazardous Waste Classification

The US Environmental Protection Agency (US EPA) has listed 450 hazardous wastes (eCFR 2021a). These waste are classified into four lists. The details are given below.

F List

The F list consists of hazardous wastes which are generated from nonspecific sources such as industrial and manufacturing operations. This list comprises of solvents generally used for degassing and metal treatment purposes, waste generated from metal plating processes, and dioxin-based chemicals (US EPA 2012). The hazardous wastes in the F-list are characterized by hazardous waste numbers from F001 to F039 allotted by US EPA (eCFR 2021a). Examples of such solvents include toluene (F001), benzene (F001), tetrachloroethylene (F002), methanol (F003), cresylic acid (F004), methyl ethyl ketone (F005), etc. (eCFR 2021a).

K List

Hazardous wastes in the K list are generated by specific industrial processes such as wood-preserving processes, manufacturing of inorganic pigments and pharmaceuticals, production of organic and inorganic chemicals, metal production, explosive manufacturing, and coking operations. The hazardous wastes in the K-list are characterized by hazardous waste numbers from K001 to K178 (eCFR 2021a).

P and U Lists

The hazardous wastes comprising of useless commercial chemicals, products, chemical intermediates, products which fail quality specifications, and container and spill residues are included in P and U lists. Examples of such waste include substances such as arsenic acid, barium cyanide, carbosulfan, diethylarsine, dinoseb, endrin, hydrogen cyanide, ziram, vanadium oxide, acetonitrile, benzal chloride, chloroform, dichlorobenzene, formaldehyde, mercury, etc. The hazardous wastes in the P and U lists are characterized by hazardous waste numbers from P001 to P205 and U001 to U411, respectively (eCFR 2021a).

3.3.2 Characteristics of Hazardous Waste

Hazardous wastes exhibit the following fundamental characteristics (eCFR 2021a).

Ignitibility

A waste is considered ignitable and hazardous if it exhibits any of the following properties:

1. For the case of liquid with alcohol less than 24% (v/v) and water at least 50% (wt./wt.) and that has flash point of the less than 60 °C as estimated by ASTM methods of ASTM D93–79, D93–80, D3278–78, D8174–18, or D8175–18.
2. If the waste is not a liquid and at standard temperature and pressure it has the ability to catch fire via friction, moisture absorption, and chemical change. Additionally, if it burns in a violent manner such that it poses a serious hazard.
3. In case of compressed gas, if it forms a flammable mixture of equal or less than 13% (v/v) with air or the flammable range with air is wider than 12% regardless of the lower limit. These limits will be considered at atmospheric temperature and pressure. The sampling and testing method will be in accordance with ASTM standard E 681–85.
4. If it is an oxidizer such as chlorate, permanganate, and inorganic peroxides and nitrates that can readily liberate oxygen to facilitate the combustion of organic material.
5. If the US EPA hazardous waste number is D001.

Corrosivity

A waste is considered corrosive if the representative sample of the waste possess any of the following properties:

1. For the case of aqueous solution with a pH less than or equal to 2 or greater than or equal to 12.5.

2. If the waste is a liquid and corrodes carbon steel (SAE 1020) with a typical composition in which carbon, manganese, phosphorous, and sulfur are 0.20%, 0.45%, 0.04%, and 0.05% at a rate greater than 6.35 mm per year at a temperature of 55 °C.
3. If the waste is solid with US EPA hazardous waste number of D002.

Reactivity

A waste is considered reactive if the representative sample of the waste possess any of the following properties:

1. If a waste under normal conditions is unstable and undergoes violent transformation without detonation.
2. If the reaction of the waste with water is violent.
3. If the waste forms explosive mixtures with water.
4. If the mixture of waste with water generates toxic gases and vapors or fumes in a significant quantity which may pose health and environmental hazards.
5. If the waste comprises of a cyanide or sulfide which can produce toxic gases and vapors or fumes within pH range of 2–12.5 in a significant quantity which may pose health and environmental hazards.
6. If the waste has the ability to detonate and explode in a confined place when subjected to heat.
7. If the waste under standard temperature and pressure has the capability to detonate or explode via decomposition or reaction.

Toxicity

A waste is considered toxic if the representative sample of the waste when subjected to a test from a certified laboratory contains contaminants such as arsenic, benzene, cadmium, etc., at levels greater than the permissible limits as presented in the list of contaminants given in Table 3.1.

3.4 Hazardous Waste Generators

A hazardous waste generator may be any person or an establishment or a site which produces hazardous wastes. US EPA has classified the hazardous waste generators in three categories based on the amount of their hazardous waste generation per month: very small quantity generators (VSQGs), small quantity generators (SQGs), and large quantity generators (LQGs) (eCFR 2021b). The details of the hazardous waste generators are described as follows:

Very small quantity generators (VSQGs). The limit for VSQGs to store a hazardous waste at a given time is 1000 kg. Additionally, they have to make sure that hazardous waste is dispatched to the approved facilities for its subsequent handling.

Table 3.1 List of toxic contaminants with specific permissible limits (eCFR 2021a)

US EPA hazardous waste number	Contaminant	Permissible limit (mg L^{-1})
D004	Arsenic	5
D005	Barium	100
D018	Benzene	0.5
D006	Cadmium	1
D019	Carbon tetrachloride	0.5
D020	Chlordane	0.03
D021	Chlorobenzene	100
D022	Chloroform	6
D007	Chromium	5
D023	o-cresol	200
D024	m-cresol	200
D025	p-cresol	200
D026	Cresol	200
D016	2,4-D	10
D027	1,4-dichlorobenzene	7.5
D028	1,2-Dichloroethane	0.5
D029	1,1-Dichloroethylene	0.7
D030	2,4-Dinitrotoluene	0.13
D012	Endrin	0.02
D031	Heptachlor (and its epoxide)	0.008
D032	Hexachlorobenzene	0.13
D033	Hexachlorobutadiene	0.5
D034	Hexachloroethane	3
D008	Lead	5
D013	Lindane	0.4
D009	Mercury	0.2
D014	Methoxychlor	10
D035	Methyl ethyl ketone	200
D036	Nitrobenzene	2
D037	Pentachlorophenol	100
D038	Pyridine	5
D010	Selenium	1
D011	Silver	5
D039	Tetrachloroethylene	0.7
D015	Toxaphene	0.5
D040	Trichloroethylene	0.5
D041	2,4,5-Trichlorophenol	400
D042	2,4,6-Trichlorophenol	2
D017	2,4,5-TP (Silvex)	1
D043	Vinyl chloride	0.2

Small quantity generators (SQGs). Their limit for the on-site accumulation of hazardous waste is 6000 kg for a period of 180 days without any permit. However, for the case of hazardous waste transportation to a distance exceeding 200 miles, SQGs can accumulate hazardous waste for 270 days. It is not mandatory for SQGs to have detailed contingency plans regarding hazardous waste; however, they are required to have one trained person to handle emergencies relevant to the hazardous waste.

Large quantity generators (LQGs). There is no limit on the on-site accumulation of hazardous waste with respect to the amount. They can store hazardous waste on-site for 90 days. Additionally, they must submit a biyearly report on hazardous waste.

It is mandatory for SQGs and LQGs to manage hazardous waste as per rules and regulations mentioned in Code of Federal Regulations (eCFR 2021b).

3.5 Hazardous Waste Sources

All the sources which generate waste (solid, liquid, and gas) listed in F, K, and P and U lists and possess characteristics as described in Sect. 3.2 are considered as sources of hazardous waste. The common sources of hazardous waste include process plants, manufacturing and agricultural industries, public institutions, scientific laboratories, mining and mineral processing sites, etc. (Tadesse 2004; Grasso et al. 2009). The details of various sources of hazardous waste are given below.

Household sources. Domestic waste contains a variety of hazardous substances such as household cleaners and detergents, aerosol sprays, gardening material, various types of paint, beauty and healthcare products, solvents, electronic waste (batteries, dry cells, etc.), medicines, herbicides, pesticides, and automotive parts (Slack et al. 2007; Mbeng et al. 2010; Dangi et al. 2011; Al-Tamimi et al. 2018).

Commercial sources. Commercial waste is typically discharged by a business, service providers, and relevant establishments such as gasoline and diesel stations, automobile workshops, etc. (Tadesse 2004; Grasso et al. 2009). The composition of any commercial waste generally depends on the services provided by them.

Institutional sources. Institutional hazardous waste sources generally include public and government offices, educational centers such as universities, research institutes and laboratories, and military establishments for manufacturing, testing, and storing ammunitions and military equipment (Grasso et al. 2009).

Healthcare units. Healthcare centers such as hospitals, clinics, blood banks, medical laboratories, etc. discharge waste comprising of human blood, infectious needles, containers, and discarded packages (Grasso et al. 2009).

Industrial sources. Hazardous waste is generated by various industrial processes. The nature of the waste depends on the type of industrial processes. For instance, waste and impurities such as tar and cyanides are categorized as hazardous waste which are typically discharged from petroleum refineries. Similarly, waste-laden agrochemicals which are generated by agricultural industries or agricultural lands such as farms lies in the category of hazardous waste (Tadesse 2004; Grasso et al. 2009).

Mines and mineral processing sites. It is a well-established fact that waste generated from mining and mineral processing which is also known as tailing contains approximately three dozen chemicals including carcinogenic heavy metals, such as arsenic, mercury, etc., and processing chemicals such as acids and cyanides, which negatively impacts human health and environment (MiningWatch 2012).

3.6 Effects of Hazardous Waste on Human Health and Environment

Improper hazardous waste management occurs in both high- and low-middle-income countries. However, it is more common in low-middle-income countries (Fazzo et al. 2017). Improper management of hazardous waste such as open dumping or dumping in nonregulated countries has a detrimental effect on human health, quality of the environment, crops and vegetation, and soil quality.

An open dump site is defined as a location or a site at which solid wastes are discarded in such a way that pose risks to nearby environment and community (FedCenter 2021). The leachate from an unmanaged dump site and waste effluent from process and manufacturing industries are typically composed of a variety of hazardous contaminants such as heavy metals and dissolved organic compounds (Amadi et al. 2017). Typical examples of such toxic heavy metals and organic compounds are cadmium (Cd), lead (Pb), mercury (Hg), arsenic (As), zinc (Zn), and copper (Cu) and vinyl chloride, benzene, benzo(a)pyrene, chloroform, 1,2-dichloropropane, beta-hexachlorocyclohexane (b-HCH), and dichlorodiphenyl-trichloroethane (DDT) (Boberg et al. 2011; Fantini et al. 2012). Also, in the last few decades, incineration of the solid hazardous waste is one of the common practices worldwide for their disposal with certain advantages such as energy recovery and volume reduction (Domingo et al. 2020). However, incineration of the solid wastes emit toxic chemicals, such as polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs), and heavy metals such as As, Cd, Hg, and Pb (Cheng and Hu 2010; Vilavert et al. 2015; Rovira et al. 2018). During incineration, heavy metals are majorly present in bottom and fly ash, with certain quantities being emitted into the atmosphere in the form of particulate matter and vapors (Peng et al. 2020).

Exposure to persistent organic compounds such as vinyl chloride and 1,2-dichloropropane causes hepatic cancer (IARC 2006). Hepatotoxic hazardous substances occur in both natural and synthetic forms. The common synthetic hepatotoxic agents in hazardous waste are aromatic and halogenated compounds which lead to hepatic cancer. Another study reported positive association of benzo(a) pyrene with bladder cancer (US EPA and IRIS 2017). b-HCH (Fantini et al. 2012) and dioxins (Fazzo et al. 2017) were reported to be associated with bladder and liver cancers. The areas contaminated by vinyl chloride (IARC 2006), b-HCH (Fantini et al. 2012), and benzene (Boberg et al. 2011) were found to be linked with non-Hodgkin lymphoma (NHL), a cancerous disease of white blood cells. PCDDs and PCDFs are known carcinogens in both human and animals (IARC 2006). Asthma was also reported among residents living near hazardous waste sites contaminated with PCDDs, PCDFs, and PCBs (Ma et al. 2005; Carpenter et al. 2008). Heavy metals are nonbiodegradable and persistent and accumulate in human body and the environment (Gonzalez et al. 2018). Additionally, some heavy metals are toxic even in extremely low concentrations and cause acute diseases such as skin lesions and neurological and respiratory disorders (Hartwig and Jahnke 2012; Menon et al. 2016; Weiss and Craver 2017). Aforementioned heavy metals such as As, Pb, Cd, and Hg are potentially carcinogenic, mutagenic, and teratogenic (Lansdown 2014). For instance, Pb, Cd, and Hg were found to be associated with liver cancer, NHL, and diabetes and respiratory diseases such as asthma (Fantini et al. 2012). Another study (Querejeta and Alonso 2019), on the linkage between air quality and cancer incidents near hazardous waste incineration plants using generalized additive modeling, reported that cancer incidents were higher near the vicinity of the plants.

Soil fertility and groundwater quality are affected by the aforementioned hazardous contaminants present in the leachate and industrial waste effluents which render them nonproductive and unhealthy, respectively. Soil fertility is directly linked to crop production. Consequently, open dump site with hazardous waste negatively impacts crop production and vegetation (Katnoria and Sharma 2020).

3.7 Hazardous Waste Management

Hazardous waste management comprises of methods, systems, approaches, guidelines, and strategies to minimize or eliminate the effect of hazardous waste on human health and the environment (Amadi et al. 2017). The ultimate aim of a hazardous waste management plan is effective, safe, and economical collection, transportation, treatment, and disposal of hazardous waste in both present and futuristic scenarios (Misra and Pandey 2005). The main steps involved in a typical hazardous waste management system are minimization, collection and transportation, treatment, and disposal as presented in Fig. 3.2.

3.7.1 Hazardous Waste Minimization

Waste minimization is a management system that targets the reduction in the amount and toxicity of generated hazardous waste. The US EPA defines the concept of waste minimization as utilization of source reduction and/or environmentally friendly recycling methods prior to energy recovery, treatment, or disposal of wastes. Waste minimization does not include any waste treatment processes such as

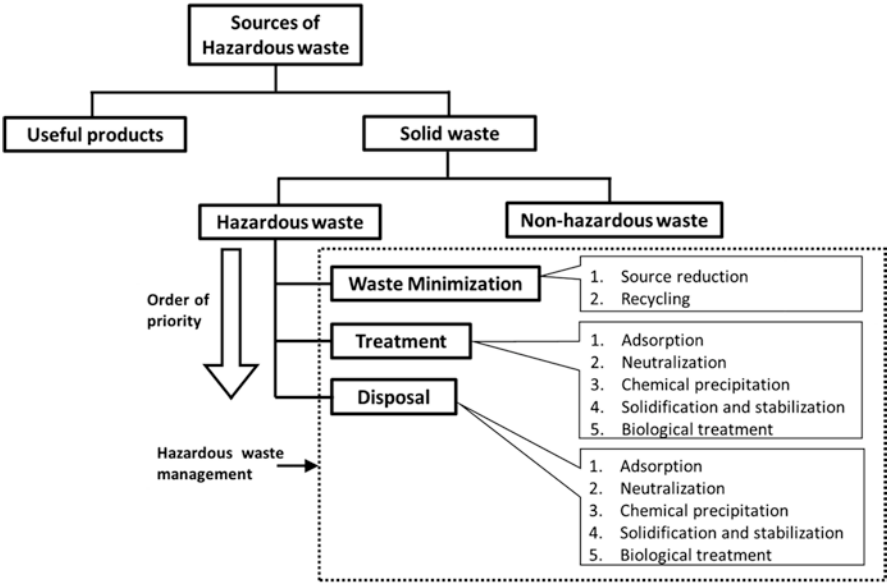

Fig. 3.2 Typical structure of hazardous waste management

neutralization, dilution, and incineration that change the physical, chemical, or biological compositions of the waste processed (US EPA 2016). Waste minimization emphasizes on less generation of the waste rather than targeting its treatment and disposal after generation.

Waste minimization offers multiple benefits. Some of the major benefits are described below:

1. As mentioned earlier in the Sect. 3.3 titled "Hazardous Waste Generators," it is mandatory for SQGs and LQGs to manage hazardous waste as per rules and regulations described in the Code of Federal Regulations. In addition to the fact that waste minimization by the waste generators is one of the best hazardous waste management practices, the inclusion of a detailed hazardous waste minimization plan further ensures their compliance with the regulatory bodies (i.e., US EPA). Furthermore, a comprehensive waste minimization plan can support the hazardous waste generators to reduce waste in certain ways that they can even "downgrade" their generator status or cannot be further subjected to the rules and regulations as given in the Code of Federal Regulations (US EPA 2016).
2. Minimizing waste aids in reducing the overall treatment expenditures associated with the treatment and disposal of hazardous waste (US EPA 2016; Green 2021).
3. Successful and robust waste reduction and recycling plans can significantly contribute to improved market share and revenues for generators (Green 2021).
4. Minimizing the amount of hazardous waste improves the overall workplace health as waste minimization substantially reduces the exposure of toxins to workers and customers (US EPA 2016; Green 2021).

5. Effective waste minimization strategies help generators to contribute significantly to a sustainable healthy environment and conserve natural resources by creating less polluted solid, liquid, and gaseous emissions (US EPA 2016; Green 2021).
6. Customers prefer utilizing products that are environmentally friendly. Thus, they are more inclined to purchase products from these manufacturers, and their purchasing is not necessarily based on the characteristic of the individual product (US EPA 2016).

To further explain the practicality of hazardous waste minimization using source reduction and recycling, two case studies regarding effective waste minimization strategies in industrial and manufacturing facilities and a scientific research institution (center or laboratory) are presented in detail as follows.

Case Study 1*:* Waste Minimization Strategies in Industrial and Manufacturing Facilities

There are various strategies which can be used by industrial and manufacturing facilities to reduce their waste generation. For instance, designated teams comprising of suitable personnel from specific areas of operations can be formed. The primary objective of such teams would be to develop and implement proposals and update senior management regarding progress of an integrated and comprehensive waste minimization plan throughout the facility (Green 2021).

In industries and manufacturing units, generation of hazardous waste can also be reduced by controlling the amount of raw materials used in the process. Additionally, required amount of raw materials should be ordered. This can be achieved by developing strict procedures comprising of guidelines for the purchasing, tracking, and managing of raw material inventory (Suprya 2021).

Waste reduction can also be accomplished by (a) utilizing more efficient and less or nonhazardous raw materials in the manufacturing process to yield a high-quality product and (b) improving the standard operating procedures and robust maintenance schedule of all equipment used in the industries. This will increase the efficiency of equipment and reduce the potential leakages and spills; (c) comprehensive training programs for the employees are one of the main elements in any waste minimization plan. Training programs should focus on standard operating procedures and process control of the equipment, recommended equipment maintenance plans and proper handling of waste material (Suprya 2021), and (d) manufacturing "green" or "sustainable" chemical products and processes to minimize toxic waste emissions which is referred to as "green chemistry" (US EPA 2021a).

In most industries, waste is discharged in the form of wastewater and sludge, and their treatment or disposal is expensive. Industries and manufacturers should find suitable methods to reduce the amount of water in their processes which would substantially reduce operational cost. In most cases, waste sludge is highly organic and thus can be reused by other companies (Green 2021). In addition, sludge can be recovered on-site or in an off-site facility using various physical and chemical techniques such as electrolysis, electrolytic recovery, centrifugation, etc., and the regenerated sludge can be further utilized for in-house manufacturing of other products commonly known as “closed loop manufacturing process” or can be used by other manufacturers (Suprya 2021; US EPA 2021a). For instance, mercury is recycled from old equipment such as switches and used in manufacturing new products such as fluorescent bulbs. In United States, mercury recycling is effective enough such that manufactures do not need to mine new mercury for its utilization (US EPA 2021a).

For companies and manufacturers that are interested in minimizing their waste, US EPA offers a voluntary program known as “WasteWise program.” Under this program, various resources including tools for planning, calculators for measuring progress, platforms to communicate results, and a free technical helpline are provided to facilities and companies in minimizing their waste in an effective and efficient manner (US EPA 2021b).

Case Study 2*:* Waste Minimization Strategies in a Scientific Research Institution

For the case of scientific research institution, strategies for waste minimization are given below.

It is important to maintain an accurate inventory of all laboratory chemicals as it facilitates in ordering the required amount of chemicals and, hence, avoids duplicate purchasing of the chemicals. Additionally, all the laboratory chemicals should be labelled with full chemical names and associated hazards (Yale 2016; The University of North Carolina at Charlotte 2019; College 2021).

Another way to significantly reduce the amount of hazardous chemicals in laboratory is to use less hazardous or nonhazardous chemicals or processes instead of hazardous ones. For instance, ethanol can be utilized instead of methanol for blotting purposes as the non-listed alcohols with concentrations less than 24% are not considered hazardous according to the US EPA. Secondly, hazardous and nonhazardous wastes should not be mixed as mixing will increase the amount or volume of hazardous waste (Yale 2016; College 2021).

“Mini or microscale chemistry” technique should be employed where applicable while performing experiments (College 2021). This is a method of performing experimental studies with small amount of chemicals without compromising on the quality and research outcomes. It offers several advantages: (1) it promotes waste minimization since small amount of chemicals are used, (2) the risk of exposure of laboratory personals to hazardous chemicals is substantially reduced, and (3) it reduces experimental cost.

Waste generated in laboratory can be recycled and reused. Common examples include commercial recycling of waste such as electronic equipment and batteries (lead acid, nickel cadmium, etc.) and purchasing gas cylinders from companies that can receive partially filled or empty cylinders. Additionally, surplus or unwanted chemicals can be utilized by other research laboratories and departments (Yale 2016; The University of North Carolina at Charlotte 2019; College 2021).

3.7.2 Transport of Hazardous Waste

Hazardous waste transporters are engaged in the off-site transportation of the hazardous waste. Off-site transportation of hazardous waste includes shipments from a hazardous waste generator's facility to another facility for treatment, storage, or disposal purpose. Transporter regulations do not apply to the on-site transportation of hazardous waste within a facility's property or boundary (RCRA 2014).

Hazardous waste transporters have to comply with transport regulations developed by the US EPA and the US Department of Transportation (US DOT) (RCRA 2014). Briefly, they are explained below:

1. All hazardous waste transporters must have respective unique EPA identification numbers assigned by the US EPA.
2. Without providing a proper manifest, a hazardous waste transporter cannot accept hazardous waste from any generator. However, recycling wastes from SQGs are exempted. Transporter should sign and date the provided manifest while receiving the waste and give a copy to the generator before leaving the hazardous waste generation facility.
3. It is mandatory for any hazardous waste transporter to deliver the exact quantity of the waste to the next designation with the manifest, which after should be signed and dated by the recipient after the subsequent handover of the hazardous waste. For the purpose of record keeping, transporter must keep signed and dated copy of the manifest for 3 years.
4. In case of accidental spill or leakage of hazardous waste, hazardous waste transporter is required to take appropriate actions to protect human health and environment. However, if the transporter does not have any US EPA identification number, then federal, state, or local authorities can authorize to take immediate measures to avoid its impact on human health and the environment.
5. In case of serious spill or leakage, it is mandatory for the transporter to inform the National Response Center (NRC) as required by US DOT regulations.

3.7.3 Conventional and Emerging Practices for Hazardous Waste Treatment

Adsorption Via Activated Carbon

Activated carbon is produced from the physical or chemical activation of carbon or charcoal obtained from the pyrolysis of lignocellulosic-based materials with high carbon content (Ahmad and Azam 2019). The physical or chemical treatment generates high surface areas of produced activated carbon to facilitate surface adsorption. In physical activation, initially bulk of the volatile content is removed, and then the resulted carbon is activated using activators such as CO_2, steam, air, or a certain combination of aforementioned activators (Sudaryanto et al. 2006). In chemical activation, various chemical reagents, such as KOH, $ZnCl_2$, H_3PO_4, KCl, $CaCl_2.7H_2O$, $FeSO_4.7H_2O$, etc., are used (Lozano-Castelló et al. 2001; Nakagawa et al. 2004; Rahman et al. 2005; Kalderis et al. 2008; Chen et al. 2013). The typical activation temperature range in chemical activation is 450–850 °C (González-García 2018) lower than 800–1200 °C for physical activation (Danish and Ahmad 2018). Also, activated carbon yields obtained in chemical activation are higher than those obtained in physical activation. The activated carbon possessing large surface areas typically in the range of 500–1500 m^2g^{-1} and electrical charge is capable of adsorbing a wide range of hazardous materials such as heavy metals (Shekinah et al. 2002; Singh et al. 2008; Moreno-Piraján et al. 2011; Bernard et al. 2013) and chemical substances such as phenols and their derivatives (Jackson 2020).

In developed countries, more than 70% of activated carbon applications in effluent waste treatment are associated with wastewater treatment (Rodríguez-Reinoso 2001). In wastewater treatment, both granular and powdered forms of activated carbon are employed. The granular activated carbon has regeneration capability and is utilized in continuous processes. Due to its regeneration capacity, approximately 10% of new granular activated carbon is required each year to sustain processes, whereas the powdered form is typically employed in batch processes (Baker et al. 2003). Activated carbon is typically used for the removal of organic compounds such as chloroethenes (Yu and Chou 2000), chloroform (Tsai et al. 2008), and organo-halogenic disinfection by-products (Lee et al. 2015) from wastewater. In addition, it is also used to treat industrial waste effluents from chemical factories, fertilizer plants, and petrochemical industries due to its ability to adsorb a variety of pollutants including heavy metals, dyes, detergents, chlorinated solvents, phenols, and biphenyls (Ayranci and Hoda 2005; Wang et al. 2008; Chen et al. 2010; Jaradat et al. 2010; Bernard et al. 2013).

Emerging Practices

Consider an example for the removal of a hazardous organic from wastewater such as phenol. Oily sludge is a notable solid hazardous waste from the petroleum sector. It has complex composition and typically comprises of hydrocarbons, water, heavy metals, and solid particles. Owing to its increased generation worldwide, scientists and researchers are investigating the prospects of its treatment and/or effective utilization. In this context recently, Mojoudi and co-workers (Mojoudi et al. 2019) prepared highly efficient activated carbon from oily sludge via chemical activation using KOH and used it for the removal of phenol from wastewater. The optimized activated carbon exhibited a Brunner-Emmett-Teller (BET) surface area of 2263 m^2g^{-1}. The maximum adsorption capacity for phenol removal was 434 mg g^{-1} as per Langmuir adsorption isotherm with an optimum pH value of 6.0. The

Table 3.2 Comparison of BET surface areas and Langmuir adsorption capacities of various activated carbons for the removal of hazardous substances (phenol and methylene blue) from wastewater via adsorption

Adsorbents.	BET surface area (m^2g^{-1})	Langmuir adsorption capacity (mg g^{-1})	References
Phenol removal			
Oily sludge-based activated carbon	2263	434	Mojoudi et al. (2019)
Cattle bone-based activated carbon	2687	431	Du et al. (2017)
Soybean straw-based activated carbon	2271	278	Miao et al. (2013)
NORIT granular activated carbon D10	778	166.6	Maroof et al. (2004)
Mesoporous carbon CMK-3-100	1260	347	Haque et al. (2010)
Active carbon	1068	257	Haque et al. (2010)
Methylene blue removal			
Flamboyant pod-based activated carbon	2854	890	Vargas et al. (2011)
Bamboo waste-based activated carbon	1896	454.2	Hameed et al. (2007)
Agricultural waste-based activated carbon	1045.6	369.3	Ahmed and Dhedan (2012)
Viscose-based activated carbon fiber felts-1600	1614	325.8	Liu et al. (2019)
Iron/cerium-based activated carbon	776.2	255.7	Cheng et al. (2018)

comparison of BET surface areas and maximum adsorption capacities for phenol removal of various activated carbons are shown in Table 3.2.

It is evident from Table 3.2 that oily sludge-based activated carbon possessed high BET surface area of 2263 m^2g^{-1} with highest Langmuir adsorption capacity of 434 mg g^{-1} (Mojoudi et al. 2019) as compared to other reported activated carbons in various studies (Maroof et al. 2004; Miao et al. 2013; Du et al. 2017). Generally, commercial activated carbons have high cost (Erdem et al. 2016). One of the alternatives to commercial activated carbons is to utilize activated carbons prepared from readily available raw materials such as solid wastes (Fu et al. 2009). Oily sludge has substantial carbon content and can be employed for activated carbon preparation. The use of oily sludge for the preparation of highly efficient and low-cost adsorbent for effective hazardous waste treatment and removal such as phenol can be considered as an emerging technique for solid waste management in an environmentally friendly manner.

Another example is the removal of methylene blue (an industrial hazardous dye) from wastewater via adsorption using activated carbon. Recently, methylene blue was effectively removed from wastewater using activated carbon prepared from the flamboyant pods (*Delonix regia*) through chemical activation of NaOH (Vargas et al. 2011). The Langmuir adsorption capacity and BET surface area were found to be 890 mg g^{-1} and 2854 m^2g^{-1}, respectively, for methylene blue removal. It exhibited an extraordinary adsorption capacity for the removal of methylene blue as compared to other activated carbons prepared from bamboo waste (Hameed et al. 2007), viscose (Liu et al. 2019), agricultural waste (Ahmed and Dhedan 2012), and iron/cerium modification (Cheng et al. 2018). A comparison of evaluated surface areas and Langmuir adsorption capacities relevant to methylene blue for a variety of activated carbons is presented in Table 3.2. It is clear that flamboyant pods' adsorption capacity and surface area are approximately 2.0–3.5 and 1.5–3.5 times higher than those of other activated carbons as demonstrated in Table 3.2. In addition to the high adsorption capacity of flamboyant pods for methylene blue removal, it is readily available in various parts of the world including Brazil, the Caribbean, the United States, Hawaii, Puerto Rico, the Virgin Islands, the Canary Islands, India, Hong Kong, Taiwan, southern China, and Australia (Vargas et al. 2011). After a maturity period, they just fall from trees, and consequently, because of their natural abundance, they can be a suitable source for the production of highly efficient activated carbon for the removal of hazardous substances such as methylene blue.

Neutralization

Chemical neutralization is an essential component of water and wastewater treatment and is a common practice over several decades for waste treatment to avoid or minimize its impact on human health and environment. Typically, it is used to balance the excess acidity or basicity which is the adjustment of pH of wastewater by adding acid or base. For the case of hazardous (corrosive) waste effluents, neutralization will be considered as a primary treatment to discharge them safely into water bodies. Additionally, neutralization also serves a pretreatment process as certain biological and physical treatment techniques significantly depend on pH (Goel et al. 2005). The US EPA has set pH standards for various types of water. For instance, the suitable and safe pH range for drinking water is 6.5–8.5 (US EPA 2020). For proper boiler operations, the pH of boiler feed water should be 11 (National Board 2015).

Neutralization is performed in both batch and continuous modes. In a batch neutralization, the hazardous waste is kept under treatment until it meets specific criteria. Batch neutralization is typically employed for small volume of hazardous wastes. For large waste volumes, a continuous neutralization process is preferred. pH of a continuous or a batch system is monitored by an online pH measurement device or by taking periodic samples for pH measurement which eventually dictates the amount of acid or base to be added.

Acidic wastes are commonly neutralized by adding lime alkalis such as quick lime (CaO) and slaked lime ($Ca(OH)_2$). In addition, sodium alkalis such as caustic soda ($NaOH$) and soda ash (Na_2CO_3) are also employed to neutralize acidic waste (National Board 2015). Calcium oxides are more commonly used as compared to sodium alkalis because the former is cheaper than latter ones (WEF and ASCE 1998).

In general, acids such as sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3) or addition of CO_2 (carbonation) is used to lower the pH of alkaline wastes. The most commonly used neutralizing agent among acids is H_2SO_4.

There are a variety of traditional neutralization practices which include in-plant neutralization, influent neutralization, in-process neutralization, and effluent neutralization (Goel et al. 2005). They are briefly discussed as follows. (1) *In-plant neutralization*, in-plant neutralization is preferred in industrial operations in which waste effluents either acidic or basic in nature are continuously generated. In in-plant neutralization, a known amount of opposite neutralizing agent is added in the system for neutralization purposes. (2) *Influent neutralization*, it is typically used in a noncontinuous industrial process in which nature of wastewater is extremely acidic or basic such that pH lies outside the permissible limits for its subsequent discharge. In carbonation, the addition of CO_2 is controlled by a pH sensor connected to a proportional controller for accurate dissolution of CO_2 for neutralization purposes. The other neutralization agents (aforementioned acids and bases) are supplied to neutralization purposes under flow control for its required amount of injection either by a pump or a control valve which is operated by a signal from pH sensor located in the neutralization tank. (3) *In-process neutralization*, in biological process, a pH control system is employed in aeration basins to protect the bacteria during malfunctioning of any mechanical or instrumentation systems. Neutralization process has its applications in hazardous waste treatment processes such as metal precipitation and acid mine drainage.

Emerging Practices

Acid mine drainage is a wastewater generated as a result of mining activities and mineral matter operations (Gault et al. 2005). It is not only acidic but also contains high concentrations of hazardous heavy metals such as Cu, Pb, Zn, Ar, etc., posing great threat to the contamination of surface and groundwaters (Silva et al. 2013). Acid mine drainage is also formed when naturally occurring sulfide mineral such as pyrite (FeS_2) is oxidized when exposed to the atmosphere. Reactions of FeS_2 with oxidants such as dissolved oxygen and ferric ion (Fe^{3+}) are given below (Tabelin et al. 2017b, c):

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2SO_4^{\;2-} \tag{3.1}$$

$$Fe^{2+} + 0.25O_2 + H^+ \rightarrow Fe^{3+} + 0.5H_2O \tag{3.2}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 16H^+ + 2SO_4^{\;2} \tag{3.3}$$

The abovementioned reactions demonstrate that acid mine drainage resulted from FeS_2 oxidation is highly acidic and has the tendency to incorporate metals with similar properties as sulfur (S) and iron (Fe) in their lattice structure (Tabelin et al. 2017a).

A conventional technique for acid mine drainage remediation is chemical neutralization. In this process, acid mine drainage is treated with basic substances such as limestone or lime to increase the pH levels of the resulting mixture, and toxic heavy metals are removed via precipitation (Johnson and Hallberg 2005). It seems a simple and effective approach for short-term purposes. However, in lengthier operations, it not only requires a continuous supply of neutralizing agent, energy resources, and manpower but also proper disposal of large amount of the generated sludge during the process. Moreover, formation of acid mine drainage as a result of FeS_2 oxidation is a lengthy and slow process equivalent to the timescales in the range of hundreds to thousands of years (Jr et al. 2000). Consequently, it renders chemical neutralization as infeasible and uneconomical process for treating acid mine drainage.

Keeping in view of the limitations relevant to the use of chemical neutralization for treating acid mine drainage, recently an alternative technology known as "passivation" has emerged. The core idea in passivation is to form a protective coating around FeS_2 surface which will inhibit its oxidation (Kang et al. 2016). Till date a number of passivating materials have been developed such as 8-hydroxyquinoline (Lan et al. 2002) and triethylenetetramine (Liu et al. 2013). Although they are effective, they have certain limitations. For instance, triethylenetetramine is toxic in nature and poses health and environmental concerns. In efforts to find environmentally friendly passivating agents, organosilanes emerged as effective passivating agent in inhibiting FeS_2 oxidation (Diao et al. 2013). In a recent study, Lui and coworkers developed a novel protective coating in which SiO_2 nanoparticles were embedded in mercaptopropyltrimethoxysilane (PropS-SH). The efficiency of this newly developed coating with respect to FeS_2 oxidation inhibition was estimated with varying concentration of SiO_2 nanoparticles within the coating. The addition of appropriate SiO_2 nanoparticles significantly enhanced the passivation efficiency of PropS-SH coating. A coating of 3% (v/v) of PropS-SH solution with 2 wt% SiO_2 nanoparticles decreased the pyrite oxidation by 81.1% and is considered as a highly efficient passivating agent. The coating mechanism of the PropS-SH coatings on pyrite surface involved the chemical adhesion of respective coating on the pyrite surface (Liu et al. 2017).

Chemical Precipitation

Chemical precipitation is the most common method used for the removal of contaminants (heavy metals and organics) from industrial effluents. In this process, solubilities of contaminants are reduced, and contaminants are precipitated as solids which are further removed using settling or filtering (Dahman et al. 2017). It includes the addition of precipitating agents such as potash alum, sodium bicarbonates, ferrous sulfate, ferric chloride, and lime (Ramachandra et al. 2005). The conventional precipitation methods employed in industries include hydroxide precipitation, sulfide precipitation, and carbonate precipitation. In hydroxide precipitation, agents such as $Ca(OH)_2$ and NaOH are used. In sulfide precipitation, sulfide compounds such as NaHS, H_2S, FeS, etc. are generally employed. In carbonate precipitation, precipitating agents such as Na_2CO_3 or $CaCO_3$ are used (Vyrides et al. 2017).

Chemical precipitation is an effective and a simple process for removal of metals from wastewater with high metal concentrations. However, it is very pH sensitive and typically ineffective for the removal of metals at low concentrations (Vyrides et al. 2017). Another drawback of this method is the accumulation of large quantities of sludge containing toxic compounds (Sethurajan et al. 2017).

Emerging Practices

Ethylenediaminetetraacetic acid (EDTA) has wide range of application in many industrial processes such as mining operations, dyeing, and electroplating industries (Huang et al. 2016). Consequently, abovementioned industrial effluents have large amount of EDTA. Additionally, EDTA is a strong chelating agent where it chelates strongly with heavy metals to form chemically stable heavy metal complexes (Van Der Maas et al. 2005). Furthermore, heavy metal complexes have significant impact on marine life (Cuprys et al. 2018). However, conventional technologies such as chemical precipitating are ineffective in removing heavy metal complexes from waste streams. Thus, emerging strategies and strategies are being developed for the removal of heavy metal complexes from wastewater (Wang et al. 2019a).

Oxidation techniques such as ozonation (Huang et al. 2016), TiO_2 photocatalysis (Lee et al. 2015), and nonthermal discharge plasma (Wang et al. 2018b) are generally utilized for releasing heavy metals from heavy metal complexes, a phenomenon known as "decomplexation." These techniques are effective but have certain disadvantages. For instance, the oxidizing potential of ozone is limited (Huang et al. 2016). The photocatalytic decomplexation using TiO_2 has limitations due its narrow absorption in UV light (Lee et al. 2015). The use of nonthermal discharge plasma is restricted due to high energy consumption (Wang et al. 2018b). Another effective technique used for decomplexation of metal complexes is Fenton or Fenton-like oxidation (Oviedo et al. 2004; Fu et al. 2009). Initially, Fenton process was used to oxidize organic compounds to CO_2, H_2O, and inorganic ions using hydroxyl radical ($^{\bullet}OH$) generated by the reaction of ferrous ions (Fe^{2+}) and H_2O_2. The reactions are presented below (Neyens and Baeyens 2003):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-} \tag{3.4}$$

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \tag{3.5}$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \tag{3.6}$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^{-} \tag{3.7}$$

The main limitations of Fenton process were associated with high cost of Fe^{2+}. Later on, to make the Fenton process cost-effective, Fe^{2+} was replaced with Fe^{3+}, and the process was referred to as "Fenton-like process." The reactions are given below (Malik and Saha 2003):

$$Fe^{3+} + H_2O_2 \rightarrow Fe\cdots OOH^{2+} + H^+ \tag{3.8}$$

$$Fe\cdots OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \tag{3.9}$$

$$H_2O_2 + Fe^{2+} \rightarrow {}^{\bullet}OH + OH^- + Fe^{3+} \tag{3.10}$$

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \tag{3.11}$$

A coupled technique comprising of Fenton or Fenton-like process followed by hydroxide precipitation proved successful in treating heavy metal-EDTA complex in wastewater. For instance, in 2009, Fu and co-workers removed Ni^{2+} from Ni-EDTA wastewater using Fenton and Fenton-like process (Fu et al. 2009). However, Fenton and Fenton-like process require low pH which will significantly increase the utilization of alkali in the later precipitation process. Secondly, metals such as Ni, Co, etc. were employed to activate H_2O_2 to enhance oxidizing efficiency, which can be a potential health and environmental risk (Bokare and Choi 2014; Zhou et al. 2019).

In the view of the abovementioned limitations, recently Wang and his team developed an innovative and environmentally friendly technique by coupling $NaHCO_3$-activated H_2O_2 (BHP) oxidation and chemical precipitation for simultaneous decomplexation and removal of Cu-EDTA and Cu^{2+} ions, respectively (Wang et al. 2019b). BHP treatment of Cu-EDTA resulted in the Cu-EDTA decomplexation efficiency of 92%. In addition, $NaHCO_3$ provided a weak alkalinity which not only facilitated Cu-EDTA decomplexation but also reduced the utilization of alkalis in post-precipitation. Thus, it is evident that this study introduced a successful green approach for heavy metal complex elimination in aqueous media.

Solidification and Stabilization

Solidification and stabilization includes cleanup techniques that minimize or restrict the potential hazards associated with the release of toxic substances from industrial hazardous waste such as waste sludge, heavy metals, and organics (US EPA 2012). Generally, these techniques do not remove harmful substances from the waste; however, they restrict contaminants from being leached out into the environment to avoid their potential health and environmental effects. In leaching, the hazardous substances are dissolved in and carried away by rain or flowing waters which can pollute soil, groundwater, and surface waters (Conner and Hoeffner 2010).

In solidification, hazardous waste materials are trapped or encapsulated in solid block or structure of a material known as solidifying or binding agent. There are two common ways of trapping hazardous substances: microencapsulation and macroencapsulation. Micro- and macroencapsulation refers to the encapsulation of fine waste particles and large vessels of wastes, respectively (Conner and Hoeffner 2010). In solidification, no chemical reaction is involved between the toxic waste and solidifying reagents, and waste is bound to the rigid structure of the solidifying agent. However, in stabilization, chemical interactions between waste materials and binding agent restrict the release of waste in environmental surroundings (US EPA 2012).

Utilizing portland/pozzolan cement is a conventional and commonly practiced technique for solidification and stabilization. In this technique, the cement material such as portland cement and pozzolanic materials such as fly ash, kiln dust, blast furnace slag, etc. that are primarily composed of oxides of calcium and silica promotes the fixation of hazardous substances in the rigid cemented matrix. Additionally, solidification enhances low permeability and low porosity to limit the leachability of the embedded toxic waste (Adaska et al. 1998). Additionally, it offers advantages such as low cost of processing, physical and chemical stability, good impact and compressive strength, and low biodegradability. The use of portland/pozzolan cement can effectively treat inorganic heavy metals such as Zn, Pb, As, etc. (Salihoglu and Pinarli 2008; Yoon et al. 2010) and organics (Leonard and Stegemann 2010; Xin et al. 2016).

Emerging Practices

However, in spite of several advantages, it has certain drawbacks. For example, portland cement-based materials can be easily damaged by sulfate and acid rain. Additionally, portland cement hydration can be compromised by the formation of metal complexes such as formation of $Pb(OH)_2$ and $PbOPb(OH)_2$ by the reaction of Pb with $Ca(OH)_2$ (Wang et al. 2018a). Furthermore, greenhouse effect substantially accelerates due to large-scale utilization of portland cement. For example, it is estimated that 900 kg of CO_2 is released per metric ton of portland cement being added to soil. Also, manufacturing of portland cement contributes to 10% of anthropogenic CO_2 emissions worldwide (Boden et al. 2017). Consequently, extensive use of portland cement for solidification and stabilization of waste material can be replaced by the highly efficient solidification and stabilization materials in an environmentally sustainable and economical manner (Shen et al. 2019).

It is evident from Fig. 3.3 that recently research studies relevant to solidification and stabilization are more focusing on environmentally friendly cement binders such as magnesia (MgO) (Jin et al. 2016; Li et al. 2019) and combination of fly ash, slag, and/or portland cement (Wang et al. 2018a; Wu et al. 2018) having low cost and good contaminant immobilization with low carbon content. Additionally, magnesia has good sulfate and acidic rain erosion (Shen et al. 2019).

As explained earlier, stabilization includes chemical interactions to bind or immobilize hazardous constituents of the waste. For the case of China, only stabilization aspect provides a practical solution to treat contaminated agricultural areas

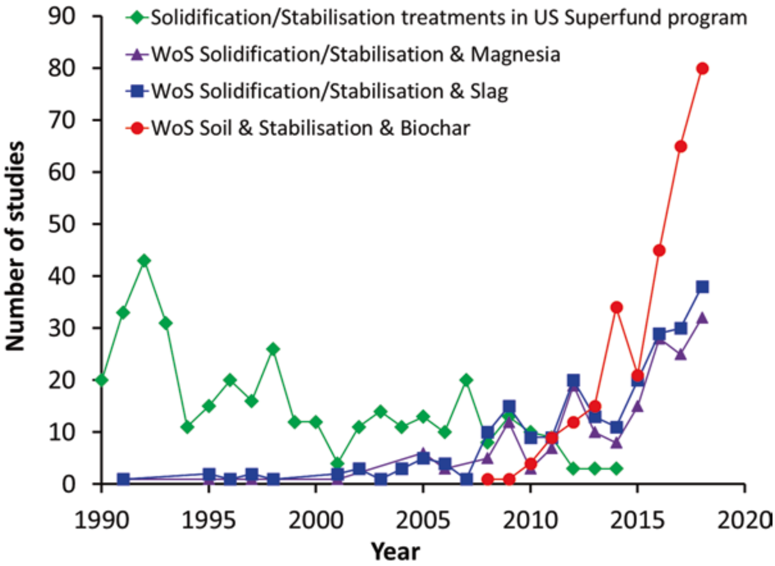

Fig. 3.3 Yearly solidification and stabilization treatments in the US Superfund program and research publications in Web of Science (Shen et al. 2019)

with extremely high concentrations of organic and heavy metal contaminants (CCICED and IISD 2015). Therefore, in this context, a variety of emerging stabilizing agents such as biochar, clay, and apatite are being studied. A wide range of novel stabilization materials, for example, biochar and zeolite (Zheng et al. 2020), ferrous sulfate and calcium polysulfide (Zhang et al. 2018), and fishbone hydroxyapatite (Nag et al. 2020), are being investigated. In Fig. 3.3, the utilization of biochar as solidification agent significantly increased from year 2015 and onward.

Biological Treatment

Application of biological systems has been exploited quite extensively for the treatment of municipal wastewater and hazardous waste. Various approaches, including bioremediation, phytoremediation, and treatment of wastewater and landfill leachate, have been suggested under the regime of biological treatment of multiple wastes. Such treatment processes employ ubiquitous living microorganisms, which may be used in natural and built/engineered systems. For a particular biological system application, characterization of environments is critical, which may be natural or built/engineered. Both, natural and engineered systems, must address carbon and energy sources for microbes, availability of electron acceptors, reduction-oxidation (redox) conditions, potential toxicity to microbial activity, nutrient availability, and surrounding environmental parameters (Council et al. 2005; LaGrega et al. 2010).

Initially, site characterization for decontamination may be carried out at two levels, i.e., at surface and in subsurface environments (in situ*)*. The latter poses challenges owing to existence of contaminants in subsurface environments in multiple phases, i.e., in free, dissolved, sorbed, and volatilized forms (Zhang et al. 2017). This may be attributed to the notion that the elimination or control of source zone, in subsurface environments, become entirely challenging. Therefore, the characterization of source zone demands extraordinary attention (Council et al. 2005). The ubiquitous nature of microorganisms in natural and built/engineered environments is indicative of the capacity of such living organisms to acclimatize to varying conditions. However, the application of microorganisms in any biological remediation system requires extensive knowledge of detailed microbial profiling in terms of growth kinetics, population dynamics, biodegradation pathways, and nutrient requirements. Generally, in situ and ex situ approaches are used for treating different waste systems. Various procedures, such as intrinsic and engineered bioremediation, liquid-, solid-, slurry-, vapor-phase treatments, etc., have been suggested. However, there are numerous factors which dictate the application of certain strategy, including anaerobic and aerobic conditions (Zhang et al. 2017).

The efficacy of any biological systems for waste treatment requires determination of biodegradability of waste, habitable environment, and rate-limiting factor. The most common limiting factor happens to be bioavailability, which sometimes may require preliminary treatment of any kind of waste for enhancing bioavailability. Contaminants need to be dissolved in aqueous phase before they could be subjected to any biodegradation pathway (Zhang et al. 2017).

For surface biological treatment of wastes, various reactors, such as membrane, integrated fixed-film sludge, moving bed biofilm, and submerged aerobic bioreactors, have been developed. As a matter of fact, the development of these reactor laid the foundation of wastewater treatment (Metcalf & Eddy et al. 2013). On the other hand, bioremediation technologies managed to provide solutions for treating soil, contaminated by oil or other petroleum-based hydrocarbons (Loehr 1978).

Emerging Practices

Developments in biological treatment of wastes have been directed to “re-NEW-able wastewater” (where NEW denotes nutrient, energy production, and efficiency), hazardous waste management, stimulation, and augmentation. Consideration of wastewater as a “re-NEW-able” resource is based on recovering the potential of chemical or hydraulic or thermal energy and nutrients, which may be contained by wastewater (Zhang et al. 2017). Extractive nutrient recovery (ENR) is an example of one of such advancements. Consequently, production of value-added chemical entities, such as biofuels, bioplastics, biopesticides, biofertilizers, biosurfactants, and bioflocculants, may be envisaged as emerging trends (Tyagi et al. 2009).

Stimulation is carried out for promoting the growth of indigenous microorganisms in a natural or built/engineered environment for biodegradation of a particular contaminant. In this scheme, the presence of native microorganisms in subsurface environment is exploited. The primary application of biostimulation is decontamination of soil and groundwater. Additionally, the contamination by volatile organic compounds, pesticides, and herbicides may also be achieved through biostimulation. Ecosystems, which are contaminated with heavy metals, have also been reported to be remediated through biostimulation (Mani and Kumar 2014). However, ensuring the availability of additives to native microorganisms in subsurface environments becomes challenging.

On the contrary, augmentation is meant for introducing selected microbial cultures or consortium to natural or built/engineered environments for decontamination processes. There are generally two ways through which the augmentation may be carried out: (1) introduction of acclimatized culture or mixed culture to a certain system and (2) introduction of genetically engineered bacteria or a vector with relevant genes to a certain system. Pure and mixed cultures were used, which included *Pseudomonas*, *Clostridium*, *Bacillus*, *Arthrobacter*, *Eubacterium*, *Desulfovibrio*, *Mycobacterium*, *Peptococcus*, *Xanthomonas*, Gram-negative rods, and slime-forming bacteria (Adams et al. 2015). Bioaugmentation has been reported to enhance the rate of cleanup process, and it may be used in conjunction with biostimulation (Kuráň et al. 2014).

The applicability of biological systems for waste management is mainly function of site survey and subsequent selection of biological treatment process, appropriateness of biological system, and process control. The appropriateness or selectivity of biological systems may indicate the limited application of such systems; however, there are various avenues which require attention and may improve acceptability of biological systems, such as molecular approaches, aimed at enhanced diagnostics, and omics technologies. Additionally, the intervention of evolving areas of nanotechnology and biosensors may also play role in sustainability of biological systems (Zhang et al. 2017).

For environmental site management, molecular diagnostics (MD) can be seen as one of the recent advances, and these employ isotope analysis and molecular biology-based techniques. The former technique provides insight into the fate of contaminant during biodegradation (Kuder et al. 2013; Kozell et al. 2015). Techniques, which are based on molecular biology, investigate relative abundance, microbial profiling of a certain environment, and their function. These techniques have been able to register their applications at multiple stages, including characterization of site, bioremediation, monitoring, and site shutdown. Based on retrieved information, techniques based on molecular biology, community profiling, and/or functional analysis of the relevant communities may be carried out (Zhang et al. 2017).

Similarly, *omics* technologies offer a wide range of studies, including genomics, transcriptomics, proteomics, and metabolomics. These technologies integrate all together into "systems biology," thus enabling us to determine the function of microbes in a system in an elaborative fashion. Among these, genomics deal in structure, function, and expression of all genes in a certain microorganism. Microbial communities, arising from contaminated soil or groundwater (by heavy metals or petroleum-based hydrocarbons), may be analyzed through metagenomic analysis.

Extensive study of expressed proteins (Proteomics), within an organism, may be aimed at protein-protein interaction, regulation, and turnover. In addition to these, emergent technologies, such as nanotechnology, novel sensors, and allied network, will have significant impact on the transformation of biological treatment systems. Nanotechnology may find applications in the treatment of hazardous waste. The principles of nanophotocatalysis and nanomembranes may be exploited (Zhang et al. 2009). Significant advancements may be expected in these emerging technologies.

Various drivers, such as financial constraints, preferred policies, etc., appear causative agents behind optimization of biological processes, leading to green remediation practices. Optimization facilitates remedy, security, efficacy, and cost-effectiveness. Green remediation refers to achievement of sustainability in terms of socioeconomic development and environmental acceptability. It may be characterized by:

1. Energy needs of a biological treatment system
2. Emissions into atmosphere
3. Contamination of soil and water resources
4. Material utilization and waste generation

The development of sustainable biological systems for the treatment of hazardous waste offers various challenges. However, with the advent of emerging technologies, monitoring and characterization techniques along with data integration will become mandatory for assessment of biological processes for hazardous waste management.

3.7.4 Conventional and Emerging Approaches for Hazardous Waste Disposal

Landfills

A hazardous waste landfill is an underground site specially constructed for the safe storage of hazardous waste for many decades. It contains special layers that prevent the leakage of hazardous materials into the soil. Hazardous landfills also contain separate cells or compartments where different waste materials are separately stored depending on their type, reactivity, and interactions with other hazardous wastes (Amadi et al. 2017).

Typically, these cells are 5–6 m high. Waste placed within these cells is commonly stored in 55 gallon drums. A 0.3 m layer of compacted soil is placed on top of the landfill to decrease dust and gaseous emissions of hazardous substances. Generally, hazardous waste sites have other facilities such as wastewater treatment plants, monitoring wells, and water-capturing structures. Landfill leachate is characterized by high organic and inorganic pollutant concentrations and is extremely toxic to the environment. Leachate is produced by two methods: (a) water penetration via precipitation (i.e., rain or snow melt) and (b) the decay of organic waste materials (i.e., organic acids) (Stefanakis et al. 2014).

The soil that makes up the bottom layer of a hazardous waste landfill site is typically clay. It is considered as a natural barrier that slows down or prevents the leaking of the leachate. Along with the clay barrier, a double geo-membrane liner developed from various plastic materials is also used for protection. A drainage system is placed above each of the liners to capture the leachate (The University of Arizona 2021). An on-site treatment plant cleans up the collected leachate to prevent the release of hazardous substances.

Another technique for the disposal of liquid hazardous waste is a deep-well disposal. In this technique, injection wells are utilized to place the liquid waste in underground rock formations that do not allow the penetration of contaminants into groundwater aquifers. High pressures are applied to force the liquid into the pores and in-rock chambers, where liquid waste is to be permanently stored. The rock unit selected to receive the waste must be relatively porous and permeable. These disposal wells are hundreds to thousands of meters deep and below the water table of a certain region (FRTR 2020).

Emerging Practices

Bedrock disposal is a landfill-based modern technique to dispose hazardous waste. The generic design of a bedrock disposal site involves multiple barrier concept. The solid waste is surrounded by layers of rock, clay, and steel that prevent the invasion of groundwater and leakage of waste material. A major limitation is the nature of the host rock. The waste forms envisaged for disposal are vitrified high-level radioactive wastes sealed into stainless steel canisters or spent fuel rods encapsulated in corrosion-resistant metals (Joshi and Ahmed 2016).

Sea Dumping

This technique is as ancient as the human life itself. Waste disposal in sea was seen as a common and easy practice as it would make all waste disappear and the land area would look tidy and clean. For instance, after World War II, 300,000 tons of chemical and conventional munitions were dumped into the oceans (Kommunernes International Miljøorganisation 2021). The weapons also included nuclear waste and cartridges. Nondegradable and one-time-use materials such as plastics often find way into the oceans because of direct dumping. It qualifies as one of the major contributing factors to ocean dumping on the account that once the materials are introduced in the oceans, they last for hundreds to thousands of years causing a potential threat to aquatic ecosystem and human health (Calmet 1989). A common example of the destructive impacts of plastic as a result of sea dumping is the Great Pacific Ocean Garbage Patch located in the middle of Hawaii and California.

Emerging Practices

The waste substances that are disposed of in the oceans can be reduced through effective management and minimization efforts. Primarily, efforts should focus on controlling and monitoring dumping activities in oceans from ships, aircrafts, and other anthropogenic activities. In this context, international treaties such as London Protocol of 1996 is in place to protect marine environment from dumping of wastes. Successful compliance of the contracting parties with London Protocol promotes waste minimization and reduction strategies which prefer recycling and reuse and innovative technologies to minimize waste (US EPA 2021c). An integrated approach is required to synchronize technology, policies, and advocacy to minimize ocean dumping and its harmful impacts on human health and aquatic ecosystem. For instance, in Republic of Korea, sewage sludge was continuously dumped in ocean between years 1993 and 2006, which negatively impacted marine life. To minimize these impacts, the Ministry of Oceans and Fisheries developed and implemented an integrated program, according to which sewage sludge dumping in ocean was phased out from year 2006. The effective implementation of this plan resulted in the termination of sewage sludge dumping in oceans by year 2012. Additionally, dumping of various types of sludge were banned in 2016. This ban not only contributed to the significant reduction in dumping of waste but also promoted recycling and energy production. For example, in year 2005 (a year before implementation of the plan), the recycling rate of total sewage sludge was nearly 5%. On terminating dumping of sewage sludge in ocean in year 2012, recycling rate of sewage sludge increased to 43%. Additionally, the energy production via incineration also increased. Thus, the success of aforementioned integrated plan can be attributed to mutual interlinkage among policies, technologies, and intergovernmental cooperation (Chung et al. 2020).

Incineration

Incineration is a method to treat waste which involves the combustion of the organic substances found in waste materials at an elevated temperature of at least 850 °C. The solid mass and volume of the original waste are reduced by approximately 80–85% and 95–96%, respectively. Incineration does not completely replace the process of landfilling; however, it does reduce the amount of waste to be disposed-off considerably (Speight 2020).

Incineration is a relatively advanced technique as compared to the sea dumping and conventional landfills, and thus, negative impacts on land and water bodies are fewer in incineration. Incineration possesses higher waste disposal rate than landfills and sea dumping. Incineration has definitive benefits when used to treat more specialist types of waste such as clinical or hazardous waste, where the high temperatures can destroy potentially dangerous toxins and pathogens. Incineration is also waste-to-energy (WTE) technology and can generate energy without relying on fossil fuels (Makarichi et al. 2018). The ash produced is being used in the construction industry (Lam et al. 2010). Metal can be extracted from the ash and reused by industries such as the steel industry (Savannah Cooper 2015).

The pollutants such as particulate emissions can travel through the air and settle on crops and water bodies, causing irreversible contamination and disrupting the food chain for humans and environment. The capital investment and running cost is higher in incineration, and it needs a supply of fuel to run combustion (Lew 2021).

Emerging Practices

An emerging technique for hazardous waste disposal is plasma arc gasification (PAG) that uses a combination of electricity and high temperatures to turn waste into usable by-products without combustion (burning). Although the technology is sometimes confused with incinerating and/or burning waste, plasma gasification does not combust the waste as in incinerators. Instead, it converts the organic waste into gas that still contains all its chemicals and heat energy. Additionally, it converts the inorganic waste into an inert vitrified glass known as slag. The process can reduce the volume of waste sent to landfills. Moreover, it will aid in electricity generation (Hosansky 2016).

In the PAG, a very high-voltage electrical current is passed through an electrical arc gasifier consisting of two electrodes, thus creating an arc between them. Inert gas, which is under high pressure, then passes through the electrical arc into a sealed container (called a plasma converter) comprising of waste materials. Temperatures in the arc column can be as high as 14,000 °C (25,232 °F), which is hotter than the surface of the sun. Exposure to such elevated temperatures transforms most wastes into gas, while complex molecules are torn apart into individual atoms. Significant by-products that PAG release are syngas (a mixture of hydrogen and carbon monoxide), slag, and residual heat. The composition of the waste stream can affect the effectiveness of the gasification procedure. Waste that is high in inorganic materials, such as metals and construction waste, will yield less syngas, which is the most valuable by-product, and more slag. For that reason, it may be worthwhile to presort waste into organic and inorganic materials (Hosansky 2016). If waste can be shredded before it enters the gasification chamber, the efficiency of the PAG can be improved.

3.8 Conclusions

The term “hazardous waste” refers to the waste comprising of toxic substances which on improper management (minimization, treatment, and disposal) pose significant threat to human well-being and the environment. Globally, the generation of hazardous waste is growing due to extensive industrialization and rapid economic expansions. The hazardous substances in the wastes include poisonous organic and inorganic chemicals, explosive and flammable materials, toxic insecticides and pesticides, heavy metals, etc. The main contributing sources of hazardous waste are industries and manufacturing units, residential colonies, public and private institutions, commercial buildings and offices, etc. The hazardous substances have four main characteristics: ignitability, toxicity, corrosivity, and reactivity. The US EPA has classified various hazardous waste on the basis of their generation into four categories: F list, K list, and P and U list representing nonspecific, specific, acute, and general hazardous wastes, respectively. Their uncontrolled release into the environment and respective persistence have detrimental effects on human health in the form of serious diseases such as liver, hepatic, and kidney cancers, non-Hodgkin lymphoma (NHL), asthma, neurological and respiratory diseases, etc. Therefore, the proper hazardous waste management is essential to minimize, limit, and/or avoid their negative impacts on humans and environmental segments such as air, water, and soil.

Globally, conventional strategies and treatment and disposal technologies are in place for the management of hazardous waste. However, they have certain limitations. For instance, conventional chemical neutralization (typically uses a neutralizing agent) for treating acid mine drainage is a simple method; however, it is only effective in short-term purposes. In long-term perspective, it is uneconomical as it requires continuous supplies of neutralizing agents. Also, for the case of stabilization and solidification of waste, portland cement is a conventional material used for treating heavy metals and organics. However, it can be easily degraded by acid rain. Furthermore, it has the ability to form metal complexes by reacting with metals in wastewater, which further limit its effectiveness. Moreover, due to population growth and economic developments, scientific community is consistently striving for improved and alternate emerging technologies and modern practices to effectively and efficiently manage hazardous waste with minimal impact on human health and environment. In hazardous waste management, waste minimization is critical not only to reduce the amount and volume of the waste but also to lower the cost associated with treatment and disposal of hazardous waste. The hazardous waste generators need to be motivated to generate less hazardous waste using modern waste reduction techniques. For instance, employing "mini or microscale chemistry" and potential recycling of hazardous substances can substantially reduce the generation of hazardous waste. Regarding treatment of the hazardous waste, certain outstanding developments have emerged in recent years. For example, in a recent study, Mojoudi and his colleagues (Mojoudi et al. 2019) have successfully developed a highly efficient activated carbon based on oily sludge (a notable waste from petroleum industry) with an adsorption capacity of 434 mg g^{-1} for phenol removal. Also, Wang and co-workers introduced an effective integrated technique by using $NaHCO_3$-activated H_2O_2 oxidation followed by chemical precipitation. This method aided in the simultaneous decomplexation and removal of Cu-EDTA and Cu^{2+} ions, respectively (Wang et al. 2019b), with a Cu-EDTA decomplexation efficiency of 92%. Moreover, plasma arc gasification (PAG) can be utilized to generate syngas for energy utilization by treating hazardous waste streams at elevated temperature of 14,000 °C without burning and generation of harmful emissions (Hosansky 2016).

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Chapter 4
Pollution Prevention Methods and Related Regulations

Zarook Shareefdeen, Elio Geara, Hassan Khan, Nooruddin Abdel Rahman, and Sarah AlNimran

4.1 Introduction

Although certain areas of the globe are more polluted than the others, pollution is spreading rapidly throughout the world, and it has become a global crisis. Pollutants are transported by movement of air, water streams in the subsurface, and through complete hydrologic cycle. Implementation of pollution prevention methods will control the spread of pollution. Pollution prevention (P2), also referred to as source reduction, protects the resources by conservation at its source. P2 consists of all aspects of waste minimization through consideration of each product throughout its complete life cycle from the initial product development to its final disposal stage.

A careful assessment is required on how each waste stream is being disposed of with the assistance of current or potential future waste-disposal techniques. In many cases, waste from one industry might be a valuable resource for another facility; thus participation in waste exchange facilities is a preferred alternative to waste treatment and disposal. If waste generation cannot be prevented, waste reduction through recycle and reuse methods can be employed (Woodard and Curran Inc. 2006).

P2 can be applied to all types of industries including the energy, agriculture, federal, consumer, and industrial sectors. In the energy sector, P2 can reduce environmental damages resulting from extraction, processing, transport, combustion of fuels, etc. Increasing efficiency in energy utilization of environmentally benign fuel sources reduces wastes in the energy sector. In the agricultural sector, reducing the use of excess water and adoption of less harmful pesticides can prevent pollution. In the industrial sector, modifying a production process in order to produce less wastes

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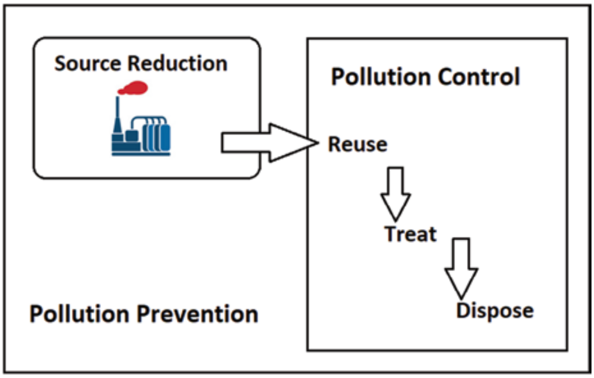

Fig. 4.1 The difference between pollution prevention and pollution control

using nontoxic or less toxic chemicals as cleaners, implementing water and energy conservation practices, and reusing materials can prevent or reduce pollution (Learn About Pollution Prevention n.d.)

P2 will not only reduce the environmental damage, but it will also decrease the financial loss and associated liabilities to waste generators. Furthermore, P2 reduces the operational expenses by decreasing waste management and cleanup expenses. It also saves the environment by conserving its natural resources and increasing its economic growth through efficient industrial productions (Learn About Pollution Prevention n.d.). There is a big difference between pollution prevention and pollution control. Pollution prevention avoids, prevents, and minimizes the generation of pollutants, whereas pollution control is focused on limiting the damages already caused by pollution. Figure 4.1 illustrates the difference between pollution prevention and pollution control. This chapter presents important details regarding various pollution prevention (P2) methods including process modification, material substitution options, recycling, and environmental regulations and case studies related to P2.

4.2 Pollution Prevention Methods

4.2.1 Pollution Prevention Hierarchy

According to the waste management hierarchy, pollution prevention is the most preferable environmental technique. However, the other techniques such as reusing the materials instead of disposing can help to save the environment from pollution. If reuse is not applicable, potential recycling options must be pursued. If reuse or recycling is not possible, waste must be treated to recover valuable products, and finally, the least favorable option is to dispose the wastes. P2 methods can be applied

Fig. 4.2 Pollution prevention hierarchy (UNEP 2011)

to all actual and potential activities that generate wastes. Figure 4.2 represents a typical industrial waste management hierarchy.

4.2.2 *Source Reduction*

Waste minimization or source reduction is a favored waste management approach because it conserves resources and contributes to a greener and cleaner environment. A simple example of waste reduction method could be by merely avoiding unnecessary packaging. There are multiple stages of source reduction methods employed to minimize the waste generation in industries. It involves common sense-based waste reduction, information-driven waste reduction, research and development (R&D)-based waste reduction, and audit-based waste reduction.

Examples of common sense-based waste reduction include segregation of wastes, labeling, reducing the amount of water use, etc. Replacing volatile organic solvent with a water-based solvent is a simple example of an information-driven waste reduction. Improvement or changes in equipment design and finding out a new chemistry (i.e., a new chemical reaction, new catalyst, etc.) are examples of R&D-based waste reduction (LaGrega et al. 2015). Lastly, audit-based waste reduction involves reviewing the purchasing and management records, preparing the list of materials that could be recycled, acquiring knowledge of waste generated in all streams, etc. The waste minimization audit can not only help in the waste reduction but also assist in reducing substantial costs involved in waste minimization projects (Hayes n.d.).

Waste minimization that cannot be handled by simple procedural modifications or improvements requires restructuring of a process or equipment. The following examples include process or production improvements: (1) changes in the production process, from batch process to continuous process; (2) changes in equipment—scrubber to adsorber; (3) changes in process control and automation; (4) changes in process conditions, such as retention times, temperatures, agitation speed, pressure, catalysts, etc.; (5) use of dispersants instead of volatile organic solvents; and (6) changes associated with the types of raw material to be used.

Several approaches consisting of physical, chemical, and biological treatment methods need to be explored so that a certain selected treatment process can also recover valuable materials for reuse or can be recycled. A waste that cannot be treated on-site may be used as a raw material by another business or factory; thus, it is worthwhile to establish a waste exchange bureau for waste reuse between industries. It may also be necessary to evaluate product enhancements or modifications that result in cleaner, more environment-friendly products for both currently manufactured products and for the proposed new products. Finally, substituting presently utilized chemicals with less hazardous raw materials is one of the most efficient strategies to reduce exposure and quantity of hazardous waste produced. Elimination, isolation, process or equipment modification, excellent housekeeping practices, administrative controls, and use of personal protective equipment are the other ways to limit waste production and avoid pollutant exposure.

4.2.3 Waste Elimination

The manufacturing section is a vital sector to any national economic development. It is connected to further divisions such as service, agricultural, and engineering sectors. Hence, if any inefficiency in the manufacturing performance occurs, it can generate a negative impact on all the other divisions. Waste elimination will guarantee that the manufacturing sector moves toward a hazard-free environment (Mostafa and Dumrak 2015).

The elimination process undergoes three phases. The first phase is documenting the waste by identifying the type and location. Wastes can be reduced to three types: (1) obvious waste, (2) less obvious waste, and (3) unobvious waste. Unreliable machines, excessive waste, excessive inventory, etc. are considered as obvious waste. Less obvious wastes are linked to delivery times, demand rates, staffing levels, etc. The second phase is analyzing the waste through finding out the root causes for waste generation. Waste can be easily reduced once it is categorized or linked to the utilization of manpower, materials and methods, measurements, or machines. The third phase is the removal process, which is initiated by producing a prioritized waste record followed by a selection of a suitable waste elimination or treatment technique (Mostafa and Dumrak 2015).

4.2.4 Material Substitution

Material substitution refers to the effective and efficient use of raw materials as well as use of substitute raw materials that generate the least amount of wastes or no wastes. This concept also involves reusing, recycling of raw materials, using of high-quality (high-purity) raw materials, and substituting raw material or products that are more environmentally friendly. For example, by substituting less toxic and/or more biodegradable materials in place of traditional degreaser solvents, the amount of waste generated can be reduced significantly. Additionally, utilizing higher-quality catalysts will increase process efficiency, while lowering the frequency of catalyst replacement. For example, replacing ceramic catalyst supports with the activated alumina supports allows activated alumina to be recycled (Speight 2020).

4.2.5 Process Modifications

Process modification or equipment modification is evaluated using the existing guidelines on pollution prevention techniques in an attempt to either alter existing methods or to develop new ones. Different approaches and modifications through either toxicity reduction or mass or volume reduction of wastes are also sought. Industrial processes often require reliable and labor-intensive equipment which have an expected lifetime that is usually measured in years (Speight 2020). This challenges economic motivation to pursue waste management through equipment or process modification. However, waste minimization eventually becomes an economically preferable method in comparison to traditional approaches. P2 requires an initial investment on certain equipment or technology; however it is guaranteed to be effective in minimizing waste generation. Additionally, it increases economic benefits. End-of-pipe treatments (or pollution control) and recovery of unconverted raw materials' costs have made process modification investments valid and pursued. Some examples of process and equipment modifications are listed below (Speight 2020):

- The backup seals are installed in order to subsequently reduce overall volatile organic compound (VOC) losses from storage tanks. Installing backup seals and reduction in the number of storage tanks are simple examples of process or equipment modifications.
- Control of carbon emissions from refineries through the installation of a vapor recovery system would reduce emissions by almost 90%. In this case, the addition of a vapor recovery system is a P2 method.
- Most industries employ old boiler systems that allow significant release of sulfur oxide (SO_x), nitrogen oxides (NO_x), and other residual materials. With the introduction of advanced technology, industries now utilize leak detection and repair (LDAR) systems to assess valves and pump seals. LDAR technology enables the industry to replace old boilers with new ones that can offer better emission control and P2.
- Installation of a bulk storage equipment can decrease the chance of spills. Bulk storage system replaces several 55 gal drums that cause undetected leakages. Bulk storage facilities require replacing underground piping with surface piping. This enables inspection of possible leaks and straightforward repairs.

- Another manufacturing problem is caused by the solid accumulation in distillation units. The goal is to maximize the removal of the residual solids from the desalting units by washing off crude oil and demulsifying residual chemicals. A process modification method is developed. This method involves substitution of existing water jets with particle rakes that minimize turbulence and allow the removal of all types of solid residual discharge.
- Sludge is formed in cooling water process units. Lime softening is a process where sodium carbonate and calcium hydroxide are added to treat the water to remove and precipitate hard ions such as calcium and magnesium ions.
- A similar problem applies to cleaning heat exchangers, where previously high-pressure water was used to eliminate solids and residue deposits. The use of high-pressure water caused the release of the solids and remnants into the wastewater treatment system causing further damage. An option would be to apply reusable cleaning chemicals that inhibit the attachment of any solids and decrease scaling. In some manufacturing companies, surfactants are used to lower the surface tension and to increase the spreading properties.

4.2.6 Waste Minimization Audit

After recognizing the need to minimize the generation of hazardous waste, waste minimization audit is carried out. Waste minimization audit consists of several phases: planning phase, assessment phase, feasibility analysis phase, and the implementation phase. In the planning phase, the first step is to obtain a clear commitment from the top management, finance, and human resources for approving the waste minimization project. Then the goals and scope of the waste minimization project are clearly defined, and the assessment task force is formed. Finally, the task force will prepare schedules, worksheets, and other necessary tools for the program.

In the assessment phase, the data are gathered by performing a thorough survey to provide information on specific sources of the waste, physical and chemical properties of the waste streams, production rate of the process, current waste management methods used from the generation to disposal steps, and the cost of each management method. The necessary information can be found from process flow diagrams (PFDs), piping and instrumentation diagrams (P&IDs), material and heat balances, operating and process description manuals, material safety data sheets (MSDS), and maintenance procedure documents.

The assessment team will then select waste minimization options for further analysis. After the selection of several waste minimization options, the technical and economic feasibility study of each option is examined. In industry, it is recognized that waste minimization projects compete for funding with other capital projects. Thus, it is necessary to look at the savings and benefits resulting from reduced cost of waste treatment and disposal as compared to the cost of a waste minimization project. Finally, feasible projects are selected for implementation (LaGrega et al. 2015). In the implementation phase, the selected projects are communicated to the top management for obtaining the necessary resources and funding. Subsequently, selected waste minimization projects are carried out, and new equipment or process is installed, evaluated, and monitored. This process is repeated by selecting new assessment targets until zero waste generation is achieved or waste generation is substantially minimized. Figure 4.3 summarizes the waste minimization procedure proposed by the US Environmental Protection Agency (EPA).

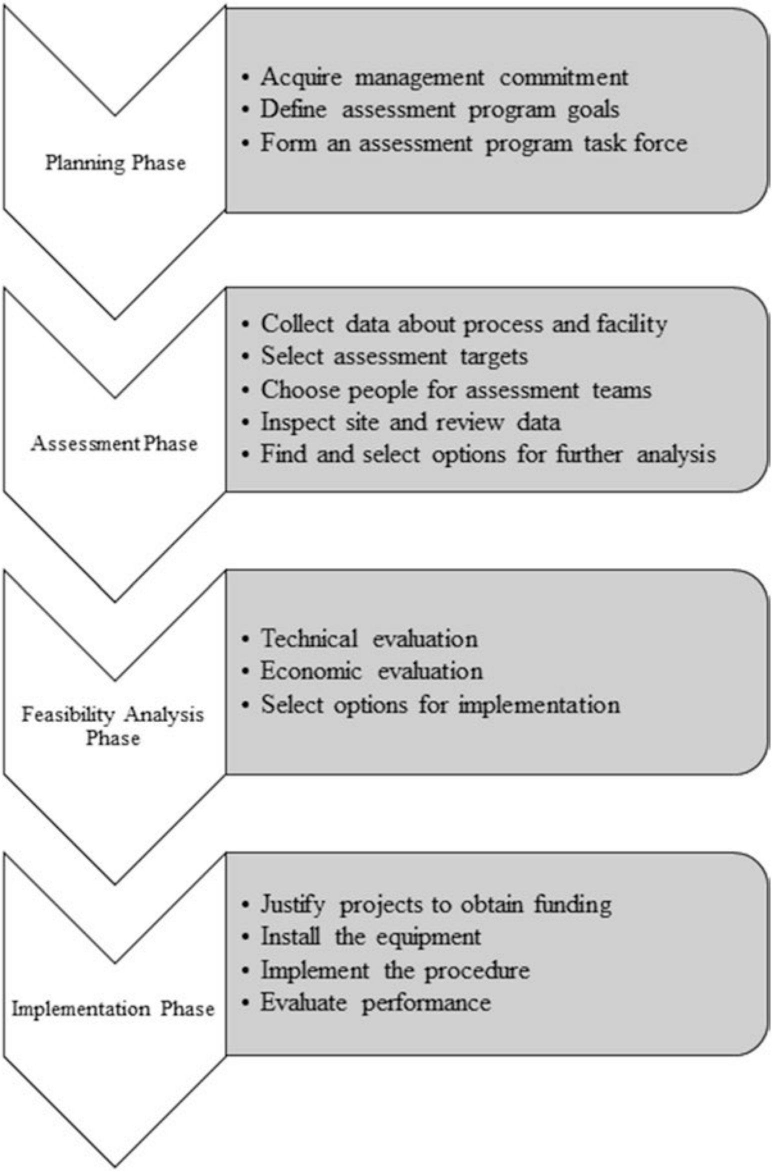

Fig. 4.3 Waste minimization procedure proposed by the U.S EPA

4.2.7 Life Cycle Analysis

Life cycle analysis (LCA) contributes in reducing the harmful environmental impacts without losing the competitive advantages. In LCA, the opportunities that benefit the environmental performance in every stage of the products are explored. The LCA stages include material selection, manufacturing, distribution, transportation, consumer use, and final disposal as shown in Fig. 4.4. The life cycle of a product starts with the raw material selection, and then it moves on to the manufacturing and packaging phases. Then, the sales, distribution, and transportation steps follow. Once the product is purchased and consumed, the product reaches its end of life, and finally it is disposed.

LCA has three phases: inventory, impact analysis, and improvement analysis. The inventory phase begins with organizing the LCA team. Certain products or processes are selected for LCA. Subsequently, LCA diagrams are prepared to identify the input and output waste streams of the selected targets. The next step is to find out the amount of waste generated and energy utilized in each stream of the process. The inventory phase is followed by the impact phase in which all the non-regulated targets, regulated chemicals, emissions, etc. are thoroughly reviewed to understand the impact of waste emissions and energy usage at each stage.

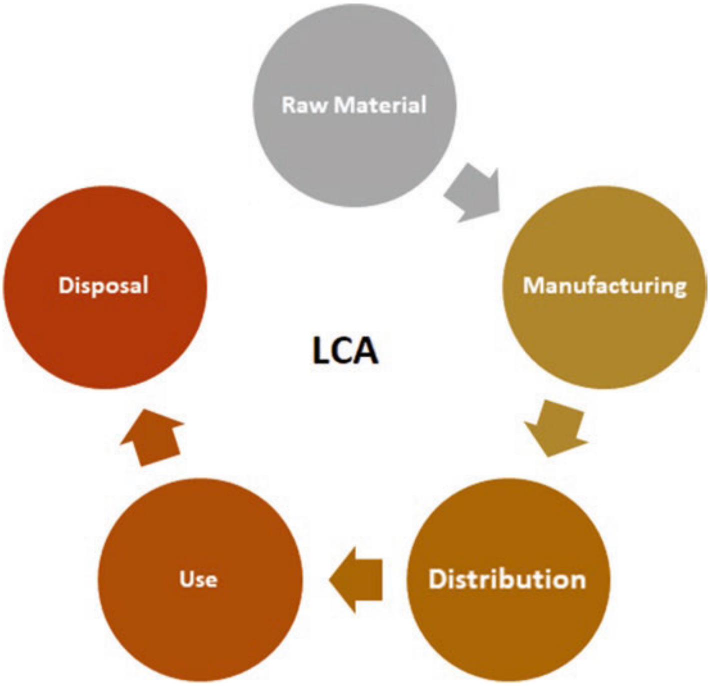

Fig. 4.4 Life cycle analysis (LCA)

Studies show that corporations can enhance the environmental, health, and safety performance through setting the priorities and expanding the effort beyond the regulatory requirements. Finally, in the improvement phase, alternative methods and technologies for improvement are selected, and each option is evaluated for its economic, technical, and regulatory feasibility before implementation (LaGrega et al. 2015).

4.2.8 Recycling, Reuse, and Reduce

Recycling restores the life cycle of a material, and it involves collection and processing materials that would otherwise be thrown away as trash. Waste recycling benefits the community and the environment. It also helps manufacturing products by conserving valuable resources (Recycling Basics n.d.).

Waste recycling starts with collecting recyclables from a curbside or drop-off center. Collection of recyclables methods include material recovery, source separation, and mixed recycling. Material recovery is extracting the recyclable materials from the mixed wastes. In source separation, wastes are segregated at the point of generation. In mixed recycling, all the recyclable materials are put together. Mixed recycling method gives higher recycling rate. In other words, the items that are normally sorted (i.e., paper, cardboard, glass, metal, plastic, etc.) in blue or green recycling bins are disposed together without separating them. After the collection step, the materials are then processed, sorted, and sold or reused for production of new products which take a new life as consumer goods (Recycling Processes 2020).

In industrial processes, solvents are commonly recycled. Solvents that are used in one process can be reused for other less sensitive processes. Water and solid materials such as metal and paper are always recycled. Oil industry practices effective recycling and reuse methods to reduce pollution as much as possible (Speight 2020). For example, caustic chemicals that are used in the removal of hydrogen sulfide and phenols from intermediate and final product streams are often recycled. Industrial process modifications may be required to enhance the concentration of the recovered products and to make it cost-effective and profitable. On-site recycling of phenol-containing caustics is also possible by lowering the pH which enables physical separation much easier (Speight 2020). If the recovered quantities and quality are at acceptable levels, used caustics or phenols can be sold. Oily sludge wastes can be used by a coking plant or a crude distillation plant. The use of sludge as a feedstock has expanded substantially in recent years, and it is more common in refineries. Similarly, coke particles are frequently seen in the vicinity of the coker unit and storage sites. Around the catalyst hoppers of fluid catalytic cracking reactors and regenerators, large amounts of catalyst fines are released. Before these particles are washed into the sewers, the fines can be collected and recycled. Coke fines may potentially be recycled and used as a source of energy (Speight 2020).

Many materials that are discarded as hazardous wastes have the potential to be reused in many ways. In certain cases, tainted materials may be suitable for use as solvents or cleaning agents in a less sensitive application. Moreover, raw materials that have been kept past their expiration dates are another form of hazardous waste if not reused. Such durations are frequently set conservatively, and the material may be requalified and used in manufacturing (LaGrega et al. 2015). For effective utilization of raw material resources and to reduce the volume and toxicity of waste products, efficient manufacturing techniques are needed. It is projected that by creating better design decisions and reusing resources, 70% of the waste materials can be eliminated (Bishop 2000).

Another useful method of waste minimization technique is "reducing" the wastes. There are several techniques that can be used to reduce the wastes. Generally, waste can be reduced by process modification, segregation, and reusing. Process modification includes changes in operating procedures and material storage methods and changes to the final products (LaGrega et al. 2015). Raw materials can be substituted with higher-quality materials to reduce or eliminate the generation of hazardous waste.

Rapid development worsens water consumption and wastewater discharge rates, resulting in the reduction of water resources. Water shortages, environmental and economic considerations, and technological advancements are the driving forces for reuse of water and wastewater. Water reclamation can enhance water supply, while reducing the amount of discharge into nearby water bodies. Furthermore, modern wastewater reuse methods employ ultraviolet radiation, maturation ponds, membrane filtration, and electrochemical treatment to remove pollutants such as salt, pathogens, heavy metals, toxins, etc. Reclaimed water is a treated effluent that has been determined to be of sufficient quality for reuse (Lyu et al. 2016).

4.3 Pollution Prevention Regulations

There are several environmental laws and regulations related to pollution prevention in developed countries such as United States, countries in Europe, etc. Prior to the Pollution Prevention Act 1990, there were directives in the US federal statutes which were related to P2. They are discussed below.

4.3.1 Clean Air Act (CAA)

The Clean Air Act (CAA) of 1970 is the federal law which regulates air emissions from both stationary and mobile sources. Additionally, the CAA authorized the US Environmental Protection Agency (EPA) to establish the National Ambient Air Quality Standards (NAAQS) to regulate emissions of ambient air pollutants and hazardous air pollutants (HAPs). The CAA was amended in 1977 and 1990 to set new limits for achieving the NAAQS. This was due to the fact that most of the country failed to meet the initial deadlines. Table 4.1 provides P2 mandates in the CAA.

Table 4.1 P2 mandates in the CAA (Pollution Prevention Law and Policies, U.S. EPA n.d.)

Section	Pollution prevention mandates in the CAA
7402	Supports collaboration among federal departments, states, and local governments for the prevention and control of air pollution
7403	EPA to establish a national R&D program for air pollution prevention and control. Additionally, the EPA must facilitate collaborations among the air pollution prevention and control agencies
7405	Enabled EPA to provide grants to air pollution prevention and control agencies
7412	Gave permit waivers for facilities that reduced their emissions of toxic substances into the air by 90–95%
7414–7418	Allowed EPA to monitor, inspect, and keep records for all facilities that emit pollutants

Table 4.2 P2 Mandates in the EPCRA (Pollution Prevention Law and Policies n.d.)

Section	Pollution prevention mandates in the EPCRA
11,001–11,005	Contain emergency planning requirements for pollution and fire control. Provides list of different substances covered under this act
11,021–11,022	Facilities which are covered under EPCRA must have material safety data sheets (MSDS) for all chemicals and must complete hazardous chemical inventory forms
11,023	Required owners and operators of the facilities which are covered under EPCRA to complete a toxic chemical release form

4.3.2 Emergency Planning and Community Right-to-Know Act (EPCRA)

The EPCRA of 1986 was made to help different communities to plan for emergencies. Additionally, the EPCRA requires industries to report their storage, use, and release of any hazardous substances to federal and local governments. This act was passed in response to the Bhopal disaster that happened in India in the year of 1984, which triggered concerns regarding the environmental and safety hazards posed by the storage and handling of toxic chemicals. Table 4.2 lists P2 mandates in the EPCRA.

4.3.3 Resource Conservation and Recovery Act (RCRA)

The Resource Conservation and Recovery Act (RCRA) grants EPA the authority to control hazardous waste generation from cradle to grave. This includes everything from the generation, transportation, treatment, storage, and disposal of hazardous waste. The RCRA was amended in 1986 to enable the EPA to address environmental problems that could result from the storage of underground tanks containing hazardous substances. Table 4.3 lists P2 mandates in RCRA.

Table 4.3 P2 Mandates in the RCRA (Pollution Prevention Law and Policies n.d.)

Section	Pollution prevention mandates in the RCRA
6907	EPA must establish waste management guidelines
6921	Requirements were established for owners and operators of the facilities which produce hazardous wastes
6922	Generators must show (in shipping manifests) that they have a plan to reduce the wastes. Additionally, they must submit biennial reports showing their efforts to reduce the amount and toxicity of waste generated
6925	Requires a permit for treating and storing hazardous wastes
6927	EPA shall offer financial assistance to federal, state, and local agencies that are researching and investigating in the areas of waste management and minimization
6981	EPA shall offer financial assistance to federal, state, and local agencies that are researching, investigating, or providing in the areas of waste management and minimization

Table 4.4 P2 mandates in the CWA (Pollution Prevention Law and Policies n.d.)

Section	Pollution prevention mandates in the CWA
1251	The national goal is to eliminate the discharge of pollutants into surface waters
1252	EPA mandated in collaboration with federal, state, and local agencies and industries to develop programs for preventing, reducing, or eliminating the pollution into surface waters
1256	Appropriation of funds to state and local agencies for pollution control
1381	EPA to provide grants to states for pollution control revolving fund for implementation of management and conservation plans

4.3.4 Clean Water Act (CWA)

The Clean Water Act of 1972 is established for regulating the discharge of pollutants to surface waters. Table 4.4 lists the mandates in the CWA.

4.3.5 Pollution Prevention Act (PPA)

As discussed above, many US legislations during the 1970s and 1980s such as the Clean Air Act (CAA), the Emergency Planning and Community Right-to-Know Act (EPCRA), Clean Water Act (CWA), etc. included pollution prevention mandates. However, in 1990, the US Congress passed the Pollution Prevention Act (PPA) which made the Environmental Protection Agency (EPA) to establish a national source reduction program that specifically focuses on preventing, reducing, recycling, and treating the source of pollution based on what each industry or facility requires. The PPA differs from the older laws because rather than controlling the waste produced (i.e., end-of-pipe control), it reduces and prevents pollution at its source (Speight 2020). Table 4.5 lists P2 mandates in the PPA (U.S. EPA n.d.).

Table 4.5 P2 mandates in the PPA (Pollution Prevention Law and Policies n.d.)

Section	Pollution prevention mandates in the PPA
13,103	The EPA to develop and implement a strategy to promote source reduction
13,104	The EPA is given the authority to provide grants to the states to promote source reduction by businesses
13,105	EPA mandated to establish a database that contains information on source reduction
13,106	Owners and operators of businesses that are required to file a toxic chemical release form must include a toxic reduction and recycling report

4.4 Case Studies

4.4.1 Sydor Optics to Recover Cerium

Park et al. (2020) studied the case of an optics company (Sydor Optics) that used a pollution prevention method to improve the recovery of cerium oxide (ceria). Cerium oxide is a rare earth compound which is used to polish glass surfaces on lenses, cell phone displays, and even vehicle windows. During manufacturing, cerium oxide residue is mostly lost due to drag out and discharge from the built up contaminants. This compound is expensive; thus, Sydor Optics opted to recover the leftovers at a lower cost.

After the assessment of the recovery process, Sydor Optics noticed that not all ceria particles were retrieved, and this resulted in major losses and damages to the sewer system. It also motivated the development of a feasible solution that would increase the recovery of ceria material, cut losses, and reduce the total suspended solids in wastewater. According to this study, it was determined that almost 23.8 kg/day of ceria was lost to sewer (77%) and only 23% was left for recovery.

Sydor Optics investigated suitable extraction methods for particle size ranging from 0.1 µm to 1.0 µm. The study showed that centrifugation process seemed to recover more ceria. Also, it is a mechanical separation technology that did not require abrasive or hazardous chemicals and high temperatures. Membrane filtration is another technology that can separate microparticles and work well with higher levels of suspended solids to minimize cost. This method uses hydrogen peroxide wash that effectively cleans the membrane and can also act as a chemical cleaner for leftover cerium. The entire process consisted of a process tank with a centrifuge at high speed and a membrane filtration with constant circulating fluid to avoid hardening of the cerium oxide particles. Based on this, the company was able to save almost $8000/year to $30,000/year with 95% recovery. This is an example of a validated P2 process modification project that is implemented to reduce wastes and cut costs relevant to the manufacturing while preserving the environment.

4.4.2 *Waste Reduction of Polypropylene Bags Using Six Sigma Methodology*

Another example of pollution prevention using process modification was studied by Sajjad et al. (2021). In this study, a polypropylene bag manufacturing plant was enhanced using the Six Sigma DMAIC (define, measure, analyze, improve, control) methodology.

Polypropylene bags are very strong, and they are made from weaved polypropylene plastic strands. An unfortunate consequence of bags' strength and durability is that they take a long time to get biodegraded. Additionally, it leads to environmental pollution when the bags are improperly disposed after use (Asmuni et al. 2015). In addition to the improper disposal, a large quantity of polypropylene bags is wasted during the production process due to rejects. The polypropylene bag plant, in this case study, had previously discarded 2.8% of all the sacks produced. This high rejection rate had negative impacts on both the environment and the profit margin of the plant.

Srinivasan et al. (2016) reported that a large number of companies are struggling to reduce the high rejection rate by utilizing different methods. One of the best strategies to improve processes is by using the Six Sigma DMAIC methodology. Using the DMAIC approach, Sajjad et al. (2021) found that the high rejection rate of this plant was due to the low strength of the fabric obtained at the weaving section of the process. Sajjad et al. (2021) designed an experiment on the extrusion section of the process and found two interacting variables which played a key role in process variations and explained the lower tape-tenacity values. These two variables were the temperature of the water bath and the line speed of the extrusion process. Using this newly found information, Sajjad et al. (2021) were able to optimize these variables and found that the optimum temperature of the water bath must be 40 °C, while the line speed must be 300 m/min. Thus, using Six Sigma DMAIC approach, the sack rejection rate of the polypropylene plant in question was brought down from 2.80% to 1.20%. This case study show that process modification using Six Sigma DMAIC methodology is effective for reducing waste which in turn provides significant cost savings and environmental benefits.

4.4.3 *LMDS: Safer Alternative to Solvent Degreasing*

A case study by the Toxics Use Reduction Institute (TURI) (n.d.) at the University of Massachusetts involves pollution prevention through material substitution. This case study is on Lockheed Martin Defense Systems (LMDS) in Pittsfield, Minnesota. LMDS design and manufacture several aerospace products for the US armed forces and their allies. This case study has focused on one of their combat vehicle transmission system. Throughout the assembly and reassembly process, the parts are cleaned frequently to remove oils, grease, and wax to ensure the highest level of reliability (Toxics Use Reduction Institute n.d.).

This process used chlorinated solvent vapor degreasers which contain ozone-depleting compounds (ODCs) such as 1,1,1-trichloroethane (trichlor, 1,1,1 TCA, methyl chloroform) and chloroflourocarbon-113 (CFC-113, Freon). A total of 39 vapor degreasers were in operation across LMDS facilities that required 125 tons/year of chlorinated solvents. From the 125 tons/year, 70 tons of chlorinated solvents were released into the atmosphere. To minimize the environmental impacts, LMDS committed to eliminate the use of ODCs. Multiple departments within LMDS including EHS, finance, procurement, and management coordinated with vendors in finding and evaluating suitable alternative techniques for degreasing process. Multiple factors such as economic feasibility, technical feasibility, safety and environmental impacts, etc. were taken into account.

LMDS replaced 36 of their existing 39 vapor degreasers with 7 aqueous systems and 2 semi-aqueous systems. By replacing their vapor degreasers with aqueous and semi-aqueous systems, LMDS reduced the use of solvent from 125 tons/year to 2 tons/year. Consequently, the emissions of ODCs were reduced from 70 tons/year to fewer than 1 ton/year. LMDS saved $497,000/year in solvent purchasing, $65,000/year in permitting and record-keeping, and $17,500/year in waste disposal. This process also reduced the water consumption of the transmission assembly and repair by 2,000,000 gallons/year. This case study shows that material substitution and process modification can not only prevent pollution but also save costs and valuable resources (U.S. EPA n.d.).

4.4.4 Plastic Pollution Prevention Measures During the 2019 COVID-19 Pandemic

Prevalence of plastics in the environment as a nondegradable and single-use material caused major issues and required immediate attention. This has translated into a form of regulations, laws, and initiatives for the disposition of plastics and halting the uncontrollable plastic pollution. These efforts were enforced by governments and international institutions; however, with the rise of the global pandemic, the laws had to be flexible as the public required single-use equipment and supplies of all sorts to protect themselves. Personal equipment of all kinds was produced utilizing plastics and thus increasing the plastic wastes on a global scale. According to Bown (2020), face mask production in China rose to 110 million units only in January to February of 2020, and this number is only a fraction of the global single-use plastic consumption.

The Plastics Industry Association has recognized that plastic bags also contribute to the spread of bacteria and viruses through surface contacts as if the bags were transmission vectors for the SARS-CoV-2 virus (Barbosa et al. 2019). This was due to the nature of the plastic surface that allowed the prevalence and survival of the virus particles on the bags for longer periods of time. Viral loads were observed to survive on polystyrene plastic, aluminum, and glass surfaces for at least 96 h but with a gradually decreased efficiency after 24 h (Pastorino et al. 2020). In order to accommodate fast-paced changes during the pandemic, a handful of rules and regulations were needed. For example, in Scotland, certain restrictions for single-use plastics were suggested, but it imposed financial burdens that were overwhelming owners of small- and large-scale businesses. Although changing the rules and regulations seemed like the most suitable short-term plan, the long-term goals need to be set to efficiently reduce plastic wastes. This case study demonstrates that P2 can be achieved by changes in the environmental regulations related to P2.

4.5 Cost of Pollution Prevention

Although there have been numerous examples showing decreased pollution through P2 methods, there are several barriers for implementation of P2. A number of P2 strategies are not self-sustaining; therefore cost is one of the major impediments. Corporate investments generally provide a sufficient return on the invested money for shareholders, and some P2 methods at particular sites may fall short of the company's criteria. For example, industrial equipment at a crude oil refining facility is extremely capital intensive and has a lengthy life cycle. This weakens the motivation to make changes to the installed equipment that is still functional.

Training programs emphasizing the significance of P2 and educating employees regarding minimizing pollution through a methodical approach will yield greater outcomes with economic incentives. Source control may be highly effective when done through public education, community planning, and regulatory standards, but it typically necessitates significant changes in human behavior. In addition to this, a comprehensive waste audit can be used to evaluate potential for better operating practices, process changes, process redesign, and recycling in a methodical manner. It should be noted that P2 programs do not always necessitate the use of sophisticated or costly equipment. A simple and low-cost approach can also be more successful.

4.6 Conclusions

Pollution prevention (P2) preserves resources by conserving them at the point of origin. P2 differs from pollution control or end-of-pipe control approach. P2 encompasses all elements of waste minimization, including careful examination of each product throughout its entire life cycle from the conception of the product to final disposal. P2 is the most desirable method of waste management due to the positive environmental impact it makes and it is demonstrated in this chapter though several case studies. Furthermore, P2 is flexible, and it can be implemented under different circumstances, through a suitable method such as elimination, reduction, recycling, etc. Moreover, the environmental regulations related to P2 described above have had a huge impact on industries and households by changing their perspective on the waste reduction.

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Chapter 5
Medical Waste Management and Treatment Technologies

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5.1 Introduction

Medical waste refers to the waste generated as a result of healthcare activities at hospitals, blood banks, veterinary clinics, medical research laboratories, or any other healthcare facilities. It includes any discarded material that is involved in the diagnosis and treatment of humans and animals, and it is usually contaminated with blood, body fluids, or any other infectious material. Figure 5.1 shows typical generated medical wastes in a hospital. Medical waste can be generally classified into general waste, infectious waste, hazardous waste, and radioactive waste (Hulley 2020). According to the Medical Waste Tracking Act of 1988, EPA defined medical waste as any type of solid waste that is created in the diagnosis, treatment, or immunization of human beings or animals, or in related research studies, or in the production or testing of biologicals (Chartier et al. 2014). The main components of medical waste are plastics, paper, and textiles, and these primary materials are used in hospitals for sanitary consumables such as bottles, drug packaging, bedsheets, toilet papers, face masks, and gloves. The bulk density of medical waste is typically 249 kg/m^3 with a moisture content of 44.75 wt.% (Zhang et al. 2016).

Medical waste poses a serious risk to the health and to the environment because it contains several pathogenic microorganisms and hazardous chemicals. Improper handling of medical waste could lead to the exposure to pathogens or hazardous material through inhalation, ingestion, or cuts or punctures by infected sharps.

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Fig. 5.1 Typical medical wastes found in hospitals (Medical wastes n.d.)

Underdeveloped and developing countries lack efficient medical waste management systems and establishments. For instance, a study was conducted in Bangladesh, which is a developing country with rapidly rising urban population and numerous health issues, and it was observed that the limited medical waste management systems were attributed to lack of education on medical waste management. Only four major cities (Dhaka, Chittagong, Gazipur, and Khulana) implemented some type of healthcare waste management methods. In other cities, the collected medical wastes are transferred to open waste dumping sites. Typically, hospital and domestic waste are mixed together and discarded or buried, without accounting for any rules or restrictions. Furthermore, it is reported that there are no specific waste treatment practices or guidelines in government hospitals within the country. The hospital employees treat all wastes as general solid wastes, without paying much attention to the possibility of the infectious nature of medical wastes (Md. Yousuf and Rezaul 2018). Due to the lack of education and awareness on the dangers of medical wastes and due to the absence of adequate waste management and control technologies or equipment, this trend will continue to persist. However, a study which focused on 900 private healthcare facilities show that the medical waste is 16.18% of the total waste, which falls within the acceptable World Health Organization (WHO) range of 10–25%. In the private healthcare sector, the average daily hazardous healthcare waste generation rate per patient was found to be 0.17 kg per bed per day. Even with the low hazardous waste generation rates in private sectors, the personnel involved in waste disposal and treatment are subject to health hazard issues, as a result of massive accumulation of medical wastes over time (Md. Yousuf and Rezaul 2018).

The objective of this chapter is to provide an overview of medical waste constituents, environmental laws related to medical wastes, management and control techniques, and medical waste management during COVID-19 pandemic.

5.2 Categories of Medical Wastes

The World Health Organization (WHO) categorized medical wastes into several groups:

- *Infectious wastes*: wastes that have a large concentration of substances or pathogens that can cause infections to humans. It includes cultures of infectious agents, as well as wastes from patients with infections. For instance, these types of wastes come from the following contaminated sources: used swabs, bandages, surgical gloves, masks, dressing, and any disposable medical equipment (Chartier et al. 2014).
- *Sharps*: wastes that do not pose an infectious hazard but a physical one instead (i.e., cut, abrasion). Sharp waste includes syringes, needles, scalpels, blades, broken glass, etc.
- *Pathological wastes*: wastes that consist of body parts of humans or animals (i.e., organs, tissues, body parts, blood, body fluids).
- *Chemical wastes*: wastes that result from cleaning or medical diagnosis processes. They include chemical solvents, disinfectants, and reagents used for cleaning and disinfecting medical laboratories.
- *Radioactive wastes*: wastes that consist of radioactive material such as radionuclides that are used for diagnosis and treatment.
- *Pharmaceutical wastes*: wastes that include unused, expired, contaminated drugs, and vaccines.
- *Cytotoxic wastes*: waste that includes genotoxic substances which can be categorized as one of the three: carcinogenic, mutagenic, or teratogenic. Cytotoxic waste can include expired or unused cytotoxic drugs used in the treatment of cancer and devices contaminated with cytotoxic substances.
- *General nonhazardous wastes*: wastes that do not possess infectious or radioactive nature and do not result in physical or chemical hazards. They are not dangerous to humans. This type of waste includes plastics, paper, and textiles.
- *Other categories of medical wastes*: these wastes include pressurized containers (gas cylinders) and waste containing heavy metal content such as broken thermometers, blood pressure gauges, and batteries.

In general, infectious waste, pathological waste, and sharps are the predominant waste types among the medical wastes generated. The WHO reported that around 85–90% of the total medical waste generated falls within the general nonhazardous waste category, while the rest of the medical waste generated is hazardous. If the waste is not segregated properly, the total volume of the medical waste generated would increase, as a result of contamination due to contact, hence increasing the overall waste management and treatment costs (Chartier et al. 2014).

Health hazards of medical wastes are mainly caused by the infectious pathogenic microorganisms that the waste contains. Other hazards are usually caused by hazardous nature of chemicals and pharmaceuticals, the radioactivity of the waste, and the cuts from sharps. The exposure to medical wastes could cause harm to anyone including medical staff, medical waste handlers, workers of waste treatment facilities, patients, and general public. Exposure to the waste can occur through direct or indirect contact with a help of a carrier like air, water, or the environment or direct contact through inhalation, ingestion, or by skin cuts or punctures. Improper management of medical waste poses significant risks on the human health and the environment.

5.3 Quantities of Medical Wastes

The quantities of medical wastes in three different developed countries including the United States, Australia, and Greece are discussed here to illustrate the enormous rate of medical waste generation.

The United States is one of the world's top contributing nations, toward prominent solid waste generation, equivalent to 624,700 metric tons in 2011 (Van Demark 2018). In terms of annual waste generation, the healthcare industry is second only to the food industry, which is known as the primary contributor in waste generation. Each year, healthcare facilities in the United States produce 4 billion pounds of trash (660 tons per day), in which their operating rooms generate up to 70%, or approximately 2.8 billion pounds (Van Demark et al. 2018).

Similarly, the Australian healthcare system has grown into being one of the greatest contributors of wastes in the country, generating up to 236 million kilograms of waste per year. According to the United Nations Environmental Program (UNEP), a single patient hospital bed can produce up to 0.87 kg of infectious waste each day. The daily output of CO_2, from incinerating the medical waste alone, is estimated to be in excess of 235,000 kg per day. Hence, the incineration process by itself releases a significant amount of greenhouse gases (GHG). To put that in perspective, 1 kg of clinical waste creates around 3 kg of carbon dioxide when burned; thus the medical waste generation directly impacts the amount of CO_2 emissions, which contributes toward the global warming effect (Wyssusek et al. 2018).

Moreover, in Greece, the generation rates and compositions of infectious and urban medical wastes, generated from private medical microbiology laboratories, were investigated using real weight measurements, which were conducted over a 6-month period. The study found that infectious medical waste (IFMW), or the hazardous percentage of total MW, accounted for 35% of the total medical waste. The study also concluded that private microbiology laboratories in Greece generate about 580 tons of IFMW each year (Komilis et al. 2017). Furthermore, it was estimated that the laboratory units from different nursing departments in Rio University Hospital in Greece add up to almost 0.149 kg/bed/day of medical hazardous waste that is highly contagious (Zamparas et al. 2019).

5.4 Regulations Related to Medical Wastes

In 1988, the US EPA established Medical Waste Tracking Act (MWTA) which provides guidelines on medical waste management (US EPA 2011). State agencies also have their own laws and regulations under the guidelines of MWTA, and the regulations of each agency differ significantly from one to the other. Federal agencies such as Centers for Disease Control and Prevention (CDC), Occupational Safety and Health Administration (OSHA), and the Food and Drug Administration (FDA) have established safety regulations on handling medical wastes (US EPA n.d.). Several international agreements such as Basel Convention also exist to control the transport of medical wastes between the countries (UN Environment Program 2011).

One of the main goals of the MWTA is the design of a cradle-to-grave tracking system based on the waste generator and the type of regulated wastes. The act also developed the tracking system that was similar to RCRA manifests for hazardous waste. In addition, necessary waste segregation, packaging, labeling, storage, and management standards were established, as well as record-keeping requirements and fines that might be imposed for waste mishandling. From June 1989 to June 1991, these guidelines for tracking and managing medical waste were implemented in four states: New York, New Jersey, Connecticut, and Rhode Island, as well as Puerto Rico. EPA also gathered data and conducted various research projects on medical waste management (Regulated Medical Waste 2015).

Determining whether the waste is infected or not has been proven to be difficult, due to the associated uncertainty. Inconsistent treatment, storage, and disposal techniques may come from various working definitions of infectious waste. Thus, inconsistencies can impact the waste management costs, treatment technology selection, and ultimately, the possible health and environmental risks (Uzych 1990). Both CDC and US EPA as well as numerous state agencies have sought to classify infectious waste based on a variety of waste characteristics. Infectious waste, for example, is defined by the EPA as the waste that can cause an infectious disease. It necessitates the examination of at least four factors linked to the disease: dosage, resistance, portal of entry, and presence of pathogen (Uzych 1990). The CDC further issued recommendations in 1987, stating that blood and body fluids should be regarded either as human immunodeficiency virus or blood-borne infections. However, the CDC eventually limited the scope of its guidelines published in 1987 only to blood and other visible blood-containing body fluids (Uzych 1990).

Implementing EPA recommendations has been a challenge for medical waste producers. For instance, the EPA categorizes communicable disease wastes as infectious, whereas the CDC recommends managing communicable disease wastes in accordance with specific guidelines of the hospital (Uzych 1990). At present, the EPA is no longer in charge of medical waste regulation; instead, the states and other government entities have acquired that responsibility.

The existing medical waste regulatory structure in the United States is summarized as follows:

- *State Medical Waste Regulations*: To some extent, medical waste laws have been implemented in nearly all 50 states in the United States. State medical waste regulations, on the other hand, differ from state hazardous waste restrictions, which are all based on federal RCRA criteria. Some state medical waste regulations are modeled after the MWTA, while others have little or no relation. In most of the states, EPA is in charge of formulating and implementing medical waste management and disposal legislation. In other states such as Missouri and Oklahoma however, the department of health may play a significant role or even act as the primary regulating agency. In situations where both agencies are involved, the department of health is primarily in charge of on-site management, while the environmental agency is in charge of transportation and disposal of wastes. Moreover, medical waste packaging, storage, and transportation are regulated in most states. Healthcare facilities in some states are required to register and/or receive a permit. The development of emergency plans, on-site treatment of waste, training, waste tracking, record-keeping, and accident reporting may all be covered by state regulations (Regulated Medical Waste 2015).
- *OSHA Regulations*: OSHA regulates several aspects of medical waste including sharps' management, medical waste container design and requirements, medical waste bags/containers labeling, and employee training. The guidelines are intended to protect healthcare personnel against blood-borne pathogen exposure. The guidelines can however assist in the systematic management of waste, which benefits both the public and the environment. There are often overlaps between the environmental authorities, department of health, and the OSHA blood-borne pathogen standards. A set of regulations can either be generic or quite detailed. In such instances, it is recommended that the healthcare facilities adhere to the more detailed or strict rules. The OSHA standards address the significant gaps where there is a lack of comprehensive medical waste regulations (Regulated Medical Waste 2015).
- *US EPA Regulations*: EPA has active regulations governing emissions from hospitals, medical/infectious waste incinerators, as well as requirements under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) for certain medical waste treatment technologies that use chemicals to treat the waste (Regulated Medical Waste 2015).
- *The Department of Transportation (DOT) Regulations*: DOT classifies regulated medical waste as hazardous. Regulated medical waste (RMW) is defined as the fraction of the waste stream that may be contaminated by blood, body fluids, or other potentially infectious materials, thus posing a significant risk of infection transmission. It is also known as "biohazardous" waste or "infectious medical" waste. Although any item that has come into contact with blood, mucus, or secretions may be infectious, it is neither practical nor a requirement to treat such waste as infectious. Guidelines and regulations, established by the federal, state, and local governments, define the types of medical wastes that are regulated, as well as the treatment and disposal standards to be followed. The degree of contamination, such as blood-soaked gauze that constitutes the discarded item, is likewise addressed by state regulations. Other specific categories of waste

generated in healthcare facilities (i.e., research laboratories that require handling precautions) are identified and categorized in the EPA's Manual for Infectious Waste Management (CDC 2003). Although understanding these standards is vital because of the liability connected with transporting to an off site, the DOT requirements largely apply to transporters rather than healthcare facilities (Regulated Medical Waste 2015).

5.5 Medical Waste Management

5.5.1 Collection, Storage, and Transportation

A proper collection and storage strategy must be devised in a waste management program. A daily collection system is needed to avoid major accumulation of wastes. Different types of wastes should be stored separately, for instance, infectious waste should never be stored in places accessible to the public. There are several criteria that should be met in order to choose a specific area of waste storage, and these criteria include the optimal temperature of the area, ease of cleaning, restriction on facility access, exposure to the sun, waterproofing of the ground, ease of access to waste transportation facilities, ventilation, amount of light, etc. The vehicles to be used for transportation of medical waste are specific. Different types of waste can, but not necessarily, use different means of transport. Moreover, on-site transportation vehicles differ from the off-site vehicles. For off-site transportation, the facility itself is responsible for packaging and labeling the waste before transporting in specifically designed vehicles. Once the waste is transported out of the storage facility, different methods are used in the sterilization and treatment of medical wastes.

5.5.2 Segregation, Labeling, and Separation

Several methods such as segregation, separation, etc. are used to minimize the volume of medical waste. Segregation is beneficial because it prevents hazardous waste from reaching and contaminating the nonhazardous ones. Thus, segregation minimizes the quantity of the hazardous wastes, and it also eases the transport of the waste to a treatment facility. The medical waste is separated into categories based on its type, amount, composition, and disposal methods. Infectious and pathological waste, as well as sharps, are stored in separate containers. For each type of medical waste, the containers are labeled as "biohazard," and they are closed and watertight and are given uniform color codes to distinguish them. Figure 5.2 shows the type of symbol used to identify medical wastes. The size of the containers is determined by the amount of waste produced, and the containers are lightweight and easy to transport (Shareefdeen 2012).

Fig. 5.2 A symbol used to describe medical wastes (Biohazard symbol n.d.)

The system for segregation, packaging, labeling, and marking of medical waste involves its separation into categories as described. Infectious medical waste, for example, is placed in yellow plastic bags and is intended to be incinerated or buried deep in a landfill. Red plastic bags or containers are used if the waste is going to be autoclaved or microwaved. Medical wastes are commonly identified by the biohazard sign, when it comes to labeling and marking. Both the packaging and the labeling are widely used around the world, and the distinction lies in the treatment method (Shareefdeen 2012). Waste containers should never be completely full; instead they should be filled till two-thirds of the capacity, as a maximum. As a precautionary measure, nonhazardous waste can be considered hazardous if the waste is placed in the wrong container (Singh et al. 2021).

5.5.3 Medical Waste Management in Different Countries: Case Studies

Iran: Medical Waste Management Practices

Kargar et al. (2020) performed a study on medical waste management practices in Iran, where a significant increase in medical centers is observed. According to the Iranian Ministry of Health and Medical Education, hospitals had a total of 120,612 active beds in 2018. In addition to 2632 rural health clinics, 2783 urban health centers provide healthcare services. In comparison to other regions of Iran, the northern part of the country has a higher population density. As a result, medical waste management in northern Iran is far more essential than in other parts of the country. Babol, a city in Mazandaran province with a population of 250,126 people, was selected as a case study. A total of 20 high-demand medical centers were considered, which consisted of 8 hospitals and 12 clinics along with 7 storage centers, 7 treatment centers, 1 transfer station, and 1 disposal center (Kargar et al. 2020). Two new treatment centers with autoclave technology as well as two storage centers were recommended for western and eastern of Babol city to manage the medical waste.

Furthermore, another study reported by Eslami et al. (2017) is based on the data gathered from Iran's 31 provinces. The study reports about 14.8% and 24.3% of private and public hospitals, respectively, lack medical waste treatment, resulting in hazardous waste being disposed without treatment which can have major impacts on public health and the environment (Eslami et al. 2017). In this study, all hospitals with access to the Ministry of Health and Medical Education network were chosen. This survey included 837 hospitals from the list. The data was obtained based on the Ministry of Health and Medical Education's instructions for the hospitals' medical waste treatment and self-reporting. Forms and questionnaires were sent to all hospitals, and the following is a list of the most crucial data that were gathered (Eslami et al. 2017):

- The number of beds in a hospital (the number of active beds in a hospital)
- The type of hospital (i.e., private, governmental, related to other organizations, etc.)
- Rate of total waste generation (kg/day)
- Rate of infectious and sharp waste generation (kg/day)
- Rate at which chemical waste is generated (in kg/day)
- Treatment procedures (i.e., autoclave)

The wastes generated were grouped into one of three categories: nonhazardous or general waste, infectious and sharp waste, and chemical waste (Eslami et al. 2017). The study pointed out that the general medical waste generation rates ranged from 0.91 to 3.27 kg/bed/day, whereas infectious and sharp waste generation rates ranged from 0.48 to 1.78 kg/bed/day. The overall waste generation rate and the infectious waste generation rate in Tehran, Iran's capital, were reported as 3.38 and 1.22 kg/bed/day, respectively. Alborz province has shown to have the highest hazardous-infectious waste generation rates, at 1.78 kg/bed/day, and Qazvin had the highest general waste generation rates, at 3.27 kg/bed/day, respectively. It was observed that the rate of medical waste generation in Iranian hospitals is significantly high.

The variation could either indicate ineffective waste segregation practices within each hospital or other factors such as external patients, higher bed occupancy, larger number of lab tests, surgeries, etc. (Eslami et al. 2017). It is obvious that the amount of infectious and sharp waste in Iran's hospitals, as well as the rate at which they are generated, is extremely high. This increase can be attributed to a variety of factors, including poor segregation, lack of waste minimization strategies, and lack of awareness on the topic. Increased generation of infectious and sharp waste eventually leads to an increase in the cost of medical waste treatment and disposal. Through this case study, the importance of implementing a precise segregation program that uses standard color-coded plastic bags or containers and educating hospital staff is emphasized (Eslami et al. 2017).

Jordan: Medical Waste Collection, Segregation, and Disposal Practices

A significant number of patients from neighboring countries travel to Jordan for medical treatment because of Jordan's rapid growth in healthcare business, which has led to the increase in the volume of medical waste generated. Jordan's hospitals have grown by 32% in the last 10 years, and the total number of hospital beds has reached 13,731 in 2017 (Al-Momani et al. 2019). Improper waste collection services and incorrect waste disposal at open dumpsites hinder Jordan's waste management methods. According to Al-Momani et al. (2019), field studies and interviews were done at some of Jordan's hospitals including educational, public, and private sectors. Public healthcare facilities are the major generators of medical waste. The northern, southern, and middle region of Jordan consist of 30 public hospitals and 1427 public medical centers which are administered by the Ministry of Health (Al-Momani et al. 2019).

The medical waste generation ranged from 0.36 to 0.87 kg per patient per day. Poor and inefficient medical waste disposal has been observed along with the large amounts of medical wastes generated in the hospitals. The case study further highlighted that there was no regulatory system in place to regulate the disposal of medical waste in Jordan. Jordan currently produces around 2,454,000 tons of wastes including municipal solid waste, hazardous industrial waste, and medical waste per year. The medical waste disposal and treatment methods being practiced include incineration and sterilization using autoclaves (Al-Momani et al. 2019). According to the study, Jordan's middle and northern areas have higher awareness on medical waste management, when compared to the country's southern regions.

The study concluded that the medical waste generation will continue to rise as Jordan's healthcare services evolve and expand; as a result, each hospital in Jordan must implement a professional medical waste management system. It has also been found that the high generation rates of waste in hospitals were due to improper segregation practices. The study proposes that healthcare workers need to be more informed of medical waste management and treatment systems (Al-Momani et al. 2019).

Myanmar: Application of Multi-Criterial Decision Analysis

The number of private and public hospitals in Myanmar is steadily increasing, which will lead to an increase in the total quantity of medical waste generated (Aung et al. 2019). In Myanmar, there are no official standards in place to ensure the treatment and processing of medical wastes. Aung et al. (2019) discusses a framework for the hospital waste management evaluation criteria using multi-criteria decision-making approaches. The multi-criteria decision analysis (MCDA) enables decision-makers to address the uncertainty that can arise while assessing the management methods and condition of medical wastes. Therefore, decision-makers have been able to compare the results and assess the performance of individual hospitals, with the help of this approach. The study revealed that open burning, incineration, and uncontrolled dumping were the common methods of waste treatment and final disposal. In public hospitals, there is also a lack of awareness and inadequate training among the healthcare staff. This study focused on the problems in Myanmar's waste management system. To enhance the waste management systems at government facilities, it is suggested that a special budget is allocated and the rate of medical waste generation is tracked in a systematic way (Aung et al. 2019).

The United States: Lean and Green Surgery Project

In a recent research study, Van Demark et al. (2018) states that the "Lean and Green" surgery project was launched in 2015 by the American Association for Hand Surgery, to reduce the amount of medical waste generated. The number of active hand surgeons in the United States is reported to be around 2000 surgeons. If each surgeon performed 100 "green" cases each year, which adds up to a total of 200,000 cases, the project would save $10.64 per case, and 5.06 pounds of medical waste per case can be reduced. This study concludes that the reusing of single-use medical devices and waste segregation are important steps to minimize the wastes from surgery rooms (Van Denmark et al. 2018).

The United States: Reuse of Anesthetic Equipment, Training, and Regulatory Requirement

Another study (Wyssusek et al. 2018) suggests reducing, recycling, reusing, rethinking, and the use of emerging technologies to achieve waste reduction. In order to reduce wastes, spreading awareness is also essential. Mandatory refresher training for employees should be conducted to keep them reminded on waste management, in conjunction with the appointment of an environmental and health and safety officer that has an impact on waste reduction. According to a survey of 413 anesthesia departments in the United States, 58% would recycle single-use anesthetic equipment only if required by law. About 83% on the other hand would participate in a recycling campaign if it was initiated by a supplier (Wyssusek et al. 2018).

Table 5.1 presents case studies that were conducted in other countries related to medical waste management (Al-Momani et al. 2019).

5.6 Medical Waste Disposal, Disinfection, and Treatment Methods

After collection and segregation of the medical wastes, medical wastes are sent to a treatment facility in securely covered and labeled containers in a highly protected vehicle (Hulley 2020). As discussed in the previous section, in many countries,

Table 5.1 Case studies of medical waste Management in different countries

Location	Aim	Method	Result and conclusion	Sources
Baghdad, Iraq	During a 4-month study, two teaching hospitals with different bed capacity were analyzed	Experimental studies, document reviews, clinical audits, and interviews	The amount of medical waste varies. The difference was due to the number of patients admitted to hospitals as a result of a variety of factors (country's current situation, explosion, and the economic situation)	Kareem Ali et al. (2018)
KwaZulu-Natal, South Africa	To determine the knowledge, attitudes, and behaviors of staff at a district hospital about healthcare waste management	Total of 241 professionals and nonprofessionals participated in this observational study. Data collection using a questionnaire was used	Healthcare waste management was not well-recognized (42.7% had poor knowledge and 53.9% had good waste management practices). Appropriate training and supervision in healthcare waste management are required to convey knowledge among personnel	Olaifa et al. (2018)
Aligarh, India	To examine management of medical waste in hospitals	Medical waste was classified according to the degree of threat	A waste management system is absent in hospitals. Most hospitals did not segregate or treat waste before disposal and lacked suitable storage facilities. There were few people in charge of waste collection and disposal, and their knowledge was insufficient	Alam et al. (2019)
Southeast Nigeria	To assess the roles and attitudes of health professionals toward medical waste management and workplace safety	A questionnaire was distributed to 54 hospital administrators	40% of medical professionals were given training on medical waste management and workplace safety. Only 1.9% followed the regular operating procedure. Standard medical waste disposal procedures and training on occupational safety measures were unavailable. Monitoring healthcare activities and proper training are required to raise awareness	Anozie et al. (2017)

treating and disposing of medical waste are a challenge. Before selecting a technology, it is critical to have a good understanding of the waste category and its volume. Selecting the disposal, disinfection, or treatment method depends on several factors including the category of the medical waste, quantity of the waste, needed budget, availability of equipment, and the laws and the regulations of the country. Medical waste can be disposed of and treated in a variety of ways including landfilling, chemical disinfection, autoclaving, microwave disinfection, incineration, plasma gasification, and pyrolysis. Nonthermal technologies release fewer pollutants and are more cost-effective, convenient, and reliable (Eslami et al. 2017); therefore, thermal technologies such as incineration which produce toxic emissions are less desirable.

5.6.1 Landfilling

Landfilling is a traditional disposal method for all types of waste; however, landfilling is unsustainable, occupies large areas, produces emissions of toxic gas, and can be accompanied with risks of spreading and transmitting diseases. Usually, a landfill site is assigned to an area which is far from the urban population and water bodies (Torkayesh et al. 2021). The factors that make a successful landfill site are proper site selection, construction, operation, and post-shutdown monitoring. Moreover, geophysical methods are used to monitor the site in all stages of operation. Geophysical surveys are used to identify any faults such as fracture zones, former mining sites, highly porous site, etc. In some cases, nonhazardous medical waste can become toxic or produce toxic by-products on-site, as an outcome of the decomposition process. This toxic waste, when mixed with the water, can form a toxic leachate that can infiltrate and pose a significant risk on the environment (Sengupta and Agrahari 2017). Thus, leachate monitoring is important to reduce negative environmental and health impacts. Landfilling, as a standalone disposal method is not adequate.

5.6.2 Chemical Disinfection

Chemical disinfection is a process that involves the use of chemical disinfectants to disinfect the wastes. This method is mostly suitable for liquid waste but can also be used to treat solids. Solid waste needs to be shredded or grinded before the chemical disinfection process, to ensure that all of the waste is exposed to the chemical agent. Chemical disinfection with prior shedding is mostly used to pretreat COVID-19-related hazardous medical waste (Ilyas et al. 2020). The shredded and crushed waste is mixed with the chemical disinfectant and is kept in a closed system in vacuum, for a certain period of time. During this period, the organic contents of the waste is decomposed, and the harmful microorganisms are destroyed. Chemical disinfection can either be chlorine based or non-chlorine based. In a chlorine-based system, sodium hypochlorite or chlorine dioxide is used as the chemical disinfectant. A non-chlorine-based system uses hydrogen peroxide (Ilyas et al. 2020). Chemical disinfection is highly effective, with a broad spectrum of sterilization possible, but it has high material and equipment cost. Moreover, the method may produce chemical leachates and it does not reduce the volume of the waste.

5.6.3 Incineration

Incineration is mostly used to treat infectious or pathological waste (Rao et al. 2017). A typical waste incineration facility includes waste storage, feed preparation, and combustion unit followed by temperature reduction with heat recovery and air pollution control; meanwhile the ash produced is sent for disposal. For medical waste specifically, the waste is stored in puncture-resistant bags in refrigerated areas preferably. The furnace should be well-maintained, the air-to-fuel ratio should be in the optimal range, and the gas mixture should have an adequate residence time (Waste incineration & public health 2000).

Medical waste treatment through incineration is fast, simple, and effective in decomposing and disinfecting the waste completely. However, incineration releases high quantities of carbon and toxic emissions which contribute to an increase in pollution. Some of the harmful pollutants released by incineration include nitrogen oxides, sulfur oxides, carbon monoxide, particulate matter, hydrogen chloride, cadmium, lead, mercury, PCBs, and arsenic (Thind et al. 2021).

5.6.4 Autoclaving

Autoclaving sterilizes the medical waste by applying steam and pressure to destroy the microorganisms prior to its disposal in landfills (Rao et al. 2017). Autoclaving is mostly used for infectious material such as sharps (i.e., syringes and scalpels) that cannot be easily combusted (Rao et al. 2017). Autoclaving ensures strong penetration of the wastes and sufficient sterilization, but it does not reduce the volume of the medical wastes. Due to the observed increase in the volume of medical wastes in recent years, there is a lot of strain put on the storage facilities. Therefore, in addition to widely used methods discussed above, other recent treatment technologies such as microwave disinfection, plasma gasification, and pyrolysis are also discussed below.

5.6.5 *Microwave Disinfection*

In this method, the microwave energy is used to break down chemical bonds between the structures; thus, molecules change without undergoing oxidation in a low oxygen, nitrogen-rich environment. Moreover, it is performed at low temperature range of only 150–350 °C (Environmental Waste International n.d.). In this treatment method, the waste is first shredded; then water is added. Consequently, the mixture is internally heated to destroy bacteria and other microbes. Some of the advanced systems allow for lesser restrictions on the type of waste and type of equipment used. Microwave disinfection has high efficiency, better control, and good sterilization capacity, while contributing to less pollution. However, this method has few disadvantages including high capital and operating cost and no significant reduction in the volume of the waste.

5.6.6 *Plasma Gasification*

Plasma gasification is a promising medical waste treatment technique that converts waste into energy, thereby reducing the volume of the waste as well as reducing negative environmental impacts, along with putting the waste into use. Plasma gasification has several stages/units which include waste handling process, the plasma gasifier, the gas cleaning process, and the waste conversion process. Plasma gasification is a thermal process that converts organic matter into a synthesis gas that consists of hydrogen and carbon monoxide, by using plasma (Erdogan and Yilmazoglu 2020). Plasma is the fourth state of matter that contains radicals, charged ions, and free electrons. When a substance is being converted to plasma, various reactions such as ionization, disassociation, and reassociation occur. Thermal plasma generators require very high temperatures up to 10,000 K (Erdogan and Yilmazoglu 2020). The residual slag produced during the gasification treatment contains recoverable heavy metals such as iron, copper, chromium, cadmium, etc.

Compared to other conventional treatment systems, plasma gasification is an environmentally friendly process that produces hydrogen syngas, reduces the volume of waste generated, and provides a good sterilization. The disadvantages of this method are (a) it produces nitrogen oxides emissions and it has (b) high capital costs, (c) high specific energy consumption, and (d) low plant life. A study by Munir et al. (2019) reports the challenges associated with utilizing plasma gasification method. The construction of a plasma gasification plant is costly, possibly because it necessitates a higher level of plant automation, special construction materials to withstand the extreme temperatures, the cost of plasma sources such as plasma torch and plasma arc, and a shortage of technical experts in the relatively new field. Plasma gasification receives a moderate community readiness level because end users are unfamiliar with the technology and are concerned about the extreme process conditions. It is important to note that the plasma gasification's commercial applicability in waste management is currently limited. Plasma gasification is currently commercially used only in five sites across the world (Munir et al. 2019).

5.6.7 *Pyrolysis*

Pyrolysis is a thermal decomposition process of material with minimal or no oxygen supply, at high temperatures. Medical waste can be converted to high-value products such as biochar and bio-oil or biofuel which can be used as an alternative to fossil fuel, whereas biochar can be used as an adsorbent due to its porous surface and high surface functionality properties (Fakayode et al. 2020). A study conducted by Jung et al. (2021) states that the treatment of disposable face masks using pyrolysis technique generated 51 wt. % bio-oil, and similarly Su et al. (2021) reported that the treatment of medical waste of plastic using pyrolysis technique generated bio-oil with a calorific value of 41.31 MJ/kg. The disadvantages of pyrolysis process are that it produces nitrogen oxide emissions, it has high capital costs and high energy consumption, and it has a short plant life. Due to the complexity of medical wastes, pyrolysis process can be affected by several factors such as heating rate, temperature and pressure range, residence time, etc.

A comparison of several treatment methods discussed above is presented in Table 5.2 (Su et al. 2021).

Table 5.2 Advantages and disadvantages of different treatment methods (Su et al. 2021)

Treatment method	Advantages	Disadvantages
Landfilling	Simple, economical	High risk of infection, large area, releases toxic gases
Chemical disinfection	Less environmental impact, high efficiency, high sterilization	High cost of chemicals and equipment, produces toxic fluids, produces residual disinfectant, does not reduce waste volume
Incineration	Simple, wide application, high volume reduction	Releases toxic gases, produces ash
Autoclaving	Good sterilization, good penetration	Produces toxic fluids, does not reduce waste volume
Microwave disinfection	Good sterilization, high efficiency, less environmental impact	High cost of operation and equipment, low waste volume reduction
Plasma gasification	High waste volume reduction, good sterilization	High cost of operation and equipment, produces nitrogen oxides
Pyrolysis	High efficiency, sustainable practice, produces high-value products, wide application	High energy consumption and pretreatment cost

5.7 Medical Waste Management and Treatment During COVID-19

Medical waste management has become a growing area of interest, due to the waste generated by the new coronavirus (SARS-CoV-2) or COVID-19 pandemic, in all fronts. Since the first case of novel coronavirus (COVID-19), the virus infection has spread rapidly to countries all over the world. COVID-19 initially emerged in Wuhan, Hubei Province, China, in late December 2019. It results in acute respiratory distress syndrome. COVID-19 was declared as a pandemic by the WHO director-general on March 11th, 2020, after 118,000 people were infected and after it spread over 114 nations. Singh et al. (2020) state that at the peak of the pandemic, the city of Wuhan generated almost 247 tons of medical waste each day, nearly six times more than the years preceding the outbreak. Prior to the COVID-19 outbreak, the city's medical waste disposal capacity was at 50 tons per day which was estimated based on an incinerator plant that operated 24/7.

The performance of the waste management systems has recently been disrupted, and serious issues have arisen in monitoring medical waste as a result of COVID-19 pandemic. An ineffective waste management system contributes to the spread of COVID-19 (Tirkolaee et al. 2021). Disposal of infectious medical wastes associated with COVID-19, as a result of the diagnosis and treatment of patients, has become a significant concern. Most of the medical waste consists of plastic which also poses a risk to the environment. The governmental authorities and healthcare professionals need to ensure that the medical waste management policies and disposal are monitored to prevent further spread of the pandemic (Tirkolaee et al. 2021).

Ilyas et al. (2020) report that South Korea generated around 2000 tons of COVID-related medical waste, since the pandemic breakout until the beginning of May 2020, and the demand for personal protective equipment (PPE) such as facemasks and surgical gloves is predicted to grow at a 20% annual growth rate till 2025. They also report an alarming rate of medical waste growth in the Unites States during the pandemic. Effective COVID waste management, including adequate disinfection and disposal strategies, is needed to restrict further spread of COVID-19 virus, as well as to reduce the medical waste generation rate and lessen the negative impacts on the heath and the environment (Ilyas et al. 2020).

The use of the personal protective equipment (PPE) became crucial to protect the frontline healthcare workers, as they treat the asymptomatic and symptomatic patients, and to allow the effective functioning of the healthcare system. According to the WHO, healthcare workers require 89 million medical masks, 76 million gloves, and 1.6 million goggles per month (Prata et al. 2020). Public concerns over this highly contagious virus have led to an increase in the usage of PPE to control the virus's transmission (Prata et al. 2020). Considering the current situation of the pandemic, the role of plastic use in the prevention of diseases has led to the vast spread of public awareness and caught the attention of regulatory authorities. Due to the persistence of plastic material, PPE residues from the COVID-19 pandemic will likely be a frequent waste item found in the environment for decades, potentially harming diverse environmental and biological systems (Prata et al. 2020).

Medical waste generated during the treatment of COVID-19-infected individuals is one route for disease transmission. This waste, if not adequately managed, will constitute a health concern to the general public as well as the medical personnel involved in the disease's treatment.

In March 2020, a study (Abu-Qudais et al. 2020) was conducted in King Abdullah University Hospital (KAUH), and it examined the transmission of coronavirus in Jordan. A descriptive statistical analysis was performed on the amounts of medical waste generated. The average generation rate was found to be 3.95 kg/bed/day, which is ten times higher than the hospital's typical daily generation rate. The increased generation rate is due to the fact that the majority of the hospital's healthcare workers are using disposable personal protective equipment (PPE). Furthermore, the constant disinfection for cleaning of equipment, floors, and hard surfaces contributes to the rise in the amount of medical waste generated. It is important to rationalize the usage of PPE and disinfectants. Healthcare workers must be given adequate training on how to reduce the hazards associated with treating COVID-19 patients, particularly on how to reduce and manage the medical waste generated (Abu-Qudais et al. 2020).

Sangkham (2020) explained a study that was done to investigate the correlation between the use of face masks and the increase in medical waste generated in Asia, during the COVID-19 pandemic. The authorities in charge should pay close attention to all elements of prevention and control, so that the spread of the virus is controlled within hospitals (Sangkham 2020). Plastics are considered widely available low-cost materials. Poor management of PPE during the COVID-19 pandemic resulted in massive environmental pollution, with an estimated monthly use of 129 billion face masks and 65 billion gloves globally (Prata et al. 2020). This is a serious health issue since used face masks or gloves are considered a vector for the spread of the SARS-CoV-2 virus. Reducing the demand for PPEs and reusing them are crucial in the minimization of medical wastes generation. The reductions of PPE use can be achieved through physical barriers, sensible use by the healthcare workers, strict quarantine practices, social distancing measures, and cancellation of non-essential activities and mass gatherings. Healthcare professionals and the public must treat PPE that has reached the end of its life as infectious medical waste. Moreover, reusing can be accomplished by producing reusable PPE, which would minimize the reliance on single-use supplies (Prata et al. 2020).

5.8 Conclusions

In this chapter, definitions, categories of medical wastes, and regulations related to medical wastes are introduced. Various medical waste management techniques such as segregation, labeling and separation, waste minimization, etc. are presented. Conventional and innovative medical waste disposal, sterilization, and treatment methods including landfilling, chemical disinfection, autoclaving, incineration, microwave disinfection, plasma gasification, and pyrolysis are discussed. The advantages and disadvantages of each method are outlined. Moreover, medical waste management during COVID-19 pandemic is presented through recent case studies. The developing countries should enforce stricter laws and regulations so that efficient medical waste disposal methods and management techniques can be enforced. Medical waste management and treatment issues should be brought to the attention of the general public through education, training, and awareness campaigns.

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Chapter 6
Advances in Waste Collection, Storage, Transportation, and Disposal

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6.1 Introduction

The exponential growth in human population, increased urbanization, and continuous expansions in the industrial, healthcare, and agricultural sectors have led to inevitable generation of ever-increasing quantities of hazardous waste. According to estimates, 2.01 billion tons of solid waste was generated globally in the year 2016, and the global waste generation is projected to increase to 3.4 billion tons by the year 2050 (Kaza et al. 2018). Out of this, approximately 400 million tons per year of hazardous waste is generated globally which translates to about 60 kg of hazardous waste per capita (Akpan and Olukanni 2020). The amount of waste generated varies significantly across the different regions of the world, and a strong positive relationship has been suggested between the amount of waste generated and the economic development. Generally, high-income economies generate more waste per capita compared to low- or middle-income economies (Zia et al. 2017; Kaza et al. 2018). In the United States, for example, 34.9 million tons of hazardous waste was generated across 22,685 sites in the year 2019 (U.S. EPA 2021). In the European Union, 101.4 million tons of hazardous waste was generated which represented 4.3% of the total waste generated in the year 2018 (Eurostat 2020). Hazardous waste typically comes from a variety of sources such as chemical, petroleum, construction, iron, steel, textile, mining, paper, nuclear, and agricultural chemical industries, households, and healthcare facilities (Rosenfeld and Feng 2011a).

In a broad sense, the term hazardous waste refers to any waste that, by virtue of its physical, chemical, biological, or infectious properties, poses threats to the environment or human health (Rao et al. 2017). Typically, hazardous waste is characterized by its ignitability, corrosivity, reactivity, and/or toxicity (Polprasert and

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Liyanage 1996). In terms of ignitibility, wastes such as liquids with flash point less than 60 °C, spontaneously combustible solids, and flammable gases that are above a pressure of 1 bar are considered to be hazardous wastes. These wastes have been designated under the waste code D001 by the US Environmental Protection Agency (U.S. EPA). Corrosive hazardous wastes are coded as D002 and include aqueous solutions with pH less than 2 or greater than 12.5 and liquids capable of corroding steel. Hazardous wastes are considered to be reactive if they can undergo a violent reaction with water, air, or under pressure. These are designated under the waste code D003 by the US EPA. Toxicity includes hazardous waste codes D004–D043, and chemicals that are harmful or fatal by ingestion or skin absorption fall under this waste code range (VanGuilder 2018). It must be noted that the toxicity characteristic is defined in terms of the ability of waste to contaminate groundwater and is experimentally measured using the standard procedure from the US EPA known as the Toxicity Characteristic Leaching Procedure (TCLP) (U.S. EPA 1992a, b). Besides these, any waste listed on the F, K, P, or U list in the Title 40, Part 261 of the US Code of Federal Regulations is identified as a hazardous waste (Rosenfeld and Feng 2011b). However, it is important to note that some wastes which are not regulated may exhibit the characteristics of hazardous waste. Examples of such wastes include, but are not limited to, household hazardous wastes, agricultural wastes, and trivalent chromium wastes. A more comprehensive list of these wastes can be found elsewhere (Rosenfeld and Feng 2011b).

Improper disposal of hazardous waste can lead to serious environmental and public health impacts due to contaminant release and exposure. This is witnessed through the historical examples such as the Minamata disease outbreak caused by methylmercury poisoning in Minamata Bay, Japan (Kudo et al. 1998; Tsuda et al. 2009), and the Love Canal incident in New York (Gill and Mix 2020). The environmental and health impacts of hazardous waste and its improper disposal are well documented. For example, evidence of correlation has been found between exposure to oil industry waste and acute neurological symptoms (Fazzo et al. 2017). Also, proximity to landfill has been reported to effect neurodevelopment in children (Sarigiannis 2017). In terms of environmental effects, improper disposal of hazardous waste can result in air, soil, and water pollution via processes such as fugitive dust emissions, erosion, and groundwater seepage, respectively (Misra and Pandey 2005). The use of effective hazardous waste management and disposal strategies is, therefore, of paramount importance in order to reduce or eliminate the potential risks to the environment and public health.

Safe disposal of hazardous waste is considered to be at the bottom of waste hierarchy. It is the last and least favorable option and, ideally, should only be utilized when the more favorable options of prevention, reuse, recycle, recovery, and treatment are not feasible (Papargyropoulou et al. 2014). Besides being the last resort, hazardous waste disposal is technically challenging and requires careful consideration for the selection and design of the best available disposal technology and method and the associated risks and costs. Several methods have been proposed for the disposal of hazardous waste such as landfilling, incineration, offshore disposal, and underground disposal using deep wells or geologic repositories. Significant efforts have been made for the advancement and improvement of these methods. This chapter outlines the prerequisites to effective hazardous waste disposal such as hazardous waste collection, storage, and transportation. An overview of hazardous waste disposal by means of incineration has been provided. In addition, the technological advancements related to different aspects of the incineration are discussed.

6.2 Hazardous Waste Collection and Storage

Before its safe disposal, hazardous waste must be temporarily collected and stored safely in a designated storage area or facility. Several factors must be considered in order to ensure safe storage of the hazardous waste. In the United States, detailed requirements and guidelines for owners and operators of hazardous waste storage facilities are provided in the Title 40, Part 264 of the US Code of Federal Regulations. Figure 6.1 summarizes the major factors and requirements that must be considered during collection and temporary storage of hazardous waste prior to its disposal. These factors and requirements are discussed in the below subsections.

Fig. 6.1 Schematic representation of the factors to be considered during collection and temporary storage of hazardous waste

6.2.1 Area-Specific Requirements

The storage area must be a separate stand-alone space that, ideally, must be located away from the point of hazardous waste generation. In case of small quantity generators, the hazardous waste may be stored on-site (Rogers et al. 2001). It is important that the storage area is clearly marked and provided with proper warning signages outside the premises. Selection of suitable location for the storage area is important, and locations with high seismic activity must be avoided. Also, public acceptance is an important consideration which necessitates that the waste storage area is not in close proximity to the public.

The storage area must have enough capacity to accommodate the hazardous waste that is expected to be generated. The storage capacity must be determined during the design phase and is typically based on factors such as the current amount of hazardous waste, the spacing/segregation requirements, the time it takes for the final disposal, and the amount of waste that is predicted to be generated in that time (Vicente 2011). The waste generation rate can be forecasted using tools such as multiple linear regression, econometric models, time-series analysis, artificial neural networks, fuzzy logic, and support vector machines (Goel et al. 2017). In addition, uncertain events such as delays in the final disposal must be considered when deciding on the storage capacity.

Operational aspects of the storage area are also important to consider. Sufficient aisle space must be provided within the storage area to allow for unobstructed movement and accessibility for the personnel, loading/unloading vehicles, and, in case of emergency, the firefighting equipment. Also, personnel and vehicles must be suitably segregated within the storage area. Separate entrances and exits for personnel and vehicles and one-way vehicle movement should be used, whenever possible.

6.2.2 Labeling

All waste containers and tanks must be properly labeled prior to storage. The labels or tags should be clearly visible and should explicitly mention the hazardous nature of the waste. The contents of the hazardous waste, the composition and physical state, filling start date, container/tank size and weight, emergency contact information, details of the generator, and the location of generation and storage must be mentioned. The labels or tags should allow for adding extra information in case the composition or contents of the hazardous waste are expected to change over time. In addition, the labels or tags should comply with the National Fire Protection Association (NFPA) hazard identification system or the Globally Harmonized System (GHS) for pictorial representation of the hazards associated with the waste (e.g., see Fig. 6.2). Labels or tags for hazardous medical or radioactive wastes must show the biohazard symbol and radioactivity warning sign, respectively. Labels or

Fig. 6.2 Hazardous waste labels (Hazardous waste symbols n.d.)

tags should also be durable with an ability to withstand any harsh conditions during transportation.

6.2.3 Segregation

Hazardous wastes must be properly segregated within the storage area. This implies that sufficient distance must be maintained between incompatible wastes. The segregation must be based on the hazard class. The same rule should be applied during mixing of hazardous wastes in containers or tanks. Incompatible wastes must not be mixed in the same container or tank. In general, wastes containing oxidizers, corrosive agents, acids, or alkalis should be segregated from flammable wastes to avoid heat generation and fire hazard. Likewise, segregation must be maintained between acid and alkaline wastes to avoid generation of heat. Comprehensive information about the compatibility of hazardous chemical wastes can be obtained using the US EPA's hazardous chemical compatibility chart (Hatayama et al. 1980).

6.2.4 Storage Systems

Typically, hazardous waste is stored in containers (portable) or tanks (stationary). Several factors need to be considered during the use and management containers and tanks for hazardous waste storage as outlined in the Subparts I and J, respectively, within Title 40, Part 264 of the US Code of Federal Regulations. The following summarized points are important for the effective use and management of containers (Batstone et al. 1989a; Blackman Jr. 2001):

- Prior to use, the containers must be in good condition without apparent physical defects, cracks, and rust. During storage, any damaged or leaking container must be replaced immediately.
- Containers must always be tightly closed except during filling or draining operations.

- Containers must not be filled to their maximum capacity to accommodate for effects of thermal expansion.
- The material of the container and its internal lining, including the lid and any residue from previous use, must be compatible with the hazardous waste to be stored.
- Care must be taken during loading, unloading, and movement of containers to avoid damage or toppling.
- Containers with liquid hazardous wastes must not be stacked.
- Containers with liquid hazardous wastes must be provided with secondary containments, such as spill pallets, for spill control.
- Some containers may require venting depending on the type of hazardous waste stored. Such containers must be identified and vented periodically.
- In case of radioactive wastes, containers must be appropriately shielded from all sides using lead metal of suitable thickness.
- Periodic inspections must be carried out to check for leaks and spills in the area where containers are stored.

In case of tanks, the following summary of points must be taken into consideration (Blackman Jr. 2001):

- Tanks must be certified for hazardous waste storage, and appropriate integrity and leak tests must be performed prior to their use.
- Appropriate corrosion protection techniques must be utilized.
- Tanks and their internal linings must be compatible with the hazardous waste to be stored.
- Tanks must be equipped with appropriate secondary containment (such as double walls) and leak detection systems.
- For tanks with continuous inflow of liquid hazardous waste, appropriate measures must be in place to stop or bypass the flow in case of a leak.
- Tanks must not be filled to their maximum capacity to accommodate for effects of thermal expansion.
- Periodic inspections must be carried out to check for leaks and spills.

Besides containers and tanks, hazardous waste may be stored as open containments in the form of surface impoundments or waste piles. Surface impoundments are shallow and bounded topographical depressions (natural or man-made) lined with clay or polymeric material that are used for holding liquid hazardous wastes. Waste piles, on the other hand, refer to bulk storage of solid hazardous wastes above the ground. Both surface impoundments and waste piles require careful design to avoid release of hazardous leachate into the underlying soil. The design must allow for leachate detection, collection, and removal. Detailed regulations related to surface impoundments and waste piles can be found in the Subparts K and L, respectively, within Title 40, Part 264 of the US Code of Federal Regulations.

Certain types of hazardous wastes require dedicated storage schemes. For example, spent nuclear fuel waste is stored in either wet or dry systems. In case of wet systems, the spent nuclear fuel is stored under water to allow for cooling and shielding. In dry systems, storage casks, constructed using stainless steel or concrete and surrounded by secondary shielding material, are utilized (Ojovan et al. 2019). Wood-preserving industries require the use of drip pads that are used for collection and temporary storage of waste preservative solution (Cheremisinoff and Rosenfeld 2010).

Containment buildings can also be employed for the storage of hazardous waste. These structures were originally developed for the storage of hazardous debris and bulky hazardous wastes that cannot be stored in regular containers or tanks (U.S. EPA 2005). However, their applicability can be extended for the storage of liquid hazardous wastes that have been filled in suitable containers. A containment building is a fully enclosed, self-supporting, and prefabricated structure constructed using a material of suitable strength and compatibility with the type of hazardous waste to be stored. The building is designed to prevent fugitive dust emissions from solid hazardous wastes and is equipped with sloping floor, secondary containment, and leak detection and collection systems in case of storing liquid hazardous wastes (Rogers et al. 2001). Containment buildings are available commercially in various dimensions and with advanced features such as weatherproof, noncombustible, and unidirectional or bidirectional fire-rated structures.

6.2.5 Inventory Management

An updated inventory must be maintained for the hazardous wastes in the interim storage facility. The inventory should record information such as the number of containers and tanks, their location, date of storage, disposal due date, and the amount (weight or volume) of the stored hazardous waste. Commercial waste management software can be used for this purpose. In addition, web-based inventory management system can be developed using PHP and MySQL (Santos et al. 2011). Barcode system can be utilized for ease of storing and tracking. In case of chemical hazardous wastes, an inventory of the material safety data sheets (MSDS) must also be maintained.

6.2.6 Safety Requirements

The following points highlight the general safety guidelines for the storage of hazardous waste:

- The floor of the storage area must be made of impervious material such as concrete or asphalt.
- In case of flammable hazardous waste, fire-proof walls and doors should be used.
- Doors must be of suitable size and must be always unobstructed.

- In case of storing radioactive wastes, proper shielding of walls and doors is necessary.
- Access to the storage area must be controlled and only limited to authorized personnel.
- Standard operating procedures (SOPs) must be developed related to the activities within the storage area such as hazardous waste handling procedure, container filling procedure, stacking procedure, spill response and cleanup, etc.
- Personal protective equipment (PPE) must be provided to the personnel. The level of protection required must be appropriate to the nature of hazardous waste to be handled.
- The personnel accessing the hazardous waste storage area must receive adequate training on the SOPs, handling and storage of hazardous waste, emergency procedures, and the use of PPE, fire extinguishers, and spill kits.
- Appropriate safety posters and warning signages must be provided within the storage area.
- The emergency contact details must be easily accessible and available within the storage area.
- Emergency evacuation routes must be clearly defined, and evacuation plan must be available in the storage area.
- Small hazardous waste containers must be placed inside safety cabinets.
- Adequate temperature must be maintained within the storage area.
- In case of flammable hazardous wastes, any source of heat, spark, and flame must be eliminated.
- The storage area must have all the required safety systems and equipment in place such as leak detection system, fire extinguishers, smoke and/or heat detectors, alarm systems, proper ventilation, air change system, spill management equipment, spill kits, first-aid kits, etc.
- Appropriate welfare facilities must be provided within or close to the storage area.
- Housekeeping must be maintained within the storage area.
- The storage area must be regularly inspected. Appropriate inspection checklists must be developed, and the frequency of inspection must be determined.
- Storage areas must be part of the health and safety audits.

6.3 Hazardous Waste Transportation

6.3.1 Transport Vehicles

Hazardous waste is typically transported to its final disposal facility via highway, rail, or water transport using, for example, trucks, rail flatcars, and barges, respectively (Peirce et al. 1998). Highway transport is the most common and versatile (Blackman Jr. 2001). The standards applicable to transporters of hazardous waste are outlined in the Title 40, Part 263 of the US Code of Federal Regulations. The general guidelines related to safe transportation of hazardous waste are summarized below:

- A manifest system must be used for tracking hazardous wastes. The manifest must show the information about the generator and the transporter, the type of waste and container being transported, special handling instructions, and emergency contact details (Blackman Jr. 2001).
- The transport vehicle must be clearly labeled to show the hazardous nature of the waste being transported.
- The hazardous waste must be loaded and unloaded carefully and, if required, must be secured using lashing strap during transportation.
- The vehicle must never be loaded beyond its maximum capacity.
- Loading must be balanced to avoid vehicle turnover.
- Segregation of hazardous waste must be maintained during transportation.
- The transporter must have the necessary competency/licensing to transport the hazardous waste.
- Online tracking system can be used for more efficient tracking of hazardous waste.
- During transportation, all the required safety systems and equipment must be available such as fire extinguisher, spill management equipment, first-aid kit, etc.
- The personnel involved in transportation, including the driver, must receive adequate training on all aspects of transportation, emergency procedures, and the use of PPE, fire extinguisher, and spill kit.
- During transportation, the safest possible route must be selected.
- Hazardous waste must not be transported through densely populated areas.

6.3.2 Radioactive Wastes

In case of radioactive waste, specialized transport packages are used. Excepted packages are used for transportation of small quantities of radioactive waste with limited activity and dose rate lower than 0.1 mSv/h (such as radiopharmaceuticals). Industrial packages are utilized for radioactive waste with low specific activity and surface-contaminated objects. Type A, B, and C packages are employed in case of transporting minor quantities of radioactive wastes, high-activity radioactive wastes, and very large quantities (usually transported by air) of radioactive wastes, respectively (Ojovan et al. 2019). Most packages are designed with hollow cylindrical body open at one end and consisting of multiple layers to provide structural strength (using steel) and protection against gamma rays (using steel, lead, or concrete) and neutrons (using water, borated polymers, or concrete). The other end of the package is closed using steel lid and seals for airtight packaging. In addition, impact limiters are employed that mitigate the effects of mechanical vibrations during transportation. Also, fins may be provided on the package surface for heat dissipation and to provide additional impact protection (Transportation Research Board and National Research Council 2006).

6.3.3 Transport Modeling and Risk Analysis

Transportation of hazardous waste has gained substantial research interest owing to the high risks involved throughout the transportation process and the severe consequences resulting from transportation incidents. Most of the research studies have focused on proposing suitable methodologies for the selection of the transportation firm, assessing and modeling the transportation risks, and developing appropriate location-routing models.

A two-step fuzzy-AHP (fuzzy analytic hierarchy process) and TOPSIS (Technique for Order of Preference by Similarity to Ideal Solution) methodology has been proposed for the selection of hazardous waste transportation firm (Gumus 2009). The evaluation criteria were determined by modified Delphi method and included hygiene and safety, service quality, complementary services, economic factors, service time, compliance with human health and environmental protection standards, problem solving ability, and the transport vehicle fleet. As an example, the methodology was applied to five hazardous waste transportation firms in order to rank them from the most preferable to the least. Overall, the methodology resulted in realistic and reliable selection of the hazardous waste transportation firm. In another study, integrated VIKOR (VIseKriterijumska Optimizacija I Kompromisno Resenje (in Serbian language) or multi-criteria optimization and compromise solution) method and fuzzy set theory was proposed for the selection of hazardous waste transportation firm (Kabir 2015).

Hazardous waste transportation risks have been analyzed by employing geographic information system (GIS). For instance, GIS has been used to model the routing, and the associated risks, of transporting aqueous hazardous waste. Transportation risks were evaluated taking into account the roads utilized for transport, the traffic level, population distribution, groundwater vulnerability, and accident probabilities (Brainard et al. 1996; Lovett et al. 1997).

A comprehensive framework for risk assessment of flammable and volatile waste transportation has been presented in one study (Das et al. 2012a). The framework used the concept of accident index (AI) that allowed for estimation of accident risk or accident probability in cases where the historical database on accidents related to hazardous waste transportation was not available. In addition, impact assessment due to volatile cloud explosion caused by accident of a hazardous waste transporter was provided. The framework also included vulnerability assessment to estimate the mortality and the morbidity to the population due to the accident. Although the proposed framework could be extended to other types of accidents such as fire pools, aerial dispersion of toxic fumes, and spills, it considered human risks only and did not account for damages to buildings and other infrastructures.

During hazardous waste transportation, the selection of the safest possible route connecting the origin to the destination is of paramount importance. This has stimulated research interest in developing routing models for hazardous waste transportation. In general, multi-criteria routing models provide a rigorous approach for simultaneous consideration of different routing requirements such as shortest route, safest route, route with least exposure to the public, etc. Fuzzy network models (Klein 1991) and GIS technology (Baaj et al. 1995) have been proposed to solve the hazardous waste routing problem. Also, a methodology for routing for simultaneous optimization of transportation cost and the associated risks has been proposed (Das et al. 2012b). Other studies have investigated combined location-routing problems that simultaneously consider both the optimal location of treatment/disposal facilities and the optimal routing strategy. One of the earliest location-routing models utilized goal programming formulation and was developed to address the trade-offs between three objectives, namely, minimization of the transportation risk, the travel time, and the disposal risk in order to determine the most desirable location of hazardous waste disposal facilities and the transportation routes (Zografros and Samara 1989). The model, however, did not account for practical considerations in real-life hazardous waste transportation and disposal. In a later study, a linear programming model was introduced for simultaneous routing and siting of hazardous waste transport, storage, and disposal operations, while taking both cost and risk into consideration (Jacobs and Warmerdam 1994). Later on, equity considerations were also included in the location-routing problem in addition to the cost and risk (Wyman and Kuby 1995; Giannikos 1998). Some studies have also included the location of treatment facilities in the location-routing problem. For example, a mixed integer programming model was proposed to identify the location of the treatment facilities and the treatment technologies used, the location of disposal facilities, the routing of hazardous waste from generation points to the treatment facilities, and the routing of waste residues (generated in the treatment facilities) to the disposal facilities (Alumur and Kara 2007). This model was applicable to real-life practical situations and was applied to the Central Anatolian region of Turkey. In addition, cost savings from the sale of recyclable wastes have been considered in the location-routing model (Boyer et al. 2013). In a recent study, a profit-based mixed integer mathematical model for location-routing problem was proposed that determined the number of recycling, incineration, sterilization, storage, and disposal facilities along with their locations and the routing of hazardous wastes and residues (Aydemir-Karadag 2018). Also, recently, the location-routing problem has been addressed under stochastic environment (Rabbani et al. 2019).

6.4 Advances in Hazardous Waste Disposal Techniques

Disposal of hazardous waste is the final step in the waste management plan. Several technologies are available for safe and effective disposal of hazardous waste. The remainder of this chapter discusses the incineration technology and the related technological advancements.

6.4.1 Incineration

Incineration is an ultimate disposal procedure that involves thermal destruction of hazardous waste. The process is based on high-temperature thermal oxidation in order to convert the hazardous waste into gases and solid residue. Typically, from economical and technical standpoints, hazardous wastes that are combustible and contain substantial organic content are considered to be ideal feeds for the incineration process. Examples of such feeds include solvent, oil, pharmaceutical, pesticide, hospital, and refinery wastes (Visvanathan 1996). However, the use of incineration can be extended to any hazardous waste that contains an organic fraction even in low amounts (Rickman 1991). Also, incineration can be used for wastes with high environmental persistence and for those that cannot be landfilled (Visvanathan 1996). Hazardous wastes that are explosive or highly radioactive are deemed unsuitable for disposal via incineration (Batstone et al. 1989b). Comprehensive information on the incineration potential of hazardous wastes on the F, K, P, and U lists can be found elsewhere (Bonner et al. 1981).

Destruction of hazardous waste by incineration involves a complex combination of volatilization, melting, boiling, sublimation, formation of reactive radicals and fragments, gas-phase reactions, and gas-solid reactions (Tillman et al. 1989). The gaseous product of incineration, often termed as flue gas, principally contains carbon dioxide and water vapor. Also, depending on the composition of the hazardous waste, hydrogen chloride, hydrogen fluoride, carbon monoxide, oxides of sulfur, nitrogen and phosphorus, metal oxide and heavy metal particulates, and polychlorinated biphenyls (PCBs) may be present in the gaseous product (Polprasert and Liyanage 1996; Williams 2005). The gaseous product, after necessary cleaning, is released into the atmosphere. Also, incineration results in the formation of solid residue, mainly containing ash, which is typically disposed in landfills.

Incineration is an attractive disposal method since it significantly reduces the mass and volume of the hazardous waste. Typically, the mass and volume of hazardous waste can be reduced up to 70% and 90%, respectively (Lam et al. 2010; Kanhar et al. 2020). For effective incineration, process variables such as temperature, residence time, turbulence, and oxygen availability must be carefully selected and controlled. Generally, higher temperature, higher residence time, increased waste/air turbulence, and presence of excess oxygen lead to a more complete destruction of the hazardous waste. The incineration process must be designed, engineered, and maintained in order to meet the constraints and performance standards outlined in the Title 40, Part 264.343 of the US Code of Federal Regulations and the Toxic Substances Control Act (TSCA) regulations. These constraints are listed below (Tillman et al. 1989; Rickman 1991):

1. The incineration process must exhibit 99.99% Destruction and Removal Efficiency (DRE) for each of the Principal Organic Hazardous Constituent (POHC). Mathematically, DRE is expressed as follows

$$\mathrm{DRE} = \left(\frac{W_{\mathrm{in}} - W_{\mathrm{out}}}{W_{\mathrm{in}}} \right) \times 100\% \tag{6.1}$$

   where W_{in} and W_{out} represent the mass flow of POHC in the feed and flue gas, respectively.
2. In case of hazardous wastes containing PCB oils, chlorinated dioxins, or similar compounds, DRE as high as 99.9999% must be achieved.
3. In cases where hydrogen chloride is generated at a rate higher than 1.8 kg/h, the emissions from the incinerator must be suitably controlled in order to remove 99% of hydrogen chloride from the flue gas.
4. Particulate emissions from incinerators must not exceed 180 mg/scm corrected to 7% oxygen in the flue gas. To correct the particulate emission concentration, the following correction factor (CF) is multiplied with the actual measured concentration:

$$CF = \frac{14}{21 - Y} \tag{6.2}$$

   where Y is the oxygen concentration in the flue gas measured on a dry basis.

The overall incineration process involves the use of an incinerator as the heart of the process along with preprocessing and post-processing requirements. The preprocessing requirements include preparation of hazardous waste feed and the use of appropriate feeding techniques. Typically, liquid hazardous wastes are blended and fed to the incinerator via nozzles or atomizers, whereas solid hazardous wastes require size reduction (crushing/shredding) and are conveyed to the incinerator by gravity or by using rams, screw, auger, or belt feeders. In case of hazardous sludge, feeding systems such as cavity pumps and water-cooled lances are employed. Post-processing, on the other hand, involves air pollution control and ash handling, treatment, and disposal (Rickman 1991). Incineration is a well-established process and several types of incinerators have been designed and made available for use. These incinerators are compared in Table 6.1 and discussed hereafter.

Table 6.1 Comparison of hazardous waste incinerators. Information presented is summarized from Bonner et al. (1981), Batstone et al. (1989b), and Rickman (1991)

	Liquid injection	Rotary kiln	Fluidized bed	Starved air	Multiple hearth
Waste physical form	Only suitable for liquid wastes that can be atomized	Suitable for wastes in solid, liquid, sludge, or containerized forms	Suitable for waste sludge, liquids, and shredded solids	Suitable for waste sludge and solids	Most suitable for hazardous sludge but can be used for solids, liquids, or gases
Design	Simple design with no moving parts	No moving parts; high turbulence; residence time can be controlled by adjusting the kiln speed	Simple and compact design with no moving parts; low temperature and air requirements; high turbulence and heat transfer	Simple design	Complex design
Operational considerations	Nozzle plugging possible for feeds containing solids; auxiliary fuel may be required	Refractory damage possible; susceptible to slug formation and air leaks	Solid shredding to uniform size required; susceptible to erosion; residual material difficult to remove	Batch operation	High residence time required
Emissions	–	High particulate loading	Allows for in situ neutralization of acid gases by addition of lime or carbonate	Lower emissions	–
Efficiency	High DRE can be achieved with effective atomization	Low thermal efficiency	Good combustion efficiency	High thermal efficiency	High fuel efficiency
Economics	Low maintenance cost	High capital cost; high cost of refractory lining replacement	Low capital and maintenance cost; high operating cost	Low capital cost	High maintenance cost

Liquid Injection Incinerators

Liquid injection incinerators are used exclusively for pumpable liquid hazardous wastes, slurries, and sludges. As a rule of thumb, hazardous waste fluids with kinematic viscosity less than 2200 cSt are the most appropriate feeds for liquid injection incinerators (Rickman 1991). Such incinerators may be designed in vertical or horizontal cylindrical configurations. Vertical design is typically suitable for wastes with high content of inorganic salts and fusible ash, while the horizontal design is more suitable for wastes with low ash content. The incinerator operates by injecting the hazardous waste in atomized form and mixing it with the combustion air. A flame zone is created, and the waste is burned within a refractory-lined combustion chamber (Rickman 1991; Williams 2005). Operating temperature is typically in the range 650–1650 °C, while the gas residence time is of fractions of seconds (Vallero 2014, 2019). The upper limit on the gas residence time (θ_{max}) can be estimated by the following equation (Bonner et al. 1981):

$$\theta_{\max} = \frac{V_T}{q_{\text{out}}} \tag{6.3}$$

where V_T is the total volume of the combustion chamber (m^3) and q_{out} is the gas flow rate at the incinerator outlet (m^3/s) measured at the operating temperature.

Several important considerations are pertinent to the design of liquid injection incinerators. The use of suitable and appropriately designed nozzles is of critical importance for achieving effective atomization and, consequently, high DRE. Atomization may be achieved by rotary cup, single-fluid pressure, or two-fluid high/low-pressure air or steam atomization techniques. Effective atomization is also realized by maintaining low viscosity of the liquid waste. This may be achieved by preheating the liquid waste or by blending it with another liquid of low viscosity. Also, to ensure effective atomization and to avoid nozzle blockage, the solid content of the liquid waste must be low. This may require solid filtration prior to introducing the feed into the liquid injection incinerator. In addition, auxiliary fuel system must be embedded within the incinerator for cases where the heating value of the waste is insufficient. Besides these, adequate mixing within the combustion chamber is an important consideration which can be achieved by utilizing baffles or allowing for tangential entry of the waste. Also, the temperature during incineration must be sustained by manipulating the feeding rate of the waste or the fuel (Bonner et al. 1981; Batstone et al. 1989b; Rickman 1991; Santoleri et al. 2000).

Rotary Kiln Incinerators

Rotary kiln incinerators are more versatile compared to the liquid injection incinerators as they can handle hazardous waste feeds in solid, liquid, sludge, or containerized forms (Rickman 1991). Also, these incinerators can be used for the disposal of explosive wastes (Duijm and Markert 2002). A typical rotary kiln incinerator consists of a refractory-lined cylinder that acts as the primary combustion chamber and is slightly inclined at one end. The angle of inclination is usually about 3–5° above the horizontal. The hazardous waste feed enters the incinerator from the inclined end. As the kiln rotates (at about 1–5 RPM), the hazardous waste is transported down the kiln and is converted into gases via volatilization, destructive distillation, and combustion. The rotation of the kiln also helps to promote mixing of the waste with the combustion air. The burner may be located at the same end where the feed enters (cocurrent mode) or at the opposite end (countercurrent mode). The location of the burner is arbitrary for highly combustible wastes. However, for wastes with low combustibility, countercurrent mode is recommended. The rotary kiln incinerator is also equipped with a stationary secondary (post) combustion chamber which acts to destruct the gaseous products from the primary combustion chamber (Batstone et al. 1989b; Rickman 1991).

Rotary kiln incinerators are typically designed with a length to diameter (L/D) ratio of 2–10. Operating temperature is in the range 800–1600 °C. The hazardous waste feed rate must be maintained to allow for operating volume that is no more than 20% of the total kiln volume. The solid and gas residence times are usually in the range 0.5–2 h and 1–5 s, respectively (Rickman 1991). Solid residence time can be estimated using the following equation (Pichtel 2014):

$$\theta = \frac{0.19L}{NDS} \tag{6.4}$$

where θ is the solid residence time (min), L is the kiln length (m), N is the kiln rotational speed (RPM), D is the kiln diameter (m), and S is the kiln slope (m/m).

The residence time for the gas to achieve DRE of 99.99% is calculated as follows (Pichtel 2014):

$$\ln\left(t_g\right) = \ln\left(\frac{9.21}{A}\right) + \frac{E}{RT} \tag{6.5}$$

where A and E represent Arrhenius constant (s^{-1}) and activation energy (J/kmol) for the compound being incinerated, respectively, R is the gas constant (J/kmol K), and T is the temperature (K).

Rotary kiln incinerators are classified as slagging or non-slagging. The slagging-type rotary kiln operates at high temperatures (>1000 °C), exhibits high DRE, and results in the formation of molten slag of the ash (Santoleri et al. 2000; Williams 2005). This type of rotary kiln is more suitable for highly combustible hazardous waste with moderate moisture and halogen content and for containerized hazardous waste (Tillman et al. 1989). The non-slagging type operates at temperatures below 1000 °C and does not attain total incineration (Santoleri et al. 2000; Williams 2005). This type of rotary kiln is more economical for use with hazardous waste feeds of low calorific value (Tillman et al. 1989).

While rotary kiln incinerators may be purpose-built, it is also possible to co-incinerate the hazardous waste in already existing units such as cement and lime kilns that provide sufficiently high temperature and residence time. The co-incineration approach is appealing since it avoids capital investments in constructing dedicated rotary kiln incinerators. Also, the alkalinity of the kiln material helps in neutralizing the acid gases such as hydrogen chloride and sulfur oxides. However, co-incineration requires careful investigation prior to the introduction of the hazardous waste. The use of the existing cement and lime kilns for co-incineration of hazardous waste should not affect the operation and product quality in the original intended process. In addition, the cement and lime kilns may not have adequate emission control equipment required for co-incineration of hazardous waste (Batstone et al. 1989b). Several case studies have reported the use of cement kilns for incineration of hazardous waste (Ishikawa and Herat 2012). For example, PCB waste oil has been incinerated in a cement kiln in Sri Lanka. The DRE was reported to be greater than 99.9999% at the highest PCB feeding rate. In Thailand, incineration of liquid hazardous waste and/or tires has been investigated. Also, obsolete insecticides, Fenobucarb and Fipronil, were incinerated at a cement plant in Vietnam. Reported DRE was higher than 99.9999% without generation of any harmful by-products such as PCB, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and hexachlorobenzene (HCB). Industrial solvents have also been incinerated in a cement kiln in Egypt. Also, pesticide-contaminated soil has been incinerated in a cement kiln in Colombia, and the reported DRE was 99.9999%. Further details on these case studies can be found elsewhere (Ishikawa and Herat 2012).

Different aspects of rotary kiln incinerators have been explored through research studies. The lifetime of the refractory lining is economically important since periodic replacement of the lining contributes significantly to the overall maintenance cost of rotary kiln incinerators. In a recent study, the use of terrestrial laser scanning has been proposed as an effective method for observing the condition of the refractory lining in order to assist in replacement decisions (Tucci et al. 2020). Experimental-based guidelines have also been provided in order to extend the lifetime of the refractory lining in rotary kiln incinerators (Villalba Weinberg et al. 2016). The study showed that the partially molten ash penetrates the open pores by capillary action leading to cracks and subsequent spalling of the refractory material. It was suggested that the lifetime of the refractory lining can be extended by depositing solidified bottom ash throughout the kiln by controlling viscosity or by employing more resistant refractory materials such as those based on andalusite. According to the experimental guidelines, it was recommended that the basicity of the bottom ash must be regularly monitored and high basicity must be avoided to circumvent pore infiltration. Also, the second half of the kiln may be cooled by ventilators or water jackets in order to diminish the infiltration. In another study, a novel mullite-zirconia-bonded refractory material was synthesized and field tested in a rotary kiln incinerator (Weinberg et al. 2021). Results showed that the novel refractory material persisted much longer than mullite- and alumina-chromia-bonded refractories. In one study, it was highlighted that fireclay and bauxite-clay refractories can suffer from corrosion due to condensed alkali and sulfur compounds in the secondary combustion chamber (Villalba Weinberg et al. 2017). In order to impede the corrosion effects, it was recommended that the refractories should contain as little silica as possible. The flame temperature in rotary kiln incinerators is an important consideration in the context of refractory lining lifetime. Solid deposition on thermocouple tend to provide poor estimation of the flame temperature and may lead to refractory lining failure. To overcome this challenge, it was suggested that accurate flame temperature measurements can be obtained by utilizing a nonintrusive thermographic method using an infrared camera where the flame emissivity setting is adjusted based on the air/waste equivalence ratio (Du et al. 2012).

Models of rotary kiln incinerators have been investigated. A mathematical model to predict the axial temperature and concentration profiles in a rotary kiln incinerator for solid hazardous waste is available (Tomaz and Maciel Filho 1999). This model is based on one-dimensional approach, considers both the kiln and the secondary combustion chamber, and takes radiation, convection, and conduction heat transfer and heat capacities, thermal conductivities, and viscosities into account. In another study, a model was developed to predict the temperature inside the rotary kiln and on its outer surface and took into account the mass and energy balances and the combustion kinetic parameters (Lombardi et al. 2013). The model results were compared with the data from a real incineration plant operating on healthcare waste and located in Rome, Italy. Also, a mathematical model has been developed to determine the flux of incinerated waste in rotary kilns in terms of its calorific values (Bujak 2015). When compared to the real facility data, the model results produced errors of only −4.1% for flux of incinerated waste and 6.8% for gas volume flux. In addition, computational fluid dynamics (CFD) models have been developed to study and describe the gas flow, heat transfer, and mixing behavior (Yang et al. 1999; YANG et al. 2005); characterize temperature and species distribution (Yang et al. 2002, 2004, 2007); predict the gas, wall, and bed temperatures (Veranth et al. 1997); and study process control of rotary kiln hazardous waste incinerators (Yang and Reuter 2001; Yang et al. 2003). Models for dynamic simulation of rotary kiln incinerators for hazardous waste are also available (Rovaglio et al. 1998; Bani-Hani et al. 2016).

Some studies have focused on the design and operation of rotary kiln incinerators. Air-enriched operation has been suggested (Melo et al. 1998). Results deduced from mass and energy balances showed that the waste feeding rate can be increased up to one order of magnitude if air is substituted by pure oxygen. Also, it was highlighted that air-enriched operation can decrease the total mass flow rate of combustion gas per unit mass of waste, thereby, reducing the amount of emitted particulate material. The use of sulfur compounds, $(NH_4)_2SO_4$ and pyrite, as co-combustion suppressants has been studied (Wu et al. 2012). Results showed that the sulfur compounds had an inhibition effect to slightly reduce the PCDD/F (Polychlorinated dibenzo-p-dioxins and dibenzofurans emissions) from the stack and to significantly eliminate PCDD/F in the fly ash. In situ detection of CO and O_2 in rotary kiln-based hazardous waste incinerators has been studied (Ebert et al. 2005). Detection of CO and O_2 is critical in assessing the degree of combustion during the operation of the rotary kiln incinerator.

Fluidized Bed Incinerators

Fluidized bed incinerators can be employed for sludges, liquids, and shredded solid hazardous wastes. A typical fluidized bed incinerator consists of a refractory-lined cylindrical vessel that is partially filled with an inert media such as sand. The inert media is preheated at a high temperature using an auxiliary burner. Combustion air is supplied through a distribution plate at the bottom of the incinerator. At sufficiently high velocity of the combustion air (above the minimum fluidization velocity), the inert bed is fluidized to create a fluid-like bubbling bed within the incinerator. The fluidized bed is characterized by high turbulence, enhanced mixing effects, and efficient heat transfer. As a result, upon feeding to the incinerator, the hazardous waste is rapidly mixed with the hot inert media and is, subsequently, combusted. The gaseous products leave the incinerator from the top. Owing to its inherently high turbulence and good heat transfer, a fluidized bed incinerator is capable of destructing hazardous wastes at a lower temperature and, consequently, with a lower excess air requirement compared to the other types of incinerators. Fluidized bed incinerators also allow for in situ neutralization of acid gases by addition of lime or carbonate during operation. Typical gas residence time in fluidized bed incinerators is between 12 and 16 s (Rickman 1991).

Several factors must be considered for the effective use of fluidized bed incinerators. It is important that the temperature is maintained below the melting point of the inert media. Also, the bed height must be carefully selected in order to avoid excessive pressure drop during the operation. In case of solid hazardous wastes, shredding/crushing must be performed to achieve the recommended nominal diameter of 2 in. Also, sludges with high water content must be dewatered to avoid a decline in temperature and a consequent increase in the fuel requirement (Rickman 1991).

It is also possible to operate the fluidized bed incinerator such that most of the bed is carried out from the top of the incinerator. This occurs when the air velocity is approximately 3–5 times higher compared to the typical bubbling bed operation (Tillman et al. 1989). The bed moving out from the top of the incinerator is transferred into an external hot cyclone where the solids are separated from the flue gas. From the cyclone, the solids are recirculated back to the incinerator by gravity. In such an incinerator, combustion also takes place within the cyclone. Due to higher gas velocity, superior heat transfer and mixing effects are achieved compared to the bubbling bed operation (Dupont et al. 2016). This type of fluidized bed incinerator is often named as circulating bed incinerator. Typical residence times for such incinerators range from 2 s for gases to 30 min or longer for large waste materials (Rickman 1991).

Fluidized bed incinerators have been investigated in various research studies. Medical waste has been incinerated using the fluidized bed technology where it was reported that coal or pyrite addition can inhibit the formation of dioxins in the flue gas (Shen et al. 2019). This study also showed that the fly ash from the incinerator can be palletized with an adhesive material and recycled for re-burning in the incinerator. Upon discharge in the form of bottom ash, the palletized fly ash was reported to be dioxin free. Fluidized bed incinerator has also been employed for the disposal of PCB-containing waste oil (Trinh et al. 2019). The process utilized ultrasonic wet scrubber, activated carbon injection, and baghouse as air pollution control devices. During incineration, calcium carbonate was injected to remove acid gases. Also, calcium hydroxide and powdered activated carbon were injected into the gas stream to remove acid gases and dioxins prior to the baghouse. The process achieved DRE values of 99.87% and 99.9998% for PCDD/F and dioxin-like polychlorinated biphenyls (dl-PCB), respectively. In another study, fluidized bed incinerator was used for the disposal of soil that was co-contaminated with lube oil and heavy metals (Samaksaman et al. 2016). In this case, a low-temperature two-stage fluidized bed incinerator was employed. The first stage was operated in the range 500–700 °C, while the second stage was operated at a constant temperature of 800 °C. Results indicated that the DRE for lube oil was in the range 98.27–99.93%. In addition, leaching tests performed on the bottom ashes revealed that the amount of heavy metals in the leachates complied with the regulatory requirements. Also, it was observed that carbon monoxide concentrations decreased with increasing sand bed height to diameter ratio in the second stage of the incinerator. The applicability of fluidized bed incinerator for the disposal of expired propellant, containing highly reactive materials such as nitrocellulose and nitroglycerine, has been studied using CFD (Cho et al. 2016). The simulation results were used to find the optimum fluidization conditions and air injection rate for the target propellant disposal rate of 20,000 tons/year.

Starved Air Incinerators

Starved air incinerators, also known as fixed hearth, air controlled, or pyrolytic incinerators, are suitable for solid or sludge wastes. Such incinerators contain two refractory-lined stages: a pyrolytic stage and a combustion stage. In the pyrolytic stage, air is maintained below the stoichiometric requirement to pyrolytically destruct the hazardous waste. The pyrolytic products from the first stage move into the combustion stage where the presence of auxiliary fuel and additional air completes the combustion. Starved air incinerators maintain low gas velocities, and particulates are mostly retained in the pyrolytic stage (Rickman 1991; Williams 2005). The gases leaving the pyrolytic stage are usually at 700–800 °C. The combustion stage is typically operated at 1000–1200 °C with 200% excess air (Williams 2005).

Multiple Hearth Incinerators

Multiple hearth incinerators are most suitable for hazardous sludge disposal but can also handle solid, liquid, and gaseous hazardous wastes (Bonner et al. 1981). Also known as the Herreshoff furnace (Santoleri 2003), a typical multiple hearth incinerator consists of vertically stacked hearths that are enclosed within a refractory-lined shell, an air-cooled central rotating shaft, and a series of rabble arms with teeth for each hearth (Dupont et al. 2016). Hazardous solid waste or sludge is introduced from the top and is distributed on the hearth by means of the rabble arms and teeth. The waste is then transported by gravity to the lower hearths through holes until it exits the incinerator in the form of ash. In case of liquid hazardous wastes, side ports are provided for feeding (Bonner et al. 1981; Vallero 2014).

Emission Control and Heat Recovery

Despite being effective for hazardous waste disposal, incineration creates inevitable risks of unwanted pollution through generation of flue gas and ash. Example pollutants such as carbon monoxide, nitrogen oxides (NOx), acid gases, particulates (fly ash), polyaromatic hydrocarbons (PAHs), PCBs, PCDDs, PCDFs, and heavy metals are of particular concern (Brereton 1996; Polprasert and Liyanage 1996; Carmen Agramunt et al. 2003; Rivera-Austrui et al. 2011). The use of suitable downstream air pollution control (APC) equipment can minimize the harmful effects due to incineration activities. In fact, most studies have established no correlation between emissions from the incinerators and harmful effects on human health (Schuhmacher et al. 2002, 2013; Mari et al. 2007, 2009; Nadal et al. 2008; Zubero et al. 2010; Rivera-Austrui et al. 2011; van Dijk et al. 2015; García et al. 2020; Iamiceli et al. 2021). On the contrary, some studies have documented the adverse effects of incineration. For instance, increased concentrations of PCDDs and PCDFs in the serum of industrial waste incineration facility workers have been reported (Kim et al. 2001) both of which are toxic, carcinogenic, and bioaccumulative with known effects on the endocrine, immune, and reproductive systems (Arisawa et al. 2005). Similar increase in the serum levels was observed for temporary workers visiting the incineration facility for maintenance work (Shih et al. 2006). Also, statistically significant increase in cancer-related mortalities has been reported in towns located near incinerators used for the disposal of hazardous waste (García-Pérez et al. 2013). One study has reported that, despite implementing emission controls, 99.4% of total PAHs (known to be mutagenic and carcinogenic) was directly emitted to the ambient air through the stack flue gas during disposal of petrochemical industrial wastewater in a liquid injector incinerator (Wang et al. 2007). Also, biomonitoring results have confirmed exposure of incinerator workers to metals such as cadmium and lead (Mauriello et al. 2017). In terms of environmental effects, arsenic, chromium, tin, thallium, and vanadium levels have been observed to increase in soils near a hazardous waste incinerator (Vilavert et al. 2012). In another study, co-incineration of sludge, coal, and hazardous waste in a cement plant was found to be a cause of increased mercury levels in the surrounding soil (Wang et al. 2018). Nevertheless, the use of appropriate APC systems in incineration facilities is highly critical to guarantee environmentally acceptable air emissions that meet the regulatory requirements and to ensure effective minimization or elimination of risks to the public and the environment.

It is important to note that the APC systems cannot operate at elevated temperatures. Therefore, as a prerequisite, the flue gas exiting the incinerator must be cooled to below 300 °C prior to feeding it to the APC systems (Batstone et al. 1989b).

Given the high temperature of the flue gas, heat recovery becomes an attractive option from the perspective of improving the economics of the overall waste management system. Conventional options for heat recovery include gas-to-water, gas-to-air, and gas-to-organic fluid systems. Gas-to-water heat recovery involves the use of waste heat boilers to generate steam which can be employed to generate power or supplement steam requirements in other processes (Rickman 1991) or utilized for district heating (Bourtsalas et al. 2019). Gas-to-air heat recovery systems use the flue gas to heat the combustion air in order to decrease the auxiliary fuel needed during incineration. Similarly, gas-to-organic liquid recovery systems are used to heat the liquid waste for incineration in order to decrease the auxiliary fuel requirement or to heat other liquids as hot streams for other processes (Rickman 1991).

The constituents of the flue gas are dictated by the incineration conditions and the characteristics of the hazardous waste being disposed. Several APC devices are available for target removal of particulates, acid gases, nitrogen oxides, and heavy metals. In addition, afterburners may be utilized in case of incomplete combustion during incineration. Afterburners essentially continue the combustion of pollutants in the flue gas, for example, by oxidizing the hydrocarbons and carbon monoxide. The overall purpose is to decrease the pollutant load on the downstream APC equipment. Afterburners may be based on direct flame, hot zone, or catalytic combustion (Bonner et al. 1981).

Particulate Control

Particulates, largely composed of ash but may also contain individual or adsorbed heavy metals, dioxins, and furans (Williams 2005), are typically removed from the incineration flue gas using dedicated equipment such as baghouse filters, electrostatic precipitators (ESPs), high-efficiency particulate air (HEPA) filters, porous ceramic filters, venturi scrubbers, or hydrosonic scrubbers (Batstone et al. 1989b; Tillman et al. 1989). In general, the selection of appropriate equipment for particulate removal depends on the flue gas characteristics (such as temperature, flow rate, and particulate loading), the particle size and the particle size distribution, and the required removal efficiency (Williams 2005). Baghouse filters, also known as bag or fabric filters, employ cylindrical fabric bags that are placed inside a casing. The bags capture the particulates and allow the flue gas to pass through the pores. The particulates build up on the surface of the bags as cake which necessitates their removal using offline (reverse air cleaning or shake/deflate) or online (pulse-jet cleaning) methods (Tan 2014). Baghouse filters are capable of reducing the particulate loading in the flue gas down to 10 mg/m^3 or less (Williams 2005). Typical collection efficiencies are 99.5% or higher for particles of size less than 10 μm (Tillman et al. 1989). Studies have also shown the effectiveness of baghouse in capturing submicronic and nano-sized particles in waste incineration flue gas with collection efficiency ranging from 98 to 99.98% (Boudhan et al. 2018). In another study, it has been shown that baghouse filtration, combined with fly ash adherence, can achieve complete removal of nanoparticles with a pressure of 500 Pa across the dust-covered filter medium (Förster et al. 2016). Studies have also highlighted that baghouse filters can simultaneously destroy dioxins and furans and collect the particulates by employing catalytic filters (Fritsky et al. 2001). Also, baghouse filtration, with prior activated carbon injection, can effectively capture heavy metals (Scala 2001) and PCDD/F (Chen et al. 2014). In terms of design, face velocity through the filter should be in the range 0.5–5 cm/s to avoid flooding (Tan 2014), and the filter medium must have sufficient permeability to the flue gas and high mechanical, chemical, and heat tolerances (Tillman et al. 1989). Common filter mediums in baghouse filters include glass and polymeric fibers such as polyphenylene sulfide (PPS), polytetrafluoroethylene (PTFE), polyamide (PA), polyimide (PI) (Tanthapanichakoon et al. 2007), and PTFE/Teflon (Sutherland 2007). In case of PPS, susceptibility to degradation by acid gases and nitric oxide is high. The operational temperature and nitric oxide concentration must be below 200 °C and 1000 ppm, respectively (Tanthapanichakoon et al. 2007).

Besides baghouse filters, ESPs (Electrostatic Precipitators) can be utilized for capturing fine particulates. In a typical ESP, the flue gas is passed between a high-voltage electrode (usually wires) and a grounded electrode (plates or tubes). The particulates, after becoming charged, move to the grounded electrode (Sinnott 1997). The collected particulates are eventually removed using mechanical vibrators (dry ESP) or using continuous water sprays (wet ESP) (Tillman et al. 1989). ESPs can remove particulates of size less than 2 μm (Sinnott 1997) as well as nano-sized particles (Holder et al. 2013). Collection efficiency is usually in the range 97–99.5% (Williams 2005). The operation of ESPs is significantly affected by the electrical resistivity of the particulates. Due to the dependence of resistivity on temperature, optimum operating temperature of ESP is an important consideration. In general, ESPs tend to exhibit lower collection efficiencies with particulates of high resistivity (Bonner et al. 1981). Best performance and collection efficiencies are observed with particle resistivity in the range 5×10^9–5×10^{10} ohm-cm (Schifftner 2013). ESPs generally have a high capital cost (Bonner et al. 1981).

HEPA (High Efficiency Particulate Air) and porous ceramic filters are of particular use for the removal of particulate radionuclides from incinerators handling radioactive wastes (Seo et al. 1990; Raj et al. 2006). HEPA filters utilize corrugated separators to capture the particulates and exhibit collection efficiencies up to 99.97% for particulates of size 0.3 μm (Tillman et al. 1989). Porous ceramic filters, on the other hand, employ ceramic-based cylindrical filter candles that are enclosed in a pressure vessel.

Venturi scrubbers are one type of wet scrubber systems that contain a converging conical section where the flue gas is accelerated, a constricted area/throat, and a conical diverging section where the gas is slowed down. Liquid water is injected at a rate of 0.001–0.003 m^3/m^3 of flue gas in either the converging conical section or the throat (Flagan and Seinfeld 1988). In both cases, the liquid is atomized, and the particulates are captured by inertial impaction (Tillman et al. 1989). Venturi scrubbers are simple in design, possess a small size, and have a low capital cost (Schifftner 2013). Hydrosonic scrubbers, on the other hand, utilize a supersonic nozzle through which steam or compressed air is ejected. The nozzle is fitted with an injection ring to deliver a water spray. Upon contacting the high-speed flue gas, the water spray is broken down into small droplets with a size 10–30 times the size of the particulates to be removed. The water droplets finally encapsulate the particulates and enter a specially designed cyclone from which the flue gas exits from the top, and the water-encapsulated particles are removed by gravity (Rickman 1991).

Acid Gas Control

Acid gases are removed from the flue gas using packed bed absorption, spray drying, or dry injection APC technologies. Packed bed absorbers are common acid gas control equipment in hazardous and medical waste incineration facilities. The absorption columns are packed with a random or structured packing material. Typically, the packing materials are ceramic based to avoid corrosion by acid gases. A scrubbing liquid (water or alkaline solution) is fed from the top of the absorber, while the flue gas is injected from the bottom (National Research Council (US) Committee on Health Effects of Waste Incineration 2000). Liquid wets the packing and provides high interfacial area for mass transfer with the acid gases. The flue gas velocity through the absorber must be carefully selected to provide sufficient contact time and avoid flooding. Packed bed absorbers are not suitable for flue gases with high particulate loading. As a result, they are typically employed for flue gas from liquid injection incinerators wherein the particulate loading is low. In case of high particulate loading, such as for flue gas from rotary kiln or fluidized bed incinerators, venturi scrubbers are employed upstream of the packed bed absorbers (Bonner et al. 1981; Rickman 1991).

Spray dryers remove the acid gases by injection of calcium- or sodium-based atomized reagent. The acid gases react with the slurry to form salts. The dryer may be designed to allow for flue gas flow in the upward or downward directions. The upflow design includes a downstream cyclone to capture a portion of the particulates. The downflow design includes a bottom hopper to remove large particulates from the flue gas (Rickman 1991). Due to the ability of spray dryers to operate with flue gases of high particulate loading (Bonner et al. 1981), particulate control equipment (baghouse filters and ESPs) are typically placed downstream of the spray dryers. The sequence allows removal of acid gases and particulates, including the reactions salts. In cases where baghouses are employed, residual acid gases can continue to react with the unreacted liquid reagent in the filter cake, thereby, increasing the overall acid gas removal efficiency (Rickman 1991). Spray dryers can also be designed to pretreat the flue gas (in a separate upstream tower or in the bottom section) with water to form an acid solution. The acid solution, in turn, helps in absorbing and removing heavy metals from the flue gas (Williams 2005). Spray dryers result in secondary pollution by generation of the polluted liquid reagent. This challenge can be addressed by employing dry injection systems where dry alkaline powder, such as calcium hydroxide, sodium carbonate, or sodium bicarbonate, is sprayed onto the flue gas to remove the acid gases via chemical reactions. In this case, recommended injection temperatures are reported to be on the order of 135 °C

(Tillman et al. 1989). Dry injection systems are used in combination with downstream baghouse filters for powder and particulate removal. Although primarily designed for acid gas removal, dry injection systems can be designed for simultaneous removal of heavy metals and dioxins by injection of activated carbon (Williams 2005).

NO_x Control

NOx emissions are controlled by catalytic or non-catalytic ammonia injection. In the non-catalytic process, ammonia is injected in a narrow temperature range of 850–950 °C in order to react with NOx to produce nitrogen and water. The temperature window in this process must be carefully maintained. At high temperatures, ammonia itself converts to NOx, while at low temperature, the reaction conversion is low (Williams 2005). Non-catalytic ammonia injection is suitable for flue gases with NOx concentrations ranging from 40 to 10,000 ppm, and removal efficiencies of up to 80% can be obtained (Tillman et al. 1989). Catalytic ammonia injection also involves conversion of NOx to nitrogen and water. The process is, however, conducted in the presence of a catalyst (platinum, palladium, vanadium oxide, or titanium oxide) and at a temperature in the range 250–400 °C (Williams 2005). Catalytic ammonia injection can reduce NOx levels by up to 95% (Tillman et al. 1989). Also, studies have shown that PCDD/F can be reduced by up to 97% (Carlsson 1992; Sam-Cwan et al. 2001). However, the process requires prior removal of heavy metals and sulfur dioxide in order to avoid catalyst deactivation. This necessitates the use of dry injection system and baghouse filter prior to the catalytic ammonia injection process (Tillman et al. 1989; Williams 2005). Compared to the non-catalytic process, the catalytic process has higher NOx reduction efficiency which results in lower direct environmental impacts (lower NOx emissions). However, it has been shown that the catalytic process has higher indirect environmental impacts due to the production and operation of the catalyst unit (Van Caneghem et al. 2016). From an environmental perspective, optimization and improvement of the non-catalytic process is preferred.

6.5 Summary

The collection, storage, and transportation of hazardous waste are important prerequisites prior to the disposal. In case of hazardous waste storage, important considerations include the storage area and its design, the storage systems and their appropriate use, safety, and proper segregation, labeling, and inventory management. Recent advances related to hazardous waste transportation have focused on developing appropriate methodologies for the selection of the transportation firm, assessing and modeling the transportation risks, and developing appropriate location-routing models. One of the available methods for hazardous waste disposal includes incineration which is based on thermal destruction. Incineration is a mature technology, and different types of incinerators, such as liquid injection, rotary kiln, fluidized bed, starved air, and multiple hearth, can be utilized for the ultimate disposal of hazardous waste.

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Chapter 7
Advances in Land, Underground, and Ocean Disposal Techniques

Muhammad Qasim and Zarook Shareefdeen

7.1 Introduction

The generation of ever-increasing quantities of hazardous waste necessitates the development and use of effective disposal strategies. Other than incineration, landfills, deep well injection systems, underground geologic repositories, and oceans represent several possible means of hazardous waste disposal options. In general, landfilling is a common disposal technique that relies on long-term containment of hazardous waste in a landfill. Deep well injection, on the other hand, involves the injection of liquid hazardous waste into subsurface porous, permeable, and saline water-bearing geologic zones. Emplacement of hazardous waste in underground geologic repositories is also an attractive option wherein the hazardous waste is isolated from the environment by means of a host rock. Finally, ocean disposal of hazardous waste involves the use of ocean incineration or ocean dumping techniques. This chapter provides an overview of the state of the art of the different hazardous waste disposal methods. The technical details are presented, and technological advancements in different aspects of the disposal methods are also discussed in this chapter.

7.2 Landfill Disposal

A landfill for hazardous waste, also known as an engineered or a secured landfill, is defined as a disposal facility where the waste is safely and securely placed in isolation from the environment and the public. Interest in the use of landfilling as a

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disposal method is mainly attributed to its low cost and unsophisticated design compared to other disposal methods (Batstone et al. 1989a; Blackman Jr. 2001; Williams 2005). Landfills must be properly designed, constructed, and operated in order to ensure safe disposal of the hazardous waste. The subsections below discuss all the significant aspects of hazardous waste landfills and their related advancements.

7.2.1 Landfill Restrictions

Most hazardous wastes can be disposed in properly designed landfills. However, there may be land disposal restrictions (LDR) for certain types and forms of hazardous wastes in order to avoid adverse environmental effects of landfills. The Title 40, Part 268 of the US Code of Federal Regulations outlines the prohibitions on land disposal, including landfilling and other methods such as well injection, unless the treatment standards have been met. Also, Title 40, Part 265 of the US Code of Federal Regulations draws special requirements pertaining to landfilling. As a summary, non-containerized hazardous waste containing free liquids and containerized liquid hazardous waste (except very small containers and small lab pack containers surrounded by absorbent material and placed in larger secondary containers) cannot be placed in landfills. When placed in containers, liquid hazardous waste can only be landfilled when it is solidified or mixed with appropriate absorbent (Wright et al. 1989). In addition, hazardous wastes on the F, K, P, and U lists, such as spent solvents, dioxin-containing wastes, corrosive wastes with pH <2, and wastes containing heavy metals or PCBs, need to meet the treatment standards before deemed suitable for disposal in landfills (Pichtel 2014). Such restrictions necessitate the use of appropriate physical, thermal, chemical, or biological treatment technologies in order to meet the treatment technology-based standards or the maximum concentration limits for specific wastes. The treatment may be based on a technology specified by the US EPA or any other technology (except dilution) as long as the maximum concentration limits are met (Pichtel 2014). As a general rule, the hazardous waste acceptance criteria for direct disposal into a landfill is as follows: calorific value: <3200 kcal/kg, nonbiodegradables: <20%, flash point: >600 °C, pH: 4–11, reactive cyanide: <250 ppm, reactive sulfide: <500 ppm, water-soluble organics: ≤10%, and water-soluble inorganics: ≤20% (Rao et al. 2017).

7.2.2 Landfill Site Selection

Selection of suitable hazardous waste landfill site must consider a range of engineering, environmental, regulatory, and economic factors. Detailed site and environmental assessments and cost studies need to be conducted before selecting a landfill site. The landfill site assessment involves extensive site survey to identify the possible pathways and environmental receptors of the releases from the landfill.

Also, it assesses the geological and hydrogeological conditions around the site in order to gather information about the soil, bedrocks, and groundwater and identify any potential foreseeable hazards such as landslides. Core samples are collected for detailed geologic and hydrogeologic evaluation. Borings are usually needed to fully characterize the soil and the subsurface geology. Determination of soil pH, cation-exchange capacity (CEC), and microbial activity is also important in order to assess the ability of soil to attenuate the constituents of hazardous waste. For instance, soils with high pH and CEC possess a superior ability to retain heavy metals (Wright et al. 1989). Also, soil microorganisms tend to decompose the organic matter present in the waste (Batstone et al. 1989b). For hydrogeologic evaluation, the depths of the water table and piezometric water levels in bedrocks/confined aquifers are determined. Also, the movement of groundwater is studied (O'Leary and Tchobanoglous 2002). Environmental assessment, on the other hand, involves a detailed analysis of the direct and indirect environmental effects that will result from the landfill and the activities involved during its construction, operation, and maintenance (Williams 2005). The data and results obtained from the site and environmental assessments are evaluated against the site selection criteria in order to decide on the suitability of the site for landfilling. In general, the landfill site selection is based on the following engineering, environmental, and economic criteria (Batstone et al. 1989a; Wentz 1989; O'Leary and Tchobanoglous 2002):

- The site selected for landfilling should have sufficient capacity to hold the quantity of hazardous waste that is generated over a long period of time.
- The site should be away from the populated areas to avoid risks to public health.
- It is preferable that the site is close to the point of hazardous waste generation to minimize transportation costs and risks.
- The site must be easily accessible through common means of transportation.
- The site should not be a high seismic activity impact zone.
- The surface/soil beneath the landfill should be impermeable or of low permeability.
- The soil at the site should have pH in the range 7–8 to allow for reduction of heavy metals and biodegradation of organic contaminants.
- Climate conditions at the site should not be severe.
- Areas such as protected lands, wetlands, floodplains, mudflats, sand dunes and those with high slopes, landslides, faults, soil erosion, subsidence, and underlying mines should not be used.
- The site should not have contact with surface or groundwater.
- Areas in contact with terrestrial and aquatic ecosystems should not be used.
- The site must meet the regulatory requirements.
- Public opinion must favor the site selection.
- The costs of site acquisition, development, operation, and maintenance must be reasonable.

It is important to note that the criteria mentioned above are not exhaustive. Several other important criteria such as social, environmental, and health costs and political and aesthetic factors related to the landfill must also be considered in selecting the most suitable site. As a result, site selection becomes a tedious and protracting decision wherein a large number of criteria, both quantitative and qualitative, must be satisfied simultaneously. This has attracted significant research interest in order to develop effective tools to assist in site selection for landfilling of hazardous waste.

The use of Delphi method to rank the site selection criteria has been studied (Zakaria et al. 2013). It has been shown that the Delphi method, which is based on surveying experts in the field, is both time and cost-effective. Results from the Delphi method have shown that the environmental criteria should be given priority when locating the landfill site followed by the social and economic criteria. Map overlayer technique has been proposed for locating suitable sites for hazardous waste landfilling (Yesilnacar and Cetin 2005). The technique involved the use of topographic, geologic, active fault, land use, earthquake zoning, erosion, climate, and transportation maps on a regional scale. Each map was evaluated to identify the potential landfill sites based on criteria related to geology, climate, temperature, precipitation, wind, topography, land use, erosion, seismicity, and transportation. The final site selection was based on over-layering and joint comparisons that were made possible through transparencies of the maps.

In a later study, the same technique was employed, however, with the use of a single geomorphological map combined with active fault and earthquake zoning maps (Yesilnacar and Cetin 2008). Advances have also been made in utilizing the spatial data from GIS for quick and reliable identification of proper landfill sites for the disposal of hazardous waste. For instance, combination of GIS and analysis hierarchical process (AHP) has been used to determine the most suitable location for landfilling of radioactive waste (Rezaeimahmoudi et al. 2014). The AHP model was based on pair comparison, and seven selection criteria were considered, namely, water resources, slope, population centers, roads, protected zones, faults, and geology. Suitable landfill sites were determined using the base maps that were created using GIS and incorporated with the expert opinion-based criteria weights from the AHP model. Similarly, in another study, GIS was used in conjunction with remote sensing to build a geospatial database (Abd-El Monsef and Smith 2019). Information for the database was retrieved from field surveys, satellite images, and literature. Using the weighted criteria (based on the Basel Convention), AHP was used to select the most suitable site for landfilling of hazardous waste.

As an alternative approach, integration of GIS and landfill susceptibility zonation methods was investigated for locating the candidate sites for hazardous waste landfills (Hafezi Moghaddas and Hajizadeh Namaghi 2011). A three-step methodology was adopted in this case. First, areas such as protected areas, urban and rural areas, fault plains, riversides, alluvial fans, main roads, dam's drainage basins, and groundwater resources were excluded. Second, landfill-suitability zonation maps were prepared. In these maps, suitable sites were first screened based on criteria such as geology, geomorphology, climate, land use, land cover, and topography. Then, a scored map was created by utilizing weighting and scoring for geology, geomorphology, land cover, slope, precipitation, and evaporation. In the last step, standard impact assessment study (Leopold matrix) combined with technical and economic considerations were used to select the final sites.

Other studies have focused on the integration of GIS and multi-criteria analysis methods for selecting suitable sites for hazardous waste landfilling. For example, in one study, GIS was used for initial screening in order to eliminate the undesirable sites (Sharifi et al. 2009). The initial screening was followed by multi-criteria decision analysis (MCDA) which was guided by a panel of experts to select the most suitable sites. Similar integration of GIS and multi-criteria analysis methods was used in other studies (Feo and Gisi 2014; Danesh et al. 2019; Stemn and Kumi-Boateng 2019). Also, integration of GIS with simple additive weighting (SAW) multi-criteria analysis method has been suggested (Khamehchiyan et al. 2011).

7.2.3 Landfill Design

The design of a secured landfill needs to satisfy several engineering and regulatory requirements in order to minimize the impacts on the environment, ecosystems, and public health. A well-designed secured landfill will completely isolate the hazardous waste and provide enough mitigation measures to deal with any releases/leaks from the disposed hazardous waste. The design of a landfill needs to incorporate several key elements (see Fig. 7.1). These key elements of design and engineering of a secured landfill are discussed hereafter.

Fig. 7.1 Landfill site preparation (Landfill design n.d.)

Landfill Capacity

The capacity of the landfill is an important design consideration. Factors such as the expected volume/amount of hazardous waste to be disposed (taking into account the current and future waste generate rates), the waste density, the amount of cover material used, the volume occupied by the liner system, the number of lifts used, and waste settlement must be taken into account while estimating the landfill capacity. Settlement of the waste is expected due to physical rearrangement soon after disposal. Also, physical, chemical, and biological degradation along with overburden pressure result in waste settlement within the landfill (Williams 2005).

Disposal Method

Hazardous waste can be disposed in landfills using the trench, area, or canyon methods (O'Leary and Tchobanoglous 2002). The trench method is the most common and is based on disposal below the ground level, for example, in a natural or an excavated depression where the water table is low (Wright et al. 1989; Pazoki and Ghasemzadeh 2020). In particular, the hazardous waste is placed inside individual trenches/cells over the active landfill area. The use of individual cells helps in segregation of incompatible wastes. The dimensions of the cells can vary depending on the amount, size, and characteristics of the hazardous waste to be disposed. The sides of the cells are sloped with a ratio of 2:1–3:1 (O'Leary and Tchobanoglous 2002). Bulk hazardous wastes are placed in the cells to create a layer of 0.61–0.91 m thickness. The layer is compacted and then covered with a 0.3 m layer of covering material, such as soil, to prevent infiltration of water or escape of potential releases from the hazardous waste. The soil cover is placed at the end of each working day and is typically termed as daily cover. In addition, an intermediate cover is used for the cells which are filled or when the site is expected to be inactive for a prolonged period. The use of daily cover is essential to control water entry into the landfill. Containerized hazardous wastes are placed vertically in the cells at a reasonable distance from one another. The space between the containers is filled with soil or compatible bulk hazardous wastes. Daily and intermediate covers are also applied on top of the containerized hazardous wastes (Wright et al. 1989). Once all the cells within the active landfill area are filled, the complete layer of cells (knows as lift) may be stacked with another layer of cells to create a series of lifts.

The area method, on the other hand, is based on aboveground disposal. It is suitable for cases when excavation of cells is infeasible due to high groundwater conditions. In the area method, daily cover is applied using soil or geosynthetic blankets (O'Leary and Tchobanoglous 2002; Pazoki and Ghasemzadeh 2020). In the case of canyon method, special landforms, such as canyons, ravines, borrow pits, and quarries, with natural features of depression and steep sides, are utilized to create the landfill (O'Leary and Tchobanoglous 2002).

Leachate Control

Leachate is the liquid that forms at the bottom of the landfill due to the initial presence of water in the waste, physicochemical changes occurring within the landfill, and infiltration of water via precipitation and uncontrolled runoff (O'Leary and Tchobanoglous 2002). The characteristics of leachate depend on several factors such as properties of the disposed hazardous waste, moisture content, temperature, site hydrology, landfill depth, and landfill age (Singa et al. 2018a; Gautam et al. 2019).

Typically, the landfill leachate is dark (black or dense brown) in color and exhibits low biochemical oxygen demand (BOD), high chemical oxygen demand (COD), and high redox potential (Gautam et al. 2019). Several studies have attempted to analyze and characterize the leachate from hazardous waste landfills. High concentrations of boron, organic phosphates, 1,4-dioxane, phthalates, bisphenol A, phenols, ethers, and chlorine have been detected in leachate samples from hazardous waste landfills (Yasuhara et al. 1999; Yamamoto et al. 2001). In another study, 190 different chemical compounds, including heavy metals, were detected in leachates from hazardous waste disposal sites (Yasuhara et al. 1997). The concentrations of organic phosphates and phthalates were found to be 0.8–10,900 ng/L and 0.1–2800 ng/L, respectively. Other constitutes of leachates from hazardous waste landfills include inorganic compounds such as iron, calcium, and magnesium and organic compounds such as acetic acid, methylene chloride, butyric acid, 1,1-dichloroethane, and trichlorofluoromethane (Ghassemi et al. 1984). Besides these, micro-pollutants such as PAHs and phthalate acid esters may be present in the leachate (Singa et al. 2020). Due to the presence of harmful constituents, leachate from hazardous waste landfills has been reported to produce toxic effects in soil, surface and groundwater, and even in humans in proximity to the landfills (Xu et al. 2018). This necessitates implementation of appropriate leachate containment, collection, removal, and treatment systems to avoid adverse effects of leachate on the environment and human health and ensure safe design and operation of the landfills.

Liner systems are employed to contain the leachate within the landfill and prevent its migration to the surrounding environment. Title 40, Part 265 of the US Code of Federal Regulations stipulates the use of two or more liners for hazardous waste landfills. A typical double-liner system is placed at the bottom and side slopes of the landfill prior to hazardous waste emplacement. The leachate accumulates within the liner system and then, by gravity, moves to one or more central collection sumps through a series of perforated drainage pipes (collection laterals). The removal of leachate from the landfill should be effective to ensure that the leachate level on the liner does not exceed 0.3 m. This requires that the bottom of the landfill is sloped and that sufficient number of drainage pipes are provided. Once collected, the leachate can be transferred for treatment or ultimate disposal. In a typical double-liner system, the bottom liner may be composed of compacted clay, a flexible membrane (synthetic) liner, or any natural material of suitable thickness and hydraulic conductivity (permeability). The top liner, however, must be a flexible membrane liner (Wright et al. 1989).

Liner systems require proper design and installation with appropriate selection of the liner material. The choice of liner material depends on the characteristics of the hazardous waste and the leachate and the geological and hydrogeological conditions (Williams 2005). The desirable liner features are as follows (Batstone et al. 1989a; Hovater 1989; Williams 2005):

- High compatibility with the hazardous waste to be disposed
- High chemical and biological resistance
- High durability
- Low hydraulic conductivity ($\leq 1 \times 10^{-7}$ cm/s)
- Optimum thickness (≥ 5 m)
- High stability against overburden pressure (low compressibility)
- High resistance to climate-induced stresses such as freeze-thaw cycles
- Absorptive or attenuative capability
- Non-decaying (long service life)
- Easy to install
- Low cost

Clay, geosynthetic clay, or flexible membrane liners can be employed. Clay liners are based on natural clay soil (composed of clay minerals) of suitably low permeability. Typical clay minerals include illite and kaolinite, vermiculite, smectite, and chlorite (Pichtel 2014). The permeability of a clay liner depends on clay mineralogy, particle size distribution, plasticity, strength, moisture content, and degree of compaction (Williams 2005). To meet the hydraulic conductivity as a liner ($\leq 1 \times 10^{-7}$ cm/s), clay soil should contain at least 20% fine particles and maximum 10% gravel-sized particles and exhibit a plasticity index greater than 10%. In addition, rocks with diameter larger than 2.5–5 cm should not be present (Pichtel 2014). To create the clay liner, naturally occurring clay soil is excavated and then sieved to remove large solids. Subsequently, the moisture content and degree of compaction of the clay soil are adjusted to control the permeability of the final clay liner. When the amount of clay minerals in the clay soil is low, bentonite clay is added to achieve a reasonably low hydraulic conductivity. These liners can be referred to as bentonite-enhanced soils (Williams 2005). It is important to note that the hydraulic conductivity of clay liners can increase under thermal cycles or wet-dry cycles induced by climate conditions. Experimental investigations under simulated landfill conditions have showed that, for soils with low plasticity index of 9.5%, the hydraulic conductivity of the resulting clay liners can increase by one order of magnitude or by 12 times after 30 thermal cycles or 2 wet-dry cycles, respectively (Aldaeef and Rayhani 2015). This necessitates the use of a cover, such as a geomembrane or soil layer, to protect the clay liner from exposure to atmosphere during construction.

Geosynthetic clay liners consist of a bentonite layer that is supported or encased by a geotextile fabric or a geomembrane. In the case of supported type liner, a layer of bentonite is placed on top of a geomembrane. Encased-type liner, on the other hand, is composed of two geotextile layers with a bentonite intermediate layer. The layers are held together mechanically via needle punching, stitching, or chemical adhesion. Geosynthetic clay liners offer low permeability, high mechanical strength, simple and rapid installation, and an ability to self-heal through swelling of bentonite (Kong et al. 2017). Also, the service life can be up to thousands of years given that bentonite loss, hydraulic conductivity loss, and desiccation are avoided (Hoor and Rowe 2013). Loss of hydraulic conductivity can be due to suppression of osmotic swelling in the bentonite layer caused by its interaction with the leachate constituents (Jo et al. 2005; Benson et al. 2010; Setz et al. 2017). Desiccation, on the other hand, is a consequence of thermal gradients caused by temperature increase during decomposition of the disposed waste. The thermal gradients cause the moisture to move away from the geosynthetic clay liner, thereby, resulting in desiccation and subsequent cracking of the bentonite layer (Southen and Rowe 2005; Azad et al. 2012; Hoor and Rowe 2013).

To avoid desiccation and loss of hydraulic conductivity, recent research efforts have directed efforts toward the use of polymer-treated bentonite in geosynthetic clay liners. When tested against low-concentration contaminants, it has been shown that polymers can enhance the hydraulic performance of geosynthetic clay liners (Elhajji et al. 2001). In particular, anionic polymer has been employed to decrease the hydraulic conductivity of calcium bentonite in laboratory experiments (Razakamanantsoa et al. 2012). Results from another study have showed that bentonite-polymer composite, prepared by polymerization of acrylic acid within bentonite slurry, exhibits higher swelling capability and lower hydraulic conductivity compared to natural sodium bentonite when tested against aggressive inorganic solutions (Scalia et al. 2014). Lower hydraulic conductivity of geosynthetic clay liners with polymer-treated bentonite has also been reported in another study (Tian et al. 2019). In addition, the hydraulic conductivity of bentonite-polymer composite geosynthetic clay liners has been found to be suitably low to suppress the migration of heavy metals (Li et al. 2020). Recently, it has been reported that a geosynthetic clay liner with polymer-treated bentonite is less susceptible to cracking due to desiccation compared to the one with unmodified bentonite. However, this behavior was only observed when the temperature on the geosynthetic clay liner was 40 °C. Above this temperature, the difference in the degree of desiccation was found to be negligible (Yu et al. 2020).

Flexible membrane liners are based on synthetic materials with low permeability such as plastics or rubber. Commonly used flexible membrane liners for hazardous waste landfills are synthesized using polyvinyl chloride (PVC), high-density polyethylene (HDPE), low-density polyethylene (LDPE), chlorinated polyethylene (CPE), chlorosulfonated polyethylene (CSPE), and ethylene propylene diene monomer (EPDM) (Hovater 1989; Williams 2005; Pichtel 2014). Table 7.1 provides a comparison of these materials as landfill liners. Flexible membrane liners must be carefully selected in order to ensure compatibility with the hazardous waste. The chemical compatibility between wastes and membrane liners can be evaluated using the US EPA Method 9090 (Hovater 1989).

Careful installation of a flexible membrane liner is critical to its successful performance. It is important that the surface supporting the liner is smooth, even, and compacted. Also, proper seaming to join the individual liner sheets or rolls is important such that free edges are eliminated and tight seals and high seam strengths are

Table 7.1 Comparison of commonly used materials for flexible membrane liners in landfills. Information presented is summarized from Bell (2004) and Williams (2005)

	PVC	HDPE	LDPE	CPE	CSPE	EPDM
Chemical resistance	Low for organics; high for inorganics	Good	Good	Poor	Good	Poor for petroleum and halogenated solvents
Mechanical strength	High	Good (but susceptible to punctures)	Good (but susceptible to punctures)	Good	Low	High
Temperature tolerance	Poor	Good performance at low temperatures	Good performance at low temperatures	Good performance at low temperatures	Good performance at low temperatures	Good performance at low temperatures
Weather tolerance	Poor	–	–	Good	Good	Good
Ease of seaming	High	High	High	High	Low	Low

obtained. Typically, seaming is performed by overlapping the edge of the liner (5–15 cm) using thermal fusion, extrusion, chemical, or adhesive seaming techniques (Hovater 1989). The size and layout of the flexible membrane liner should be properly selected in order to minimize seaming of individual sheets or rolls. Also, as a recommendation, horizontal seams on slopes and transverse seams at the toe of slopes should be avoided. Seams on slopes should be parallel to the slope, and transverse seams should be 1–1.5 m away from the toe of slopes. Seam tests are of critical importance in order to assess the seam strength and integrity. These tests can be destructive, such as shear or peel tests using a field tensiometer, or nondestructive, such as dual seam, vacuum chamber, air lance, or ultrasonic methods (Cossu and Stegmann 2019). In addition, the liner should be anchored to the surface beneath (Hovater 1989). To support and protect flexible membrane liners, geotextiles (polypropylene or polyester fibers) and geonets (plastic drainage nettings) are employed (Hovater 1989; Williams 2005). As a secondary function, geotextiles also act as filtration media to remove solids from the leachate and avoid blockage of the drainage layers (Williams 2005). At the end of installation, hydraulic test should be conducted to identify any leakages from the liner. In addition, electrical leak location (ELL) survey can be conducted where high voltage across the liner (electrical insulator) is applied and the flow of current is used to detect the precise location of leaks. This method is well described in ASTM D6747 and D7002 standards (Cossu and Stegmann 2019). When installed properly, the design life of flexible membrane liner can range from many decades to many centuries (Rowe et al. 2019).

Besides the conventional liners discussed above, several research studies have proposed novel liner materials for hazardous waste landfills. Liner composed of a compacted mixture of bentonite and zeolite with optimized water content has been explored (Tuncan et al. 2003). Results indicated that the ideal landfill liner, with low hydraulic conductivity, was obtained when the bentonite to zeolite ratio was 0.10. Also, volcanic soil, with allophane as the main pedogenic mineral phase, has been investigated as landfill liner (Navia et al. 2005). The hydraulic conductivity was found to be suitable for use as landfill liner (in the range 5.16×10^{-9}–6.48×10^{-9} m/s). In addition, the volcanic soil liner possessed an ability to adsorb the pollutants in the leachate. Liners from crushed shales have been investigated (Mohamedzein et al. 2005). These liners had hydraulic conductivity in the order of 10^{-7} cm/s and showed good performance when subjected to calcium chloride solution. In another study, a mixture of sand and attapulgite (a natural clay) was employed as landfill liner (Al-Rawas et al. 2006). Scanning electron microscope (SEM) images revealed that attapulgite formed a coating between and around the sand grains which resulted in low porosity and, therefore, low hydraulic conductivity of the liner. It was reported that sand with 30% attapulgite and water content 2% above the optimum value satisfied the landfill liner requirements. In another study, marine clay soils were proposed as landfill liners (Chalermyanont et al. 2009). These liners exhibited hydraulic conductivities in the range 4.8×10^{-9}–1.1×10^{-8} cm/s and possessed ability to retain heavy metals such as chromium, lead, cadmium, zinc, and nickel. The use of marine clay as landfill liner was also investigated in a recent study, and hydraulic conductivity of $\leq 10^{-8}$ m/s was reported (Emmanuel et al. 2020b). In another recent study, olivine-treated marine clay was suggested as landfill liner material (Emmanuel et al. 2020a). Treatment of marine clay with 30% olivine was reported to produce the lowest hydraulic conductivity. In another recent effort, carboxymethyl cellulose (CMC) was used to decrease the hydraulic conductivity of bentonite liner (Fan et al. 2019). Results indicated that, for a given void ratio, CMC-treated bentonite possessed 20 times lower hydraulic conductivity compared to untreated bentonite. Also, the hydraulic conductivity of CMC-treated bentonite remained unchanged when exposed to real landfill leachate. A recent effort proposed a sustainable liner material composed of fly ash and bentonite (Garg et al. 2020). With 70% fly ash and 30% bentonite, the liner was able to meet the strength and hydraulic conductivity requirements. Numerical model studies suggested that the liner could be employed for 100 years when the applied thickness was 126–154 cm.

Leachate Treatment

Once collected, the leachate from hazardous waste landfills can be treated using a combination of biological, physical, and chemical techniques. The choice of treatment technique and the development of treatment train depends on the characteristics of the leachate, the constituents that need to be removed, and the required removal efficiency. Biological treatment processes are cost-effective and utilize microorganisms to degrade the nutrients and organic constituents present in the leachate. Both aerobic and anaerobic biological processes can be utilized for the treatment of leachate from hazardous waste landfills (Morgan 1990). However, care must be taken since the presence of toxins, heavy metals, and bio-refractory compounds and high concentration of sulfates and dissolved solids in the leachate tend to decrease the effectiveness of the biological treatment processes (O'Leary and Tchobanoglous 2002; Gautam et al. 2019). Aerobic processes for the treatment of leachate from hazardous waste landfills have been investigated. For example, lagoon with intermittent aeration has been utilized to treat phenol-containing oil shale ash heaps leachate (Orupõld et al. 2000). Results showed that the lagoon was able to achieve COD removal of 70% and phenol, methyl phenols, and dimethyl phenols removal of 95–99%. Also, activated sludge systems have been employed. For example, sequencing batch reactor (SBR) has been employed to treat leachate form an industrial waste landfill where 85–95% of total organic carbon (TOC) was removed (Irvine et al. 1984). SBRs are time-oriented systems that operate over repeated cycles (fill, react, settle, decant, and idle) and allow for flexible operation that can be easily controlled (Ozturk et al. 2019). Similarly, sequencing batch biofilm reactors (SBBRs) have been employed which utilize a packing to carry the activated sludge in SBR (Yuan 2014). These reactors have many advantages over conventional activated sludge processes such as larger surface area for bacterial growth, stable operation, and generation of smaller quantities of excess sludge (Chang et al. 2000). SBBRs with either membrane oxygenation system or bubble aeration have been used for leachate treatment (Dollerer and Wilderer 1996). Experimental studies with leachate from a hazardous waste landfill have shown that these reactors are able to reduce the dissolved organic carbon (DOC) by 60–68%. Also, combined anaerobic-aerobic SBR has been used to treat oil shale ash dump leachate (Kettunen et al. 1996). Besides removal of BOD and COD (97–99% and 73%, respectively), it was found that combined anaerobic-aerobic conditions can achieve phenol removal of up to 83–86%. Upflow anaerobic sludge blanket (UASB) reactors represent another option for the treatment of landfill leachate, specifically for the abatement of ammonium and nitrite (Mainardis et al. 2020). In a typical UASB, anaerobic sludge is suspended at the bottom of the reactor, and the flow of leachate is upward through the sludge blanket (Tiwari et al. 2020). It has been reported that UASB can remove 10.5–23.6% of influent COD and up to 78.7% of biphenyls in landfill leachate (Ismail et al. 2020).

Physical processes for leachate treatment include dissolved air flotation (DAF), carbon adsorption, air stripping, and membrane-based processes such as reverse osmosis (RO) (Renou et al. 2008). DAF is employed to remove suspended materials and microorganisms. In the context of leachate treatment, flotation has been utilized as a posttreatment after the biological treatment step for the removal of humic acids from synthetic landfill leachate (Zouboulis et al. 2003). Removal efficiencies as high as 99% were reported. Adsorption via activated carbon is a conventional water treatment technology that can efficiently remove the COD (organics). Air stripping, on the other hand, can effectively eliminate ammonium-nitrogen (NH_4^+-N) in wastewaters. Activated carbon adsorption and air stripping techniques have been applied to leachates from municipal solid waste (sanitary) landfills, and removal efficiencies of 91% (COD) and 99.5% (NH_4^+-N), respectively, have been reported (Renou et al. 2008). However, studies employing these techniques for the treatment of leachate from hazardous waste landfills are nonexistent. Nevertheless, both of these are well-established technologies for wastewater treatment and can be applied to leachates from hazardous waste landfills. The RO process utilizes a semipermeable membrane and high pressure to separate the contaminants (such as organics and inorganics) present in the leachate. It has been reported that RO can effectively treat industrial landfill leachate pre-treated using evaporation. Results showed that organics and ammonium reductions of 90% and 97%, respectively, can be achieved using RO (Di Palma et al. 2002).

In the case of chemical treatment processes, well-established methods such as coagulation/flocculation, chemical precipitation, and advanced oxidation processes (AOPs) can be utilized for leachate treatment. Coagulation/flocculation is typically used as a pre- or post-processing step for the treatment of leachate (Bakraouy et al. 2017). This treatment process can be used to remove suspended materials and organic and inorganic matter by addition of a coagulant to the leachate (Teh et al. 2016). The process results in agglomeration of small particles and colloids which are eventually removed as large particles. Typical coagulants that can be employed include aluminum sulfate, ferrous sulfate, ferric chloride, and ferric chloro-sulfate (Renou et al. 2008). Research studies have utilized coagulation/flocculation for the removal of humic acid (85%) (Zouboulis et al. 2004), turbidity (97%) (Amokrane et al. 1997), and COD and color (67% and 96%, respectively) (Monje-Ramirez and Velásquez 2004) from sanitary landfill leachates. Research studies have not utilized coagulation/flocculation specifically for the treatment of leachate from hazardous waste landfills. However, coagulation/flocculation is a well-established technology for wastewater treatment and can be utilized for the treatment of leachates from hazardous waste landfills. Chemical precipitation can be employed to remove specific contaminants from the leachate. For example, it can be used to remove NH_4^+-N using magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) and sodium phosphate dibasic dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$) (Li et al. 1999). Also, chemical precipitation, performed using ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12}.26H_2O$) and barite ($BaSO_4$) minerals, has been utilized to remove 99% of sulfates in leachate from hazardous industrial waste landfill (Barbosa Segundo et al. 2019). AOPs rely on the generation of rapidly reacting hydroxyl radicals to remove contaminants and toxins from the leachate. Different types of AOPs have been utilized for the treatment of leachates from hazardous waste landfills. One possible option is ozonation which utilizes ozone to alter the molecular structure and oxidize the organics to biodegradable compounds that can be easily removed via biological posttreatment (Gautam et al. 2019). Ozonation of industrial waste landfill leachate has been studied where 50% reduction in COD was achieved (Haapea et al. 2002). Results from a recent study highlighted that ozonation can be used to remove up to 34.5% of dissolved organic carbon (DOC) from leachate sample obtained from a hazardous industrial waste landfill (Segundo et al. 2021). In the same study, it was shown that ozonation combined with hydrogen peroxide (H_2O_2) addition can increase the DOC removal to 45.2%. Other options include catalytic ozonation and ozonation combined with UV radiation or persulfate. These methods have been employed for the treatment of sanitary landfill leachates and may also be applied to leachates from hazardous waste landfills (Gautam et al. 2019). Due to its low treatment efficiency, ozonation is typically employed for pre- or posttreatment of landfill leachates. Fenton process is another type of AOP that can be employed for leachate treatment. In this process, H_2O_2 is activated in the presence of a ferrous catalyst to generate hydroxyl radicals. When used for the treatment of hazardous waste landfill leachate, the Fenton process has been reported to exhibit 56.49% COD removal (Singa et al. 2018b). In another study by the same authors, Fenton process in the presence of UV light (photo-Fenton process) was employed to achieve 68% removal of COD (Singa et al. 2018a). Also, heterogeneous Fenton oxidation, electrochemical oxidation, electrocoagulation, and electro-flotation (applied extensively to sanitary landfill leachate) may be employed for the treatment of hazardous waste landfill leachate (Gautam et al. 2019; Usman et al. 2020).

Some studies were done on combined processes for treating leachates from hazardous waste landfills. Combined process such as Fenton treatment followed by activated sludge process or activated sludge process followed by Fenton treatment has been found to be effective for the treatment of semicoke (hazardous waste rich in phenols) landfill leachate from an oil shale thermal treatment plant (Kattel et al. 2016). Besides efficient removal of BOD and COD, both processes exhibited lower treatment costs compared to the ozonation process. Also, the combination of activated sludge process and microfiltration has been investigated for treating leachate from a hazardous waste landfill (Setiadi and Fairus 2003). Results showed that the COD, BOD, and ammonia-N removal efficiencies of the combined process were 31.3%, 66%, and 98%, respectively.

A recent study has employed a combination of forward osmosis (FO) and membrane distillation (MD) to treat high salinity hazardous waste landfill leachate. The FO process utilized a sodium chloride (NaCl) draw solution (of high osmotic pressure) to transfer the liquid molecules in the leachate across a semipermeable membrane. The MD process, on the other hand, was used to treat the draw solution from the FO process. In the MD process, a temperature gradient was employed to allow for permeation of vapors (generated from the heated draw solution) across a hydrophobic membrane. The combined process showed TOC, salt, and total nitrogen (TN) removal efficiencies higher than 98%, 96%, and 98%, respectively. In addition, NH_4^+-N and heavy metals (mercury, arsenic, antimony) were completely removed. The biological, physical, and chemical treatment methods and their combinations discussed above are summarized in Table 7.2.

Due to the complex composition of landfill leachate, complete remediation necessitates the use of a multistage treatment strategy that combines different physical, chemical, and biological methods. A six-step treatment strategy has been recently proposed for the treatment of a hazardous industrial waste landfill leachate (Barbosa Segundo et al. 2020). The proposed treatment process consisted of (1) catalytic oxidation using H_2O_2 to remove sulfides and sulfites, (2) chemical

Table 7.2 Summary of studies related to the treatment of leachate from hazardous waste landfills

Treatment method	Treatment details	Main leachate characteristics	Removal efficiency	Reference
Biological	Aerated lagooning, intermittent aeration, nutrients: KH_2PO_4 (34–136 mg/l) and NH_4Cl (146–590 mg/l), activated sludge: 0.2 g mixed liquor suspended solids (MLSS)	BOD_7: 1650 mg/L, COD: 3090 mg/L, pH: 12	COD: 70%, phenol, methylphenols, and dimethylphenols: 95–99%	Orupõld et al. (2000)
	Sequencing batch reactor (SBR) (aerated), MLSS: 2600 mg/L, pH: 7.9–8.6	TOC: 2300 mg/L	TOC: 85–95%	Irvine et al. (1984)
	Sequencing batch biofilm reactor (SBBR) (aerated)	TOC: 2500 mg/L, COD: 5295 mg/L, BOD_5: 2600, pH: 9.1	DOC: 60–68%	Dollerer and Wilderer (1996)
	Sequencing batch biofilm reactor (SBBR) (combined anaerobic-aerobic)	BOD_7: 810–2700 mg/L, COD: 2000–4600 mg/L, pH: 12–13, phenols: 130–230 mg/L	COD: 73%, BOD: 97–99%, phenol: 83–86%	Kettunen et al. (1996)
	Upflow anaerobic sludge blanket (UASB) reactor, working volume: 10.8 L, sludge volume: 6 L	COD: 3421 mg/L, pH: 7.75	COD: 10.5–23.6%	Ismail et al. (2020)
Physical	Flotation, air flow: 200 cm^3/min	Humic acid: 50–300 mg/L	Humic acid: 99%	Zouboulis et al. (2003)
	Reverse osmosis (RO), polyamide membrane, pressure: 60 bar	BOD_5: 5000 mg/L, COD: 19900 mg/L, TOC: 5244 mg/L, pH: 8	Organics: 90%, ammonium: 97%	Di Palma et al. (2002)

(continued)

Table 7.2 (continued)

Treatment method	Treatment details	Main leachate characteristics	Removal efficiency	Reference
Chemical	Chemical precipitation using $BaSO_4$, $[Ba^{2+}]:[SO_4^{2-}] = 2:1$, pH: 8.5	BOD_5: 1100 mg/L, COD: 7063 mg/L, TDC: 3670 mg/L, pH: 8.7	Sulfate: 99%	Barbosa Segundo et al. (2019)
	Ozonation, dosage: 0.5 mg O_3/mg of COD	COD: 500 mg/L, pH: 10	COD: 50%	Haapea et al. (2002)
	Ozonation, dosage: 40 mg O_3/min	BOD_5: 360 mg/L, COD: 2809 mg/L, TOC: 3670 mg/L, DOC: 966 mg/L, pH: 8.4	DOC: 34.5%	Segundo et al. (2021)
	Ozonation with H_2O_2 addition, dosage: 50 mg O_3/min	BOD_5: 360 mg/L, COD: 2809 mg/L, TOC: 3670 mg/L, DOC: 966 mg/L, pH: 8.4	DOC: 45.2%	Segundo et al. (2021)
	Fenton oxidation process, pH: 3, H_2O_2/Fe_2^+ molar ratio: 3, reaction time: 150 min	BOD_5: 960 mg/L, COD: 3715 mg/L, pH: 9.53	COD: 56.49%	Singa et al. (2018b)
	Photo-Fenton oxidation process, H_2O_2/Fe_2^+ molar ratio: 3, reaction time: 90 min, UV source: 16 W	BOD_5: 850 mg/L, COD: 4123 mg/L, pH: 8.42	COD: 68%	Singa et al. (2018a)
Hybrid	Activated sludge/Fenton treatment, $COD/H_2O_2/Fe^{2+}$: 1/1/0.2 (w/w/w)	BOD_7: 330 mg/L, COD: 851, TOC: 367 mg/L, DOC: 243 mg/L, pH: 9.3	COD: 78%, BOD: 96%, DOC: 78%, NH_4-N: >99%, total phenol: 94%	Kattel et al. (2016)
	Fenton treatment/activated sludge process, $COD/H_2O_2/Fe^{2+}$: 1/0.5/0.1 (w/w/w)	BOD_7: 330 mg/L, COD: 851, TOC: 367 mg/L, DOC: 243 mg/L, pH: 9.3	COD: 62%, BOD: 91%, TOC: 56%	Kattel et al. (2016)
	Activated sludge/microfiltration, sludge retention time: 32 days, transmembrane pressure: 0.3 bar	COD: 2036 mg/L, BOD_5: 350 mg/L	COD: 31.3%, BOD: 66%, ammonia-N: 98%	Setiadi and Fairus (2003)
	Forward osmosis (FO)/membrane distillation (MD), FO draw solution: 4.82 M NaCl, MD feed temperature: 62.5 °C	TOC: 726.9 mg/L, salinity: 100,000 mg/L, NH_4^+-N: 18.5 mg/L	TOC: 98%, salts: 96%, TN: 98%, NH_4^+-N and heavy metals (mercury, arsenic, antimony): 100%	Zhou et al. (2017)

BOD biochemical oxygen demand, *COD* chemical oxygen demand, *TOC* total organic carbon, *TDC* total dissolved carbon, *DOC* dissolved organic carbon, *TN* total nitrogen.

precipitation to remove the sulfates, (3) biological treatment to remove organics and nitrogen species, (4) coagulation to remove suspended solids and some organics, (5) photo-Fenton process to degrade organics and enhance biodegradability, and (6) biological treatment to remove the biodegradables. The complete treatment train was able to reduce the COD to less than 1000 mg/L, a limit commonly acceptable for discharge to municipal wastewater treatment plants.

Landfill Gas Control

Unlike municipal waste landfills, gas release from landfills dedicated for hazardous waste disposal is uncommon. This is because most hazardous waste is received in stabilized or solidified form without biodegradable constituents (Pichtel 2014). However, in the case of organic hazardous waste disposal, landfill gas can be generated through anaerobic biodegradation of the organic matter. Typically, landfill gas contains methane and carbon dioxide (greenhouse gasses) as major components along with small amounts of volatile organic compounds (Williams 2005). With methane as one of the principal constituents, landfill gas can cause asphyxiation or form explosive or flammable mixtures with air. Also, the gas has an ability to travel vertically or laterally through the soils due to pressure and concentration gradients (Wright et al. 1989). Given these characteristics, monitoring and control of landfill gas become important in order to avoid harmful effects on site workers and the surroundings.

Landfill gas can be monitored via surface or subsurface monitoring techniques. Surface monitoring is based on the use of portable and wearable gas detectors with single or multi-gas sensors. Subsurface monitoring, on the other hand, utilizes probes for monitoring gas within the landfill and in the surroundings. The probes also allow for surface transfer and collection of gas (through a sampling valve) for laboratory analysis (Williams 2005). Some recent studies have proposed novel systems for monitoring of landfill gas. For instance, the use of infrared cameras/infrared thermography for the detection of landfill gas leaks has been suggested (Lewis et al. 2003; Tanda et al. 2017). Also, unmanned aerial vehicle (UAV) with embedded gas detectors has been utilized for landfill gas monitoring (Kim et al. 2021). Control of landfill gas is achieved via passive or active control systems. Passive control reduces the lateral migration of landfill gas by using atmospheric venting systems that are installed through the final landfill cover. This type of control is only recommended when the gas generation rate is low and toxic components are not present. Active control systems, on the other hand, rely on extraction of landfill gas by creating a negative pressure, for example, using a blower. Both vertical and horizontal extraction wells may be utilized for this purpose (O’Leary and Tchobanoglous 2002). The extracted gas is either collected or flared.

Final Cover

A final cover (cap) must be applied upon completion of the landfill or an individual cell. The final cover is an integral component of the landfill that serves a multitude of purposes listed below (Batstone et al. 1989a; O'Leary and Tchobanoglous 2002; Williams 2005):

- Contain, protect, and isolate the disposed hazardous waste.
- Prevent wind dispersion of the disposed hazardous waste.
- Reduce the infiltration of rainwater and surface water.
- Minimize the uncontrolled release of landfill gas.
- Minimize the ingress of air.
- Provide a surface for vegetation of the site.
- Suppress the proliferation of disease vectors and other organisms.

The final cover should meet the following criteria (O'Leary and Tchobanoglous 2002):

- Exhibit a low permeability.
- Maintain integrity, and possess an ability to withstand conditions such as erosion, abrasion, extreme climate, earthquakes, subsidence, and settlement within the landfill.
- Promote surface runoff.
- Allow for drainage of any percolated water.
- Have a low-maintenance requirement.

The final cover for secured landfills is constructed from a series of layers. A dense and compacted clay layer is first placed directly on top of the disposed hazardous waste. This layer functions to prevent the infiltration of water into the landfill. Next, a geomembrane cap, with chemical and physical properties similar to synthetic liners, is placed on top of the clay layer. The geomembrane cap also prevents the infiltration of water into the landfill. Unlike synthetic liners, the geomembrane cap is not exposed to landfill leachate, and, therefore, its chemical compatibility is not a serious concern. However, the geomembrane cap may experience strains due to waste settlement within the landfill. Nevertheless, its repair is easy due to proximity to the surface. Above the clay-geomembrane layer, a surface water collection and removal system is provided. This system is composed of granular soils, geonets, or geocomposites with drainage pipes and serves to direct the infiltrated water away from the bottom layers. Finally, a vegetative soil layer is added to complete the final cover for the landfill. The vegetative layer prevents wind and water erosion, enhances evapotranspiration, and improves the aesthetic features of the landfill. Typically, the minimum depth of each individual layer in the final cover is as follows: clay layer: 0.61 m, geomembrane cap: 0.02 m, drainage layer: 0.3 m, and vegetative layer: 0.6 m (Pichtel 2014). The final cover is typically sloped (3–5%) to promote runoff, minimize infiltration, and accommodate for waste settlement within the landfill (Wright et al. 1989). The suitability of the final cover (as well as the liner system for leachate control) and its susceptibility to percolation can be evaluated using the "Hydrologic Evaluation of Landfill Performance" (HELP) model. This model is a computerized water budget program that performs water balance on the landfill system using a quasi-two directional flow. It considers the flow in vertical direction, due to infiltration and evapotranspiration including saturated and unsaturated vertical flow, and in the lateral direction, due to lateral drainage and surface runoff, and takes into account the weather and the soil layer data (Piskin and Demirer 2007; Chabuk et al. 2018).

Advances have been made in order to utilize alternative, low-cost, and sustainable materials for the final cover in landfills. Evapotranspirative cover has been designed and employed in hazardous waste landfill (Zornberg et al. 2003). Unlike typical landfill cover that acts as a barrier, an evapotranspirative cover acts as a sponge to store the moisture during precipitation and then release the moisture back to the atmosphere as evapotranspiration. This type of cover is technically superior and is less vulnerable to desiccation and cracking compared to the clay layers, requires low maintenance, and can be easily constructed from a broad range of soils. In order to mitigate the effects of settlement and the resulting cracks in the final cover, using a self-recovering sustainable liner has been suggested (Kwon and Cho 2011). In this type of final cover, impermeable precipitates are formed from chemicals (such as diatomite and slaked lime with sodium carbonate catalyst) contained within the cover. In the case of crack formation or water infiltration, the final cover undergoes a self-recovery process in which the precipitates fill up the pores to maintain the hydraulic conductivity. In recent studies, the use of waste materials in the final cover has been explored. For example, the use of steel slag in landfill final cover has been investigated (Herrmann et al. 2010; Andreas et al. 2014). Mixtures of electric arc furnace slag and cementitious ladle slag were used within the final cover. The performance of the final cover in terms of infiltration and stability was found to be promising. Also, it was estimated that 60–70,000 thousand tons of construction materials required annually for landfill cover can be replaced by steel slags. Overall, the use of steel slag in the final cover allows for its economic recycling, reduces its quantity to be disposed, and decreases the material requirements for the construction of the final cover. Likewise, some recent studies have shown the possibility of using final covers containing mixtures such as clay/biochar (a carbon-rich solid obtained from pyrolysis of biomass) (Wong et al. 2016, 2017) and clay/fly ash (Shaikh et al. 2021).

Environmental Monitoring

Environmental monitoring is an important aspect of hazardous waste landfills. Routine monitoring of the vadose zone, groundwater, and air quality is critical to identifying any contaminant release from landfills and taking corrective actions to avoid harmful effects on the environment and public health. Several well-established techniques are available for environmental monitoring at landfills. These techniques either involve collection of samples for laboratory analysis (sampling techniques) or rely on some chemical and physical change to monitor the environment (non-sampling techniques) (O'Leary and Tchobanoglous 2002).

The vadose zone represents the unsaturated soil zone beneath the hazardous waste landfill. Monitoring of the vadose zone helps identify any release of leachate or gas from the landfill and provides early warnings of groundwater contamination. Liquid in the vadose zone can be monitored by sample collection using lysimeters (Wright et al. 1989; Singh et al. 2018). Typically, suction lysimeters are installed in the vadose zone. These are cylindrical devices consisting of a porous cup attached to a nonporous tubing. Vacuum is applied to collect a sample of the soil solution into the lysimeter through the porous cup. The collected sample is withdrawn into a sampling flask on the surface for laboratory or field analysis. Gas monitoring, on the other hand, may be performed via soil gas probes that obtain the gas samples from the vadose zone for analysis (O'Leary and Tchobanoglous 2002). Some research studies have focused on advancing the non-sampling methods for monitoring of the vadose zone. For instance, electrical leak detection method has been suggested (White and Barker 1997). In this vadose zone monitoring method, permanent grid of electrodes is installed beneath the landfill, and increase in electrical potential is used to detect leakages from holes in the liner system. In addition, time-domain reflectometry (TDR) has been suggested for continuous real-time monitoring of the vadose zone (Dahan et al. 2003; Aharoni et al. 2017).

Groundwater monitoring allows for detection of changes in the water quality caused by landfill leachate or gas. Monitoring wells with inert/corrosion-resistant casings are used for this purpose. Typically, four groundwater monitoring wells are installed (one up-gradient and three down-gradient). The required number of monitoring wells and their location must be decided, taking into account factors such as the nature of the aquifer, leachate characteristics, and groundwater depth, flow rate, and flow direction (Wright et al. 1989). Samples of groundwater can be collected using piezometers, and the groundwater quality can be monitored through hydrochemical analysis of the samples. Besides monitoring wells, recent studies have proposed alternative groundwater monitoring techniques. Electrical resistivity imaging (ERI) has been used for groundwater monitoring in landfills (Park et al. 2016). This technique relies on the fact that the electrical resistivity of landfill leachate is lower than that of clean groundwater. As a result, changes in the electrical resistivity of the groundwater can be related to contamination due to landfill leachate. This technique is attractive since it provides fast and reliable groundwater monitoring without the need for well drilling. Also, groundwater contamination at landfill sites and the spatial variation of contaminants have been studied using the very-low-frequency-electromagnetic (VLF-EM) survey (Monteiro Santos et al. 2006; Al-Tarazi et al. 2008). This survey utilizes radio signals with frequency ranges between 5 and 30 kHz to obtain and identify subsurface domains of low resistivities in which landfill leachate may have contaminated the groundwater.

Ambient air quality at hazardous waste landfills and in the vicinity can be monitored by collecting gas samples for laboratory or field analysis. Air samples can be collected using grab or active samplers. Grab samplers collect the gas in a collection chamber at regular intervals. Active samplers, on the other hand, allow for continuous collection and analysis of the air stream (O'Leary and Tchobanoglous 2002).

Post-Closure Care and Remediation

Post-closure care of a hazardous waste landfill should consider the following (Wright et al. 1989; O'Leary and Tchobanoglous 2002):

- Periodic inspection and maintenance of final cover in order to maintain its integrity.
- Continuous monitoring of vadose zone, groundwater, and ambient air.
- Periodic inspection and maintenance of environmental monitoring facilities.
- Analysis of samples from environmental monitoring facilities.
- Continuous operation and maintenance of leachate collection and removal system.
- Continuous operation and maintenance of gas control system.

Remedial action plan is required in order to take appropriate corrective actions in case any contaminant (leachate or gas) release is identified during post-closure environmental monitoring. The following points should be considered while developing the remedial action plan:

- Emergency procedures, such as site closure, evacuation, and liaison with emergency responders during flammable/toxic atmospheres.
- Methods and procedures for limiting the spread of contaminants in case of groundwater pollution.
- Procedures to rebuild or repair leachate control systems.
- Methods for treatment of contaminated groundwater.

7.2.4 Miscellaneous Landfill Considerations

Other requirements pertinent to the design and operation of a hazardous waste landfill are summarized below:

- The infrastructure around the landfill should be carefully planned. Access roads to the landfill site and to the disposal area should be provided.
- Equipment requirements should be evaluated, and appropriate equipment for excavation, soil compaction, and loading/unloading should be made available.
- A system should be in place to inspect the incoming hazardous waste and record and track the amount disposed.
- Equipment for loading, unloading, and transferring wastes should be provided.
- Unauthorized access to the landfill should be prevented by using fences and security measures.
- Wherever appropriate, safety and warning signs should be provided.
- The landfill operators should be adequately trained.

- Adequate PPE should be provided to the site operators.
- Safety equipment, such as first aid kits, should be available.
- Site offices and storage rooms for equipment should be provided.
- Appropriate welfare facilities should be provided.

7.3 Deep Well Injection

Deep well injection technique is applicable for the disposal of liquid hazardous wastes. It involves the injection of waste into subsurface (underground) porous, permeable, and saline water-bearing geologic zones that are confined vertically by impermeable strata (Warner 1989; Shammas and Wang 2010). Typically, the injection well consists of a series of concentric pipes that extend several thousands of feet from the surface level. The outermost pipe (surface casing) extends below the base of underground sources of drinking water (USDW). It is entirely cemented to the surface to avoid contamination of USDW. A long casing, extending into the injection zone, is provided within the surface casing. This casing is filled with cement up to the surface to prevent the flow of injected waste back to the surface. Liquid hazardous waste is injected into the well via injection tubing that is provided inside the long casing. The annular region between the inner casing and the injection tube is filled with a pressurized inert fluid (such as kerosene or diesel) and is sealed at the bottom using a removable packer to prevent the liquid backflow into the annulus (Shammas and Wang 2010; Pichtel 2014). At the surface, a wellhead caps the injection well which is provided with valves and gauges for injection control and monitoring (Batstone et al. 1989c). Detailed requirements related to injection wells (Class I wells) are outlined in the underground injection control program (UIC) program established by the US EPA, and the related regulations can be found in Title 40, Parts 144–148 of the US Code of Federal Regulations. As examples, deep well injection has been employed for the disposal of liquid radioactive waste (Rybalchenko et al. 2005), mercury-contaminated sludge (Yod-In-Lom and Doyle 2002), mercury sulfide and residual ash (Brkic et al. 2003), and acidic waste (de Graaff 1998).

7.3.1 Site Selection

Selection of a suitable site for deep well injection should consider the technical factors summarized below (Batstone et al. 1989c; Warner 1989; Shammas and Wang 2010):

- The injection zone should be saline water-bearing, sufficiently thick, and permeable enough to accept the wastes at safe injection pressures.

- The injection zone should not contain mineral resources of economic significance.
- The confining strata above and below the injection zone should be impermeable and sufficiently thick in order to confine the disposed waste.
- Geologic features such as faults, folds, and joints must be avoided to prevent escape of the injected waste.
- Fluid movement conditions in the injection zone should not allow for movement of waste in vertical and lateral directions.
- The injection and confining zones should not be penetrated with abandoned or unplugged wells.
- Sites with high seismic risk must be avoided.

As mentioned above, the confinement zones should ideally be impermeable. However, in practice, the confining zones are typically of low permeability that act to retard the movement of the injected hazardous waste. During its movement, the hazardous waste undergoes several geochemical processes that include ion exchange, osmosis, filtration, adsorption, and transformation. The velocity of the hazardous waste leaking through the confining zone is given by the following equation (Shammas et al. 2009):

$$v = \frac{Q}{A\varphi} = \frac{PI}{\varphi} \tag{7.1}$$

where v is the velocity (ft/day), Q is the leakage rate (ft^3/day), A is the leakage area (ft^2), φ is the porosity, P is the permeability (ft^3/day/ft^2), and I is the hydraulic gradient (ft/ft). The vertical permeability of the confining zone can be determined by analyzing the core samples obtained during drilling. When combined with the confining zone thickness and the pressure difference across the confining zone, the vertical permeability can be used to estimate the velocity of hazardous waste traveling through the confining zone. Besides permeability, the ion exchange capacity is often measured for the core samples from confining zone. The ion exchange capacity provides an estimate of the degree of subsurface treatment and attenuation which is of particular importance in the case of toxic wastes (Shammas et al. 2009).

The injection zone at the selected site should be able to receive the expected volume of hazardous waste to be injected. The hazardous waste and the injection zone should be characterized to avoid situations where undesirable changes in the injected waste and the injection zone may occur. These changes can be in the hazardous waste due to the injection zone conditions, chemical reactions between the waste and the injection zone formation or the injection zone fluids, or changes in the injection zone due physical/chemical interactions with the waste. Also, the dynamics of fluids in the injection zone is an important consideration since it affects the direction and rate of movement of the injected hazardous waste (Shammas et al. 2009).

7.3.2 Waste Characteristics

The characteristics of the liquid hazardous waste are important in assessing the suitability for disposal by deep well injection. The following factors should be taken into consideration (Warner 1989; Shammas and Wang 2010):

- The waste must be compatible with the materials used in the injection well system, with the confining and injection zones, and with the natural formation water. To ensure compatibility, pre-treatment of waste may be required prior to disposal.
- Wastes with high turbidity can cause plugging of the injection zone.
- Corrosive wastes should be neutralized as they can undergo undesirable reactions with the injection system components, the formation, and the formation water.
- High iron concentrations can also cause plugging/fouling due to changes in solubility caused by changes in the valence state.
- Organic carbon in the waste can result in fouling by aggravating the growth of microorganisms.

7.3.3 Deep Well Injection Design

Injection wells are typically drilled using the rotary method (Shammas and Wang 2010). An important design aspect is the bottomhole completion method that depends on the type of subsurface formation. Open-hole completion can be used for competent formations such as limestones, dolomites, and consolidated sandstones due to their ability to stand unsupported. In the case of incompetent formations, such as unconsolidated sands and gravels, gravel-packed completion is used. Also, perforated casing can be utilized for competent and incompetent formations where casing and cement are extended into the injection zone and perforations are provided to allow for waste injection (Warner 1989; Shammas and Wang 2010). The casing provides the necessary support to prevent collapse of the formation into the wellbore. Besides the bottomhole completion method, corrosion control and mechanical integrity are important design considerations. Corrosion control measures may include cathodic protection, use of corrosion-resistant materials in the well, and neutralization of corrosive wastes. Internal and external mechanical integrity tests are conducted to check for leakages in the casing, tubing, or packer and outside the casing, respectively. Internal mechanical integrity tests are conducted using the standard annulus pressure test (SAPT), the standard annulus monitoring test (SAMT), and the radioactive tracer survey (RTS). External mechanical integrity tests, on the other hand, include the use of temperature log, noise log, oxygen activation log, cementing records, or RTS (Gaurina-Medjimurec 2015). The procedures and the required equipment for conducting these tests can be found in the guidance documents prepared by the US EPA Region 5 UIC Branch (U.S. EPA 2008). The type of wellhead is another important design consideration. In the case where high backpressure is expected, for example, due to chemical reactions in the injection zone, the wellhead must be designed to bleed off the back flows to avoid excessive buildup of pressure and prevent the potential for blowout (Shammas et al. 2009).

Besides the injection well, the complete deep well injection disposal system requires the use of auxiliary upstream equipment. The waste is typically collected in a sump tank where an oil layer (in an open tank) or an inert gas (in a closed tank) is used to prevent air contact. For wastes containing oil, an oil separator is used downstream of the sump tank. The removal of oil is required to avoid plugging of the formation. A clarifier is then employed where particulates are allowed to settle under gravity. The residual particulates in the waste are removed using filtration. Metal screens coated with diatomaceous earth or cartridge filters can be used for this purpose. Filtration step is typically employed in the case the waste is injected into formations of low porosity. After filtration, the waste may be treated with a bactericide if the susceptibility to plugging due to high microorganism levels. The treated waste is collected in a holding tank from where it is finally injected into the injection zone using an injection pump. For highly porous formations, the liquid head may be sufficient for injection, and the injection pump may not be required (Shammas and Wang 2010).

The well design should also incorporate the necessary elements required for the protection of aquifers that are of domestic, industrial, or agricultural value. The aquifers may be contaminated by the injected hazardous waste or the displaced formation fluids. The necessary steps required for aquifer protection depend on the migration pathway taken by the contaminants. Defects in the casing can provide pathways for the injected hazardous waste to escape into the nearby aquifers. To avoid this, the casing material should be compatible with the hazardous waste. In addition, periodic casing integrity tests should be carried out. Techniques such as downhole camera and high-resolution Vertilog can be employed for casing inspection and identification of defects. Also, the use of separate tubing for injection can minimize casing defects by isolating the casing from the injected fluids. Vertical migration of contaminants through the annular region between the casing and the wellbore can also result in aquifer contamination. To eliminate this, the casing is cemented to the wellbore. Also, leakage through the confining zone (due to the presence of fractures) can contaminate the aquifer. This can be avoided by ensuring that the injection zones are deep, carefully selecting the deep well injection site, and thoroughly studying the geology of the confining zone (Shammas et al. 2009).

7.3.4 Monitoring Requirements

Typically, the volume, flow rate, chemistry, and biology of the hazardous waste; injection and annulus pressure; corrosion rate; and leakages need to be monitored during deep well injection operation. The volume and chemistry of the injected hazardous waste provide an estimate of the distance traveled by the waste within the injection zone. Biological monitoring and analysis of hazardous waste, on the other hand, is required to ensure that microorganisms are not being introduced into the well. The injection and annulus pressures are monitored continuously to avoid excessive pressures that may result in hydraulic fracture of the injection and confining zones and cause damage to the well facilities. In the case of corrosion monitoring of the well tubing and casing, corrosion coupons are typically installed in the well. These weight-loss specimens are made of the same material as the tubing and the casing. The weight of corrosion coupons is measured periodically to estimate the corrosion rate. To monitor and detect leakages in the casing-tubing annulus and the tubing, conductivity probes are employed. These probes can detect changes in the fluid chemistry caused by leakage of the injected waste. Alternatively, the inert fluid in the annulus region can be cycled continuously, and the return flow can be analyzed to detect the presence of hazardous waste that leaked into the casing-tubing annulus (Batstone et al. 1989c; Warner 1989).

7.3.5 Modeling of Deep Well Injection

Most of the recent advances are related to disposal by deep well injection and are related to the development of mathematical models that describe different aspects of deep well injection systems. Stochastic modeling of flow and transport in confining layers of deep well injection systems has been presented (Rhee et al. 1993). In this model, the confining layers were assumed to be binary random structures of pure sand and pure shale and were defined using Monte Carlo methods.

MODFLOW finite difference model was used to simulate three-dimensional flows in the confining layer. Results indicated that rapid transport may occur through the confining layer if the average shale fraction was less than 0.65. In addition, two-dimensional finite element model was used to model diffusion and advection-dispersion in the confining layer. With shale fraction greater than 0.65, the simulation results showed that the model waste (dilute acetonitrile solution) did not extend beyond the confining layers over a period of 10,000 years.

Numerical model for studying the movement of injected waste within the hydrogeologic system has been presented (Jin et al. 1996). The model is available in both cylindrical and Cartesian coordinates and was developed by creating a convection cell around the injection well with a buoyant injection that formed a lens within the injection zone. In another study, a well injectivity decline (WID) simulator was developed for modeling the well performance during deep well injection (Saripalli et al. 2000). The simulator was employed to study the well performance by considering factors such as the waste quality and suspended materials, formation characteristics, completion type, injection rate, injection pressure, initial well or formation damage, and gravels surrounding the wellbore. Simulation results showed that well plugging and, consequently, poor injection performance is caused by high concentration of suspended solids in the waste, low injection rate, low injection pressure, formation heterogeneity, and low formation porosity and permeability.

Recently, a mathematical model with an analytical solution was presented to describe the contaminant plume movement at injection disposal site of liquid radioactive waste (Malkovsky et al. 2019). The model considered both topography-driven (regional) and buoyancy-induced components of the groundwater flow. The results from analytical solution were found to be in good agreement with the numerical solution.

Besides the models related to the well, the cost of deep well injection has been mathematically studied (Mogharabi and Ravindran 1992). In this study, a model for selecting the best disposal system design and operating policies was proposed based on linear goal programming techniques. The proposed method resolved the conflicting objectives such as cost, environmental regulations, equipment utilization, and waste quality requirements before injection and produced 40% savings by utilizing the design predicted by the model.

7.4 Underground Geologic Repositories

Emplacement of hazardous waste in deep underground geologic repositories or mines is considered to be one of the best disposal techniques. Historically, geologic repositories were employed for disposal and isolation of radioactive waste, such as reprocessing effluents and spent fuel-rod assemblies, in salt host rocks (Testa 1994). With advancements in the field, geologic repositories of alternative host rocks have been explored, and the use of geologic repositories has been extended to other types of hazardous and toxic wastes. Disposal in geologic repositories is an attractive option given the ever-increasing regulatory requirements and prohibitions placed on landfilling and deep well injection techniques. In general, disposal by emplacement of hazardous waste in geologic repositories offers the following advantages (Testa 1994; Kaliampakos et al. 2006):

- Complete isolation and protection of hazardous waste.
- Very low probability of hazardous waste leakage.
- Very low probability of leakage to the surface environment.
- Protection of hazardous waste from severe weather conditions and effects of earthquakes.
- Limited or no generation of wastewater/leachate.
- Easy segregation of hazardous waste which makes future inspections easier.
- Limited need for long-term and aftercare monitoring due to high level of protection provided by the geologic medium.
- Lower operating cost compared to landfills due to lower monitoring requirements.
- Low land and construction costs in the case abandoned underground mines are utilized.
- No concerns related to aesthetic and visual impacts of disposal.

7.4.1 Site Selection

As with landfilling and deep well injection, selection of an appropriate site is a critical part of disposal in underground geologic repositories. The type and characteristics of the host rock and the stability and hydrogeological characteristics of the site are among the key criteria that influence the decision on selecting the most suitable geologic repository for the disposal of hazardous waste (Testa 1994; Kaliampakos et al. 2006).

The host rock, into which the repository is excavated, is the main geologic barrier that isolates the hazardous waste from the biosphere. In general, the host rock should exhibit the following characteristics (Testa 1994; Pusch 2006a):

- Low permeability to ensure high isolation capacity.
- High thermal conductivity to maintain low temperatures.
- High strength and stability to endure the effects of geologic activities such uplift and seismic events.
- Absence of unfavorable geologic features such as discontinuities, faults, folds, and joints or other features allowing infiltration of groundwater.
- High degree of homogeneity (both vertical and lateral).
- Large lateral area to allow for excavation of the repository and provide adequate protection to the waste.

Potential host rocks for geologic repositories include crystalline, argillaceous, and salt rocks; basalts; volcanic tuffs; and anhydrites (Testa 1994; Pusch et al. 2018). Crystalline rocks are composed of tightly packed grains of minerals and are formed from solidification of magma of molten or partially molten rocks (igneous rocks) or from sedimentary rocks under high pressures and temperatures (metamorphic rocks) (Pusch et al. 2018; Ewing and Park 2021). Crystalline rocks such as granite and gneiss are composed of quartz (10–40 wt%), feldspars (10–75 wt%), and heavy minerals (5–20 wt%) (Pusch et al. 2018). In general, crystalline rocks possess excellent stability for underground repository construction but exhibit high permeability (Pusch 2006a).

Also, granite offers high chemical stability, low water content, and good sorptive capacity. However, the use of granite in repositories is challenging due to frequent presence or generation of faults and high excavation costs (Testa 1994). Argillaceous rocks, on the other hand, exhibit very low permeability but poor stability when compared to crystalline rocks (Pusch 2006a). Shales are well-known examples of argillaceous rocks. Besides their low porosity and permeability, shales possess a high sorptive capacity and an ability to seal fractures due to plastic flow. However, due to the inherent presence of water, shales may release water into the repository under thermal loads.

Salt rocks (salt domes) have been widely utilized for the disposal of radioactive wastes. These rocks are formed from salt deposits under high pressures and temperatures and are essentially homogeneous, free of discontinuities, impermeable, geologically and chemically stable, and typically possess a large lateral area.

However, the presence of brine in rock salts can corrode the waste containers. This is specially of concern in the case of radioactive wastes where the thermal field can cause migration of brine toward the waste canisters. Also, the solubility of rock salts in groundwater or other water sources, waste sinkage due to creep, and compatibility of salt with the hazardous waste may limit the utilization of rock salts as the preferable choice of host rock in geologic repositories (Testa 1994; Pusch 2006a).

Basalts possess intermediate thermal conductivity, high thermal load capacity, good sorptive capacity, high strength, and low permeability. However, basalts typically consist of zones of secondary permeability which may enhance their ability to allow infiltration of water. Volcanic tuffs (welded or zeolitic) can also serve as geologic barriers in geologic repositories. Welded tuffs, formed from volcanic ash, possess low porosity and permeability and high thermal load capacity and have strength and thermal conductivity values comparable to those for basalts. Zeolitic tuffs contain zeolites and exhibit high sorption capacity due to their open structure. The open structure, however, imparts them with high porosity and permeability and moderate strength. Anhydrite deposits, composed of anhydrous calcium sulfate, are homogenous and impermeable and possess high thermal conductivity and chemical stability, making them suitable for geologic repositories. However, interactions with water can convert anhydrites to gypsum which can induce changes in porosity and permeability (Testa 1994).

The stability of the repository structure is an important consideration during site selection. High structural stability is critical to ensure safe and long-term disposal of hazardous waste. The suitability of the site is also dictated by its hydrogeologic characteristics. The presence of artificial penetrations and their depths and locations at the proposed site should be identified. Visual inspections and geophysical methods can be employed for this purpose. In addition, laboratory analysis should be carried out to study the mineral content and its composition, heterogeneity of the host rock, and the presence of fluids and their characteristics. In general, the environment in the geologic repository should be dry with little or no groundwater. Also, the geo-mechanical properties of the host rock such as density, porosity, permeability, water content, plasticity, strength, compressibility, and swelling potential should be determined via laboratory analyses. Any structural discontinuities, faults, and tectonic activities should also be identified using, for example, field mapping (Testa 1994).

Besides the aforementioned factors, it is important that the proposed site is located away from ore deposits and oil and gas fields and areas of high population density. In the case the proposed site is an abandoned mine, the remaining exploitable ore and its current and future economic significance should be considered before converting the mine into geologic repository for hazardous waste disposal.

Selection of sites for geologic repositories has been explored in some recent research studies. To avoid local and regional opposition, the importance of public participation in site selection processes of nuclear waste repositories has been highlighted (Krütli et al. 2010). In this study, a functional dynamic view of public participation was proposed that combined the decision-making process with specific types and extents of public participation. Different levels of public participation were considered (information, consultation, collaboration, and empowerment) and were combined with the decision-making process in a temporal and phased framework.

In a very recent study, a new approach to site selection was proposed that utilized GIS technology (Perković et al. 2020). The proposed approach utilized site exclusion and comparison criteria. Exclusion criteria included flooding safety, seismotectonics and seismology, lithological and geomorphological characteristics, hydrogeology, population density, protection of natural and cultural heritage, mining and mineral exploitation, and protected areas. Comparison criteria, on the other hand, included technical aspects, installation safety, and location acceptance. Using the selection criteria and merge layers and symmetrical difference layers in GIS technology, a map of potential sites was finally created.

7.4.2 Repository Design

The geologic repository should be designed with sufficient capacity to accommodate the expected volume of hazardous waste to be disposed. The design should also consider the repository life span which depends on the characteristics of the hazardous waste to be disposed. For certain wastes, the hazard will decrease with time (e.g., radioactive wastes), while other wastes may require a much longer repository life span (e.g., wastes with indefinite toxicity). In general, the geologic repository should be designed to isolate the disposed waste over a long period of time (Testa 1994). The design and dimensions of drifts (horizontal or nearly horizontal openings or tunnels within the repository) and rooms are also important considerations. The geometry and dimensions of drifts and rooms should provide adequate clearance to accommodate and move the waste and the equipment. Typically, horseshoe- or rectangular-shaped drifts and rooms are utilized (Pusch 2006a).

Three types of geologic repositories can be used for hazardous waste disposal, namely, existing mines, salt caverns, and new mines. Existing mines that have been abandoned after extraction of the exploitable ores can be utilized for hazardous waste disposal. These mines are usually mined using the conventional room-and-pillar method (Testa 1994). Abandoned mines require careful examination before hazardous waste disposal since stabilization may be required depending on the presence of unstable rocks and internal stresses due to tectonics and glaciation (Pusch 2006a). Several inactive underground mines have been reused as waste repositories in Europe. A comprehensive list of these mines can be found elsewhere (Kaliampakos et al. 2006).

Salt caverns, on the other hand, are cavities in salt formations that are developed by drilling and cementing concentric casings into the salt formation. An uncased hole is also drilled to expose the salt formation to leaching. Water introduced via the annulus dissolves the salt which, in the form of brine, returns to the surface via the outing casing. Waste is disposed into the caverns via solution mining which can be achieved using one of the several possible methods. For example, brine-balanced method can be used for the disposal of liquid and slurry wastes. Once injected into the cavern, the brine is displaced and forced up the casing for collection. It is important that the specific gravity of the liquid or slurry waste is higher or lower than the brine so that the waste remains at the bottom or top of the cavern, respectively. If the specific gravity of the waste is close to that of the brine, cross-contamination of brine limits the applicability of the brine-balanced method. To avoid cross-contamination of brine, the gas-balanced method can be utilized where the brine is displaced using an inert gas at high pressure. The cavern is sealed at the minimum design pressure after which the gaseous, liquid, or slurry waste is injected until the design pressure is reached. However, in this case, the size of the cavern should be limited to maintain structural integrity.

In situ disposal of solidified waste is another option where the waste is mixed with a cement of polymer slurry prior to injection into the cavern. The size of the cavern is also limited in this method to ensure the structural stability. In addition, string-of-pearls method can be utilized. In this method, a series of stacked caverns are constructed. Brine is removed from the deeper cavern and filled with the waste. The top portion of the cavern is then sealed with a cement plug after which the waste can be directed to the upper cavern. Again, to maintain structural integrity, the size of the cavern is limited in this method (Testa 1994). Besides existing mines and salt caverns, new mines can be constructed given that the selected site meets the selection criteria discussed earlier.

Depending on the nature of waste to be disposed, geologic (mine) repositories may require engineered (man-made) barrier systems which supplement the natural barrier provided by the host rock for effective isolation and containment of the waste. For instance, disposal of radioactive waste typically requires the use of a multi-barrier system. Waste containers/canisters, placed inside the repository, can be considered as part of the engineered barrier system. However, to ensure effective isolation of the waste from the biosphere, more sophisticated engineered barrier systems are required. These barrier systems around the waste are typically constructed using clay and cement/concrete (Pusch 2006b). In the case of clay barriers, bentonite and bentonite/sand mixtures are typically used due to their inherently low permeability in saturated state and self-healing ability (Sellin and Leupin 2013).

Recent advances related to disposal in geologic repositories are related to the design, use, and performance evaluation of the engineering barrier systems in radioactive waste repositories. The physicochemical properties of bentonite barriers are susceptible to changes due to factors such as humidity, temperature variations, and fluid interactions. A model to describe long-term diffusion reaction in bentonite barrier for radioactive waste confinement is available (Montes-H et al. 2005). This model utilized thermokinetic hydrochemical code (KIRMAT: kinetic reactions and mass transport) to simulate the chemical transformations due to geochemical and cation exchange reactions, the diffusion of chemical species into the barrier, and the changes in the swelling capacity. Results indicated that the bentonite barrier was significantly affected after 10,000 years due to contact with geologic fluid. Also, the results highlighted that the swelling capacity declined significantly within the geological barrier-engineered barrier interface. In another study, KIRMAT was used to study the changes in the bentonite barrier due to the geologic fluid and Fe^{+2} ions from the radioactive waste canisters (Marty et al. 2010). The results again highlighted significant changes in the bentonite barrier due to interactions with the natural barrier. Also, feedback effect of corrosion products resulted in slow diffusion of Fe^{+2} through the bentonite barrier and reduced the corrosion rate from 5 to 0.2 μm/year. The presence of bacterial communities in bentonite barrier layers has been established (Lopez-Fernandez et al. 2015), and the effects sulfide-producing bacteria on the barrier performance has been studied (Pedersen et al. 2017). It was found that bentonite clays immobilized the corrosive sulfide from sulfide-producing bacteria and the rate of sulfide diffusion depended on the bentonite density. The immobilization of sulfide reduced the transport of sulfide toward the metal canisters, thereby, reducing the corrosion susceptibility. However, the sulfide also reduced ferric iron in contact with the bentonite clay to ferrous iron. This was found to cause destabilizing effects of ferrous iron on the dioctahedral clay smectites. Also, additives for bentonite barriers have been proposed. It has been shown that addition of activated carbon in bentonite barrier helps in sorbing technetium radionuclide (Makarov et al. 2021). The performance of cement/concrete barriers has also been explored using modeling studies. In one study, the geochemical interactions between concrete barrier and mudrock were investigated using the reactive transport code Hytec, and it was shown that sulfate can strongly alter concrete engineered barrier based on pure Portland-based cement (Trotignon et al. 2007). In another study, the reactive chemical transport model of HYDROGEOCHEM 5.0 was utilized to show that hydrogen ion, sulfate, and chloride can significantly degrade the concrete barrier in radioactive waste repositories (Lin et al. 2016).

7.5 Ocean Disposal

Although technically feasible, offshore disposal of hazardous waste in oceans is highly constrained by regulatory requirements. Theoretically, ocean disposal can be in the form of ocean incineration or ocean dumping. Compared to land-based incineration facilities, ocean incineration on ships is of lesser concern to the public due to its operation far from the coast. Also, gas cleaning facilities are typically not required since hydrogen chloride can be effectively diluted in the seawater (Batstone et al. 1989c). Ocean incineration is regulated under the “Convention on the Prevention of Marine Pollution by Dumping of Wastes and Other Matter” of 1972, also known as the London Convention. As per this global convention, which has 87 Contracting Parties as of January 2021 (U.S. EPA 2021), ocean incineration of sewage sludge and industrial waste is completely prohibited.

Ocean dumping, on the other hand, is based on the principle of dilution and dispersion of waste that is dumped directly into the ocean. In this disposal technique, it is assumed that, once discharged into the ocean, the waste is immediately diluted to very low concentrations such that its environmental impacts become negligible. To avoid environmental impacts, the use of ocean dumping should be limited to the disposal of wastes that can be naturally degraded, neutralized, or transformed by the chemical and biological process occurring within the ocean. Ocean dumping can be carried out in shallow or deep sea. Shallow-sea dumping has low transportation cost and localizes the adverse impacts of the disposal. Deep-sea dumping, on the other hand, allows for higher degree of dilution and dispersion (Visvanathan 1996). However, similar to ocean incineration, ocean dumping of industrial waste and sewage sludge has been prohibited under the London Convention. In the USA, under the Marine Protection, Research, and Sanctuary Act of 1972 (MPRSA, which implements the requirements of the London Convention) and its 1988 amendment, the Ocean Dumping Ban Act (ODBA), it is unlawful to carry out ocean dumping for wastes such as high-level radioactive wastes, sewage sludge, medical wastes, industrial wastes, known carcinogens, mutagens, or teratogens and certain heavy metals (U.S. EPA 2020). Due to the stringent requirements and prohibitions placed on offshore hazardous waste disposal, recent advances in this area have not been witnessed.

7.6 Summary

Landfills, injection wells, and underground geologic repositories can be used for the safe disposal of hazardous waste. However, selection of suitable site and proper design is of critical importance to ensure the effectiveness of these disposal methods and guarantee long-term isolation of the hazardous waste. Recent research studies have made significant efforts in providing the necessary guidelines and methodologies for the selection of suitable site and improving the design of landfills, injection wells, and underground geologic repositories. In the case of ocean disposal, its use for hazardous waste disposal is highly constrained due to imposed prohibitions.

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Chapter 8
Waste-to-Energy Technologies

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8.1 Introduction

With an exponential growth in the human population comes the challenges of meeting the demands in terms of food and agriculture, water, electricity, and other basic needs. In order to meet the drastic rise in demand for products and services, the industrial revolution had emerged; as a result, the first steam engine was invented. The initial steam turbines were quite basic, in which they operated on coal and other nonrenewable energy sources. Following the boom of the first industrial revolution came the second and third industrial revolutions that managed to bring in and create a variety of man-made products and goods ranging from manufactured food products to vehicles (Industrial Revolution 2019). With all the advantages that were brought in with these industrial revolutions, little was known about the importance of waste management in terms of packaging wastes, reusing valuable by-products, recycling and recovering wastes, and conserving energy means. The majority of the generated wastes is grouped under the title of Municipal Solid Wastes (MSW) which include food wastes, disposed packaging containers, glass, plastics, metals, rubber, textiles, wood, etc. (Funk et al. 2020).

With the evolution of technology and inventions, environmental awareness began to emerge and eventually started gaining the public interest. Its importance was recognized almost nearly after the publication of *Silent Spring* in 1962, by Rachael Carson (Geary 2018), which mainly discussed the impacts of pesticides on agricultural crops. Hence it managed to raise the environmental awareness among the public on different levels. Consequently, a more conservative approach was adopted by company owners and investors toward the fields of green or renewable energy, waste management, material recovery, and sustainability. Thus, waste

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management methods such as recycling, recovery of materials, means of waste size reduction, and storage became legal requirements among different developed countries. Though the waste management methods brought in added value in terms of resource sustainability and preservation, they were energy consuming and undergoing challenges of meeting the continuous rise of waste generation. Furthermore, the landfills are predicted to face shortages in handling these wastes, and the demand for energy for waste management is consequently rising. This chapter discusses modern solutions not only to get rid of the generated wastes but also to convert them into energy. In this chapter, the main waste-to-energy (WtE) technologies are discussed along with the air emissions resulting from WtE plants.

8.2 Waste-to-Energy (WtE) Technologies

There are five main WtE processes: incineration, gasification, pyrolysis, anaerobic digestion, and torrefaction (or carbonization) (Gumisiriza et al. 2017; Badgett and Milbrandt 2020). WtE processes rely on energy supply to decompose the waste at elevated temperatures, into gas and/or char and/or oil, which are then converted to electrical energy and useful products (Leng et al. 2021). The general steps include waste pretreatment, thermal waste breakdown and decomposition, waste conversion and product formation, and energy conversion (Su et al. 2021). The major differences between the five processes would be the amount of oxygen fed into each of them. Incineration relies on complete oxygen feed, whereas gasification relies on partial oxidation feed, and pyrolysis, torrefaction, and anaerobic digestion processes rely on limited or no oxygen feed (Leng et al. 2021; Badgett and Milbrandt 2020).

The wastes initially undergo a form of size reduction, in several steps including shredding, screening, compaction, dehydration, and/or pelletization. The waste that undergoes these steps is called the refuse-derived fuel or “RDF.” These steps facilitate the handling of the waste, minimize the storage requirements prior to thermal decomposition, and enhance the efficiency of the energy generation. In addition, the utilization of RDF as a process feed also helps in achieving a higher calorific value of the feed, as well as a more homogeneous feed, with a consistent composition (Giugliano and Ranzi 2016). Regardless of the technique used in converting the waste into energy, the waste must be handled manually and by the help of a belt conveyor, as an initial step to transport it to the reaction chamber (Purnomo et al. 2021).

8.2.1 Incineration

Incineration process is considered the earliest waste-to-energy technology. When compared to other WtE processes, it is known to deal with a wider range of wastes including medical wastes, polyvinyl chloride plastics (PVC), discarded equipment/

sharps, etc. (Messerle et al. 2018). However, incineration produces more pollutants when compared with the other WtE technologies. The heat of combustion is expected to vary based on the constituents of the wastes fed into the incineration chamber.

There are certain criteria for verifying the eligibility of wastes to undergo incineration, and these include a minimum resultant heating value of 8370 kJ/kg, less than 20% fraction of noncombustible left out particulates, less than 5% fraction of noncombustible material, at least 60% fraction of combustible material, a moisture content of 30%, etc. (Shareefdeen et al. 2019). Incineration is a thermal decomposition process that relies on full oxygen supply, and it requires an operating temperature ranging from 750 to 1200 °C. It produces fly ash, flue gases, and particulate matters (PM) (Beyene et al. 2018; Leng et al. 2021; PEPFAR 2010). The resultant polluted flue gas produced due to combustion consists of several pollutants that are required to undergo treatment in a series of air pollution control (APC) units. There are eight common types of incineration chambers which include simple incinerators, rotary kiln incinerators, fixed grate incinerators, fluidized bed incinerators, multiple hearth incinerators, catalytic combustion incinerators, moving grate incinerators, and liquid injection incinerators.

Simple Incinerators

Simple incinerators are the oldest types of incineration chambers that operate in a batch process at a temperature of 1000 °C or more (Harvey et al. 2002). They are brick-lined and have a metal grate, or fire bars at which the combustion process takes place, along with a clinker which is an ashtray to collect the incombustible residues (Speight 2020). The most common design comes with two openings from the top and sides, in order to input the feed and to remove the combustion residues (ash), respectively (Speight 2020; Harvey et al. 2002). Additionally, they consist of a chimney to exhaust the resultant flue gas, a solid concrete top, and a base to prevent the particulates and resultant gas from escaping into the ground or soil. It has a base size of approximately 1 m × 0.5 m and a capacity of 100 Kg/hr. of feed wastes (Harvey et al. 2002). Its main disadvantage is that it functions in a batch operation, and it is difficult to regulate and maintain the operating temperature within the incinerator (Speight 2020; Harvey et al. 2002).

Rotary Kiln Incinerators

A rotary kiln incinerator has a rotating cylindrical steel tube which is heated in order to burn the waste feed while constantly rotating to ensure that the waste is mixed and supplied with oxygen (Al-Salem 2019). It consists of an arm or roller to insert the feed from the top of the kiln, known as the incineration chamber. The end of the kiln consists of a tall stack in order for the resultant combustion flue gas to exit the incinerator after APC units (Al-Salem 2019).

The rotating cylindrical steel tube comprises of steel shells placed on rollers that rotate horizontally on an incline, usually 5° incline above ground level, and this is referred to as the rake. This is done in order to increase the mixing rate in parallel with the cylinder's rotation (El-Haggar 2007). The parameters can be altered to either increase or decrease the residence time within the combustion chamber, based on the nature of the feed. The waste rotates along the axis of the tube while the combustion is taking place. The rotary kiln incinerators may also consist of one or two chambers, depending on the design (Al-Salem 2019; Rathna et al. 2018). The one with two chambers consists of a primary and a secondary chamber, in which the primary one is the cylindrical rotary section, which is used for combustion of the solid or liquid feed into gas, and the secondary one ensures further combustion of the remains which includes both particulates and gases (Rathna et al. 2018; El-Haggar 2007). The primary chamber is supported with baffles, in order to ensure the mixing of the feed and to increase its turbulence and reaction with oxygen (Al-Salem 2019). Rotary kiln incinerators can handle a wider range of feed including solids, sludge, and liquid waste feed and operate at a temperature range of 800–1650 °C (Rathna et al. 2018; Al-Salem 2019). The resultant ash is usually collected at the bottom. They can be operated either as a batch, semi-batch, or continuous modes. The capacity is about 0.1–20 tonnes of waste/hr., with an efficiency of 80% (Al-Salem 2019).

Fluidized Bed Incinerators

Similar to rotary kiln incinerators, fluidized bed incinerators are also commonly used in incineration plants, and they function at temperatures ranging from 800 to 900 °C (Van Caneghem et al. 2012). Their combustion efficiency reaches up to 90% (Al-Salem 2019). Within the incinerator, a packed bed media is subject to heat at the required operating temperatures. Usually, sand is used as a packing medium within fluidized bed incinerators. In order for combustion to take place, air (or any other inert gas) is pumped from the bottom of the bed in between the packing media, all the way to the top. This ensures the required turbulence and combustion reaction within the incinerator (Van Caneghem et al. 2012). The waste is usually fed at the top of the packing media where it remains in contact with the heated packing media along with the air/oxygen supply (Van Caneghem et al. 2012). Depending on the design of the fluidized bed, air can either be supplied as primary air, secondary air, or tertiary air. The air can either be pumped from the bottom, from the bottom and top of the packing media, etc. (Moharir et al. 2019). There are three common types of fluidized bed incinerators/combustors: bubbling fluidized bed combustors (BFBC), circulating fluidized bed combustors (CFBC), and rotating fluidized bed combustors (RFBC) (Van Caneghem et al. 2012; Moharir et al. 2019).

The BFBC is the most commonly used one, in which it is designed with a cyclone attachment in order to increase the combustion efficiency by carrying over the un-combusted particulates (Van Caneghem et al. 2012; Moharir et al. 2019). The chamber consists of packing media, which are set to a fluidization state by the help of the distributors, located at the bottom of the chamber. The distributors usually pump air, or any other preferred gas, evenly between the packing media in an upward direction in order to bring the inert packing media into a fluidized state (Van Caneghem et al. 2012; Moharir et al. 2019). The distributors provide air at a speed of 0.5–3 m/s in order to ensure the fluidization effect (Van Caneghem et al. 2012). Usually, a BFBC works with both primary and secondary air supply (Moharir et al. 2019). A disadvantage of using this technology is that the waste feed has to be converted into RDF at a maximum particle size of 10 mm diameter (Moharir et al. 2019). BFBC can handle limited variations of waste feed including wastewater sludge, plastic waste, coal, and biosolids (Van Caneghem et al. 2012).

RFBC functions in a similar manner to BFBC; however, the air supply should be distributed unevenly, which creates two zones within the bed: one of strong aeration and the other is of low aeration. The strong aeration zone forces the packed bed materials to move upward, and the low aeration zone induces a downward movement of the packing media. This process enhances the mixing between the feed and the packing media and encourages the utilization of a more variant waste feed mixture. The maximum recommended particulate size of the waste feed is less than 30 mm (Van Caneghem et al. 2012; Moharir et al. 2019).

CFBC has a primary or a secondary cyclone attachment depending on the design (Van Caneghem et al. 2012). Unlike RFBC and BFBC, CFBC operates at higher velocities of air/gas supply. The distributor pumps the air/gas at a speed of 3–9 m/s (Van Caneghem et al. 2012). In a CFBC, both the packing media and the waste feed are pumped separately into the chamber. The combustion reaction occurs vertically upward. The chamber is designed to have at least one cyclone; thus a recycling effect is established as the carried over particulates are brought back to the bottom of the fluidized bed (Van Caneghem et al. 2012). Additionally, the cyclone ensures the separation of the sand/packing media from the flue gas as it rises (Moharir et al. 2019). The recycle step helps to save up on the cost of supplying fresh sand/packing media. The resultant ashes of smaller particles get carried away along with the flue gas as a result of the process (Van Caneghem et al. 2012). Studies have shown that the efficiency of a CFBC is higher compared to other fluidized bed incinerators and can reach up to 99.99% in a 2-s residence time (Van Caneghem et al. 2012). Additionally, due to the nature of the CFBC, limestone can also be fed within the fluidized bed, along with the waste feed and packing media, which results in saving up on the capital and operational costs of an acid gas scrubber (Li et al. 2014).

Multiple Hearth Incinerators

Multiple hearth combustors/incinerators (MHCs/MHIs) work on burning the waste feed, which is fed from the top of the chamber all the way to the bottom, by the effect of gravity. They operate at a temperature ranging from 300 to 980 °C. MHIs can handle various types of waste feed including sludge, hazardous liquids, hazardous gases, and solids, where the solids and sludge can be fed from the top and hazardous liquids and gases can be pumped from the side of the MHC. An MHI is shaped as a vertical stack with multiple chambers (usually two chambers) that are leveled (Letcher and Vallero 2019; Dentel and Qi 2014). The levels are divided into three zones, and each zone is subject to a different heating pattern. The top section is subjected to moderate temperatures, followed by the highest temperatures at the middle section and lowest temperatures at the lower section. Solids and thick sludge are fed from the top of the chamber, which operates at high temperatures, approximately 550 °C. This causes reduction in the feed size and overall moisture content, allowing the feed to move forward to the next hearth and so forth (Dentel and Qi 2014). As the feed reaches the middle section, it is subject to higher temperatures reaching approximately 900–1000 °C, due to the fact that additional liquid and gas wastes can be fed into the chamber through nozzles from the side (Dentel and Qi 2014; Letcher and Vallero 2019). As the feed reaches to the lower section of the MHC, the incineration process of all the wastes is usually completed. The lower section operates at temperatures reaching up to 350 °C (Dentel and Qi 2014) which brings the ash to cooler temperatures before it collects at the bottom. The flue gas is passed through APC units for the removal of air pollutants (Letcher and Vallero 2019).

Fixed Grate and Moving Grate Incinerators

Fixed grate and moving grate incinerators are similar in terms of process but differ slightly in design; hence their efficiencies differ (Yan et al. 2021). Moving grate incinerators are proven to have higher efficiencies as they ensure more mixing (Blijderveen 2011). Both fixed and moving grate incinerators are widely used in the industry due to their ability to handle raw waste feed without having the wastes to be converted to RDF (Kabugo et al. 2020). They work with breaking down various wastes; however they are distinctively used with MSW (Yan et al. 2021). Both fixed and moving grate incinerators have incineration chambers that are composed of grates. Both incinerators are either designed horizontally or diagonally on an incline, where they are subject to temperatures higher than 950 °C (Moving Grate 2021; Blijderveen 2011).

There are three types of grates: rolling grates, forward-acting grates, and reverse-acting grates. Forward-acting grates move in the same direction as the feed, whereas reverse-acting grates move in the opposite direction. Waste feed can either enter the unit from the side or from the top. If the grates are shaped horizontally within the combustion chamber, the feed is usually fed from the sides to allow the grates to carry them. Otherwise, the waste feed enters from the top through a throat-shaped stack that allows it to fall into the heated grates for the combustion to occur (Yan et al. 2021). In a grate incinerator, the grates are heated from the bottom of the unit, and the air is pumped either within the grates or in between them depending on their design (Blijderveen 2011). Primary air is passed between the rollers or grates or within special openings embedded in their design. Secondary air is pumped on top of the feed that is being transported, in order to ensure the presence of sufficient oxygen (Speight 2020; Blijderveen 2011). The flue gas that exits the chamber is passed through APC units and turbine, which are responsible for treating the pollutants and generating electricity, respectively.

Liquid Injection Incinerators

Liquid injection incinerators are cylindrical incineration chambers and are less preferable due to the fact that they are used to incinerate only liquid wastes, slurries or sludge (US EPA 1998). In order for the combustion to take place, air is pumped using a fan, and the heat is supplied using a flame (Vallero 2014; US EPA 1998). The liquid injection incinerator can utilize additional fuel/natural gas as a supplementary heating source in order to enhance the ignition (US EPA 1998). The operating temperatures range from 650 to 1650 °C, and the residence time ranges from 0.5 to 2 s (Vallero 2014; US EPA 1998). The design of the liquid injection incinerator can either be vertical or horizontal, and the capacity can reach up to 1500 gallons/h of liquid feed (US EPA 1998).

Catalytic Combustion Incinerators

Catalytic combustion incinerators utilize catalysts that speed up the combustion reactions taking place within the combustion chamber, by lowering the activation energy, hence bringing the reactions to completion in a shorter time (US Energy Department 2021). An advantage of catalytic combustors over the other combustors is that they release less NOx content due to lower operating temperatures which favor the production of less NO, NO_2, N_2O, and CO (US Energy Department 2021; Razak 2007). The catalyst provides more control over the oxidation reaction, hence favoring more complete combustion reactions (Matthey 1984; US Energy Department 2021; DieselNet 2021).

The most common metal catalysts used include either platinum group metal catalysts, platinum metal itself, or palladium metal (Matthey 1984; DieselNet 2021). An important factor that is accounted for when choosing catalysts is the catalyst support system which is referred to as the washcoat (Paul Day 1998). The washcoat system is a refractory oxide porous layer that holds the catalyst in place, and it provides the catalyst with a large surface area for the reaction to take place effectively with high conversion of NO_x into N_2 and CO into CO_2 (DieselNet 2021; Paul Day 1998; Razak 2007). The washcoat allows for the dispersion of the catalyst, in addition to physical segregation of the reactants, thus leading to the formation of more desirable reactions (Razak 2007; DieselNet 2021). Thermal stability is a major factor that determines the efficiency of a washcoat substance, in which the substance is exposed to extreme heat, and it demonstrates the ability to stay rigid without decomposing for the long time period (DieselNet 2021). Washcoat material consists of inorganic metal oxides, and some of the most commonly used ones include Al_2O_3 (alumina or aluminum oxide), TiO_2, SiO_2, zeolites, etc. (DieselNet 2021).

The catalysts can either be fed into the incinerator or they can be embedded within the washcoat material prior to the combustion process. The process that requires the catalyst to be fed into the reactor is called impregnation process, and it occurs with the help of an aqueous (water-based) solution containing the catalytic precursors, which decompose to form the final form of the catalyst (DieselNet 2021). The catalytic combustors consist of a combustion chamber which is sectioned into the following: a mixing region, the catalytic region, and the dilution region (Matthey 1984; Andrews 2013; Razak 2007). The operating temperatures are determined by the type of catalyst used. Different catalysts operate at different temperatures ranging from 426.85 to 1650 °C (Andrews 2013; Matthey 1984).

8.2.2 *Gasification*

Gasification process is a thermochemical process that converts carbonaceous wastes into synthetic gases, bottom ash, fly ash, and vitrified slag (Shareefdeen et al. 2015; Min-Jun Choi et al. 2021; Dong et al. 2018; Seo et al. 2018). It is a process that has both endothermic and exothermic reactions taking place within the gasifier resulting in syngas production between 75% and 88% of the original feed, mainly due to the generation of hydrogen gas (Seo et al. 2018).

There are two main types of gasification processes: direct and indirect gasification. The main difference between them is the gasifying agent utilized (Seo et al. 2018). A gasification process that relies on the supply of oxygen or air is referred to as a direct gasification process, whereas a gasification process that relies on other inert gases is referred to as indirect gasification. Direct gasification relies on oxidation reactions that originate from the supply of oxygen; however the oxygen/or air is fed partially (Seo et al. 2018; Shareefdeen et al. 2019). The low-temperature gasification occurs at temperatures ranging from 700 to 1000 °C at which the majority of the gaseous components are formed. High-temperature gasification occurs at 1200–1600 °C, and at this temperature range, significant amount of CO and H_2 (referred to as syngas) are formed (Shareefdeen et al. 2019). The produced flue gas or synthetic gas is used to produce heat and electricity. Gasification is usually accompanied by rapid quenching of the syngas, which is the process of cooling down a gas to condense the condensable components, leaving the non-condensable ones in the vapor form (Seo et al. 2018; Stals et al. 2010; Piemonte et al. 2016; Al-Haj Ibrahim 2020). Quenching results in decreasing the NO_x as well as dioxin contents that normally result from the thermal decomposition of the carbonaceous wastes (Seo et al. 2018).

The most commonly used gasifying agents include steam, supercritical water and CO_2 for indirect gasification, and air for direct gasification, respectively (Seo et al. 2018; Purnomo et al. 2021; Jangsawang et al. 2015; Zhang et al. 2019). The direct gasification generates CO, CO_2, H_2O, and H_2 gases. The indirect gasification (i.e., usage of steam to decompose the waste feed) mainly results in the production of high concentrations of H_2 gas, as well as CO and CO_2. Furthermore, the reaction with H_2 generates CH_4 and H_2O gases (Seo et al. 2018). One of the main disadvantages of using the indirect gasification is that nitrogen content can affect the quality of the produced syngas. However, the utilization of steam results in high amount of hydrogen gas, and this eventually leads to saving up on energy costs. Additionally, indirect gasification is considered less costly in terms of gasifying agent supply, as steam is readily available compared to pure oxygen (Seo et al. 2018).

The main factors that affect the efficiency of the gasification process include the reaction temperature, gasifying agent, residence time, oxygen level (lower than that of combustion), moisture content, the type of gasifier, and the equivalence ratio (ER), i.e., the ratio of the actual flow rate of the air-flue gas (during gasification) to the stoichiometric flow rate of the air-flue gas ratio (during complete combustion). ER is used in determining the resultant syngas quality and composition, tar content, and gas yield and energy output (Rai et al. 2020; Shareefdeen et al. 2019; Salaudeen et al. 2019; Kuo et al. 2020). The higher the ER, the more complete the oxidation reactions are; hence the cracking of char and hydrocarbons is assumed to be much higher with a higher yield of tar content, and the concentration of CO is predicted to be lower due to sufficient amount of oxygen supplied. This in turn results in a lower syngas quality and value (Salaudeen et al. 2019; Kuo et al. 2020).

When compared to incineration, the gasification process is considered more environmentally friendly (Seo et al. 2018). Less air pollutants such as dioxins, furans, etc. are emitted as a result of the partial oxidation process. The produced synthetic gas consists of carbon dioxide, methane, water vapor, hydrogen gas, nitrogen gas, carbon monoxide, hydrocarbons (i.e., methane), inert gases, trace amounts of hydrogen sulfide, contaminants (including tar), and ammonia (Zhang et al. 2019). Gasification does not only result in the thermal degradation of wastes and their size reduction, but it also results in the production of valuable chemicals that can be used in various manufacturing goods including adhesives, bioethanol, methanol, fatty acids, plasticizers, ethylene, and surfactants (Zhang et al. 2019; Shareefdeen et al. 2015). The disadvantages of the gasification process include higher operational cost, higher solid residue and tar cleaning costs, and interruptions to the operation of the unit (Shareefdeen et al. 2019). The gasification process does not treat all types of waste unlike the incineration process. For example, polyvinyl chloride plastics (PVC) waste is not an ideal feed for this process. There are five main types of gasifiers: fluidized bed gasifier, plasma gasifier, fixed bed gasifiers (or moving bed gasifiers), rotary hearth gasifiers, and entrained flow gasifiers.

Fluidized Bed Gasifier

Fluidized bed gasifiers are gasifiers that function with the help of packing bed material and a gasifying agent in order to thermally decompose the feed which is usually fed from the top (Zhu and Frey 2010). The packing materials are supported by a distributor plate which allows the gasifying agent to flow upward and pass through its pores (Zhu and Frey 2010). Within the reactor, there are two different zones: the dense zone and the freeboard zone (Dutta and Acharya 2011). The dense zone is where the thermal degradation occurs. In order for the feed to decompose, the gasifying agent is passed through the packing material all the way to the top until it reaches the feed, thus setting the feed into a fluidized state (Hofbauer and Materazzi 2019). The freeboard zone is located along the upper part of the unit where hydrocarbons and VOCs (volatile organic compounds) in the produced syngas are thermally decomposed (Speight 2015).

When considering the design, there are two main criteria that should be taken into account: minimum fluidization velocity and “bed agglomeration and sintering prevention” (Hofbauer and Materazzi 2019). The minimum fluidization velocity is the minimum velocity that should be exceeded in order to fluidize the particles, and it occurs when the upward drag force of the gasifying agent’s particles is equivalent to the downward gravitational force of the feed particles (Zhu and Frey 2010; Pang 2016; Hofbauer and Materazzi 2019). This induces high turbulence and mixing and provides high heat and mass transfer between the solid and gasifying agent (Speight 2015; Hofbauer and Materazzi 2019; Zhu and Frey 2010). Agglomeration and sintering prevention is the second main factor. It occurs as a result of achieving low ash melting points. The ash particles would melt to form a slag as it gets in contact with the heated gasifying agent causing the slag to stick on the packing bed material (Dassisti and Brunetti 2020). Furthermore, the slag starts forming aggregates as it spreads around and increases in size (Miller 2016; Dassisti and Brunetti 2020). Not only does achieving a low melting point for the ash particles result in agglomeration and sintering, but also it can result in erosion, deposition, and corrosion (Arvelakis et al. 2002). This is due to the fact that the slag has a liquid nature that gets to spread at a faster rate than the solid form of dry ash, and it constitutes of acidic or alkaline substances (Richardson et al. 2015; Arvelakis et al. 2002). Hence, preventing this effect can significantly enhance the performance of the gasifier. The packing bed material can either be of inert type such as silica sand, olivine, and dolomite, or it can be of a catalytic nature including CaO (Speight 2015; Niaounakis and Halvadakis 2006; Pang 2016).

Fluidized bed gasifiers usually operate at high temperatures, ranging between 800 and 1200 °C; hence, they result in significant cracking of the char and tar (Zhang et al. 2019; Wei et al. 2020). This in turn results in negligible tar content (Wei et al. 2020). Additionally, fluidized bed gasifiers result in high carbon conversion efficiency reaching up to 70% and are mainly used to generate methane and other hydrocarbons (Wei et al. 2020). Fluidized bed gasifiers usually support medium capacity feed, and they maintain uniform temperature distributions within the unit (Zhang et al. 2019).

The main advantage of using a fluidized bed gasifier is that the unit provides the feed with sufficient contact time with the gasifying agent. This results in a high heat and mass transfer establishment and generation of low particulate matters (Zhu and Frey 2010; Zhang et al. 2019). The main disadvantage of using a fluidized bed gasifier is that some ash particles, depending on the operating conditions, turn into slag and cause sintering and agglomeration, as discussed previously (Miller 2016; Dassisti and Brunetti 2020). According to a biomass gasification study conducted by Richardson et al. (2015), the constituents of syngas have been observed to consist of metal oxides, acids, and bases including HCl, H_2S, and alkali substances.

Variations in the Fluidized Bed Gasifiers

Fluidized bed gasifiers are further divided into three main types: bubbling fluidized bed (BFB), circulatory fluidized bed (CFB), and double (dual) circulated fluidized bed (DFB) gasifiers (Zhang et al. 2019; Richardson et al. 2015). The main difference between BFB and CFB gasifiers is the fluidization velocity of the gasifying agent. In a BFB gasifier, the velocity of the gasifying agent is slightly above the minimum fluidization velocity, and it only causes the packing material to bubble in place, as the gasification agent makes its way to the top of the unit. The CFB gasifier operates at much higher fluidization velocity (Bermudez and Fidalgo 2016; Hossain and Charpentier 2015).

The CFB gasifier is designed to have a low efficiency separator (cyclone) attached to it, which acts as a recycle stream for the large suspended particles, more specifically the tar particles (Hossain and Charpentier 2015). The tar particles are then recycled back to the gasifier for further decomposition. A CFB gasifier is more suitable for large capacity operations, when compared to the BFB due to the fact that it utilizes all of the freeboard area within the gasifier (Grace and Lim 2013). The BFB gasifier is the older version of the CFB gasifier, and it results in a lower carbon conversion efficiency (Bermudez and Fidalgo 2016). CFB is known to result in a higher efficiency (Hossain and Charpentier 2015). The carbon conversion efficiency of a CFB is reported as 90–99% (Doherty et al. 2009).

A BFB gasifier is known to generate low to medium tar content (Bermudez and Fidalgo 2016). There are two main stages within a BFB gasifier: bubbling stage and emulsion stage (Pereira and Martins 2017). Bubbling of the packing material and feed takes place in the bubbling region where the actual solid-gas contact occurs. At the emulsion zone, the released syngas is subject to further cracking (Pereira and Martins 2017). As the bubbles are making their way to the top, they grow in size and carry a huge amount of particles that enhances the heat and mass transfer between the solids and the gasifying agent (Pereira and Martins 2017).

The double fluidized bed (DFB) gasifier, which is also referred to as dual fluidized bed gasifier, consists of two interconnected gasifiers in which the first is an endothermic gasification chamber and the second is an exothermic one. The first chamber works with steam as a gasifying agent in order to gasify the waste feed, and the second chamber works with air to incinerate the char that results from the gasification process. As the flue gas rises to the top, the heavy and large-sized tar particles fall off which are fed into a built-in cyclone that recycles the particles back for further decomposition to produce a higher-quality syngas (Richardson et al. 2015; Evans and Smith 2012; Sikarwar and Zhao 2017). The resultant products from the first chamber are the syngas and char. The second chamber results in the production of a methane-rich gas with a high calorific value (Evans and Smith 2012).

Plasma Gasifiers

Plasma gasification requires elevated temperatures either in the form of a thermal arc or a torch. An inert gas is passed between electrodes generating extremely high temperatures which leads to the breakdown of the waste feed as well as the conversion of the inert gas into plasma, which is known as the fourth state of matter. The particles of the inert gas that are subject to extremely high temperatures become ionized and decompose into plasma, i.e., free radicals, ions, charged particles, and free electrons (Erdogan and Yilmazoglu 2020). The process results in physical and chemical decomposition of the inert gas as well as the waste feed which is set in contact with the gas due to the fact that the gas undergoes the following chemical reactions: dissociation, ionization, and reassociation reactions (Erdogan and Yilmazoglu 2020; Kuo et al. 2020).

Plasma arc gasification decomposes the waste feed by converting it partly into syngas and slag (char) with some of the wastes being converted into atoms in the plasma state (Seo et al. 2018). The operating temperatures of a plasma gasifier reach up to 5000 °C, which is extremely high compared to other gasifiers (Kuo et al. 2020). Its high performance translates inversely to a high operational cost. A main disadvantage is that it operates at extremely high temperatures, in which the core of the plasma torch reaches up to 13,900 °C. The operating temperature of the plasma arc gasifier ranges between 2700 and 4427 °C (Seo et al. 2018). There are two main types of plasma gasification: one that utilizes microwave plasma torches and the other is transferred/non-transferred arc plasma torches. The most commonly used plasma media are air, carbon dioxide, steam, water, nitrogen, or a mixture of these gases (Erdogan and Yilmazoglu 2020). An advantage of plasma gasification over other types of gasification is that it allows for some of the metals' recovery. The metals are captured within the resultant residual slag, in its molten form, and are detained in various compounds containing iron, mercury, chromium, cadmium, copper, graphite, and other carbon-saturated compounds (Erdogan and Yilmazoglu 2020). Plasma gasification does not result in the production of tar or produce only insignificant amounts (Kuo et al. 2020; Seo et al. 2018).

Fixed Bed Gasifier

The fixed bed gasifier, also known as moving bed gasifier, is a vertical unit that consists of a thermal degradation chamber at which the waste feed is passed from the top of the unit under the effect of gravity. As the feed is passed, it is subject to varying temperatures that dehydrate and decompose the feed into a smaller size until it reaches the bottom of the unit (Wei et al. 2020; Sikarwar and Zhao 2017). The gasifier operates with the help of a gasifying/oxidizing agent, and the operating temperature of a fixed bed gasifier ranges between 950 and 1150 °C (Wei et al. 2020).

A fixed bed gasifier mainly consists of three main zones: drying, pyrolysis zone, and combustion/gasification zones (Sikarwar and Zhao 2017). The bottom of the unit is accompanied by an ash collection chamber. Fixed bed gasifiers result in a flue gas of relatively low temperatures ranging between 450 and 650 °C (Zhang et al. 2019). The main advantage of using a fixed bed gasifier is that it is simple and easy to operate (Zhang et al. 2019; Sikarwar and Zhao 2017). One of the main disadvantages is that it operates on small to medium scale and is not suitable for industrial scale. Additionally, fixed bed gasifiers result in the generation of high ash content (slag or dry ash) and have the potential to generate large quantities of tar ranging between 0.01 and 150 g/Nm^3, and they consume large quantities of gasifying agents (Zhang et al. 2019; Wei et al. 2020). The unit generally has high carbon conversion efficiency ranging between 40 and 85% (Wei et al. 2020).

There are five main types of fixed bed gasifiers: updraft (counter current) gasifier, downdraft (cocurrent) gasifier, and horizontal (cross) draft gasifier, which are distinguished from each other based on the direction of the flow of the feed, the resultant syngas, and the gasifying agent (Dutta and Acharya 2011; Wei et al. 2020; Sikarwar and Zhao 2017; Zhang et al. 2019; Nuamah et al. 2012). An updraft flow gasifier is referred to as a counter-flow gasifier due to the fact that the syngas leaves the unit from the top, and the gasifying agent is fed from the bottom. A downdraft fixed bed gasifier functions in a contrary manner to an updraft gasifier, and it is referred to as a cocurrent flow gasifier due to the fact that the syngas outlet and gasifying agent inlet are located at the bottom of the unit, which eventually leads to higher degradation efficiency of the tars and generated solids (Nuamah et al. 2012; Dutta and Acharya 2011).

Horizontal draft gasifiers are similar to updraft gasifiers, with the inlet of the gasifying agent and the outlet of the syngas placed nearly at the middle of the unit, in a horizontal manner (Dutta and Acharya 2011). An updraft gasifier is distinguished from the other fixed bed gasifiers, as it has the ability to handle feeds of high moisture content, up to 40–50% moisture, and it results in higher hydrocarbon content. Unlike downdraft gasifiers, updraft gasifiers are not recommended to be used with gas turbines due to the high tar and slag content that results post gasification (Nuamah et al. 2012). Tar content is within the range of 10–20 wt% in an updraft gasifier (Sikarwar and Zhao 2017).

Updraft gasifiers cause a higher hydrocarbon content, due to the fact that the resultant syngas flows in an upward manner; hence, it initiates the gasification and thermal decomposition process even before the waste feed lands at the gasification zone. The downdraft fixed bed gasifier releases less pollutants within the syngas and results in minimal formation of slag and tar (Nuamah et al. 2012; Dutta and Acharya 2011). Hence, downdraft gasifiers can be optimally used with gas turbines (Nuamah et al. 2012). Horizontal fixed bed gasifiers generate more tar content when compared to updraft gasifiers as the syngas generated exits within the same level as the gasifying agent; hence tar cracking is not sustained for a long time (Sikarwar and Zhao 2017).

Rotary Hearth Gasifiers

Rotary hearth gasifiers are round (doughnut)-shaped gasifiers that function under partial oxidative conditions. A rotary hearth gasifier generally consists of a rotary disc where the feed initially enters, and the gasifier or the heated thermal degradation chamber (Woodard, and Curran, Inc. 2006). Depending on the design, the feed can enter the rotary discs from a vertical stack, at which it can be subject to an initial size reduction prior to feeding into the heated gasifier (Letcher and Vallero 2019). As the feed enters the gasifier, the thermal decomposition begins to take place, thus resulting in syngas and ash. The gasifier has a vent that would constantly direct the released gas out of the chamber for syngas treatment, with the help of APC units and electricity generation (Woodard, and Curran, Inc. 2006).

Entrained Flow Gasifiers

Entrained flow gasifiers gasify the waste feed by setting the feed and gasifying agent in a cocurrent flow either from the top of the unit or from the side. The gasification reaction takes place as soon as the feed and gasifying agent enter the gasifier (Basu 2018). The entrained flow reactor operates on a large scale; however it requires the waste feed to be of extremely fine size, 200 μm, in order to ensure efficient and adequate heat and mass transfer (Wei et al. 2020; Higman 2011). It operates at high temperatures ranging from 1200 to 2000 °C and high pressures varying between 20 and 80 bars (Nuamah et al. 2012; Higman 2011).

The most commonly used gasifying agent is oxygen and steam (Basu 2018; Zhu and Frey 2010). Furthermore, entrained flow gasifiers are not recommended for a feed that is expected to generate large amounts of ash, and they are ideal for slurry and liquid-based feed (Wei et al. 2020; Zhu and Frey 2010). An advantage of using entrained flow gasifiers is that they result in negligible amounts of tar. The generated ash gets converted into a liquid molten slag (Wei et al. 2020; Nuamah et al. 2012). The resultant slag is usually quenched with water (Zhu and Frey 2010). In addition to this, they result in a high carbon conversion efficiency up to 99% conversion (Mvelase and Majozi 2015). Furthermore, they are known for their short residence time lasting up to only a few seconds (Higman 2011; Wei et al. 2020). One of their main disadvantages is that they result in the melting of ash that turns into slag due to the high operating temperatures and pressures (Nuamah et al. 2012). This significantly increases the cleaning costs. Moreover, they require a very high amount of gasifying agent due to the fact that the unit operates at very high temperatures, which in turn results in increasing the operational costs (Wei et al. 2020; Nuamah et al. 2012). In addition, converting the RDF into a finer size of up to 200 μm is not necessarily practical and results in increasing the operating costs significantly (Higman 2011; Nuamah et al. 2012).

8.2.3 *Pyrolysis*

Pyrolysis process is a thermochemical decomposition process that utilizes heat in anaerobic conditions (i.e., in the absence of oxygen), to break down the organic carbonaceous wastes fed into polluted gas (or biogas), biochar, tar, hydrocarbons and chemical products (consisting mostly of hydrocarbons ranging from C8 to C46), volatile organic carbons (VOCs), polycyclic aromatic compounds (PAHs), pyrolytic oil (or bio-oil), and water vapor) (Dharmaraj et al. 2021; Su et al. 2021; Lee et al. 2021; Messerle et al. 2018; Beyene et al. 2018; Park et al. 2021).

Out of these products, a fraction of the VOC produced is condensable using quenching techniques. The remaining constituents (i.e., solid tars, chars, some gases) are non-condensable (Al-Haj Ibrahim 2020). The main types of pressurized gases used for quenching are air, nitrogen, argon, and helium. Not only does gas quenching result in gaseous condensation into the desirable liquid product, but also it results in less cleaning costs as it leaves the compartment nearly free of residues (Troell et al. 2014).

Tar and char are two by-products of the pyrolysis process (Dharmaraj et al. 2021; Chen et al. 2015). Char contains a high heating value, similar to that of coal, and it resembles activated carbon in terms of physical properties. The char may contain heavy metals (Ni, Cr, Zn, Mn, Mo, and Al) as a part of their constituents which require treatment prior to obtaining a raw heavy metal-free char. Tar is another by-product of pyrolysis and mostly consists of hydrocarbons which have the tendency to deactivate catalysts and have a carcinogenic nature. Tar can stick on the surfaces of engines or turbines (Dharmaraj et al. 2021).

Pyrolysis takes place at relatively lower temperatures when compared to gasification and incineration, and the thermal decomposition occurs between 300 and 1300 °C (Beyene et al. 2018), hence resulting in lower operational costs. Due to the fact that it operates at lower temperatures, negligible amounts of dioxins, benzo[a]pyrenes, etc. are produced; hence, it is considered a more environmentally friendly process compared to incineration (Messerle et al. 2018). Pyrolysis requires less APC equipment or smaller-sized APC equipment. The operating temperatures are determined based on the desirable product required and the types of wastes being fed. One of the disadvantages of the pyrolysis process is that it functions at a smaller scale when compared to other WtE technologies.

In addition to the waste reduction and waste-to-energy conversion process, pyrolysis is distinguished from other WtE processes as it generates useful products including water vapor, bio-oil, hydrocarbons (ranging from C8 to C46) and chemical products, and biochar (Beyene et al. 2018; Su et al. 2021). Each of these products can be used to serve different processes either as high-value raw products or as high energy density fuel. By altering the process parameters such as the moisture content within the feed, the operating temperature, the operating pressure, feed quantity, feed composition, residence time within the reactor, type of catalyst, type of reactor, heating rate, etc. product yield can be altered (Su et al. 2021; Lee et al. 2021; Beyene et al. 2018; Purnomo et al. 2021; Shareefdeen et al. 2015; Al-Haj Ibrahim 2020).

Studies have shown that the higher the moisture content in the feed, the lower the bio-oil content formed. Bio-oil can be used as a source of fuel to replace the depleting fossil fuels currently in use around the world (Su et al. 2021). Additionally, at low temperatures, ranging from 300 to 550 °C, the formation of higher liquid content is favored, whereas at higher temperatures exceeding 700 °C, the formation of higher gas content (syngas) is favored (Al-Haj Ibrahim 2020; Shareefdeen et al. 2019). The residence time in a pyrolytic chamber varies from a few seconds to 2 h (Shareefdeen et al. 2019; Chen et al. 2015). Another factor that affects the production of higher solid, liquid, or gaseous content is the pressure within the reactor. Pyrolysis is ideally carried out at vacuum conditions; however in practice, it takes place at atmospheric pressure to lower the operational costs (Al-Haj Ibrahim 2020). The pressure within the unit leads to higher solids (char) (Al-Haj Ibrahim 2020). There are four main pyrolysis process types which are distinguished on the basis of operating temperatures and vapor residence time, and they include conventional pyrolysis, fast pyrolysis, catalytic pyrolysis, and slow pyrolysis (Chen et al. 2015; Beyene et al. 2018; Dharmaraj et al. 2021). Among these methods, the lowest operating temperature is utilized in conventional pyrolysis (ranging from nearly 277 to 627 °C). Fast pyrolysis works at operating temperature ranging from 650 to 1000 °C with a reaction time of 3 s.

Fast pyrolysis can be split into three main types: flash, rapid, and ultrarapid pyrolysis (Chen et al. 2015; Beyene et al. 2018; Dharmaraj et al. 2021). Flash pyrolysis operates at 777–1027 °C with a reaction time of 0.03–0.15 s (Beyene et al. 2018; Dharmaraj et al. 2021; Chen et al. 2015). Rapid pyrolysis operates at 800–1000 °C (Zanzi et al. 2002; Chen et al. 2015), and lastly ultra-rapid pyrolysis operates at 700–1000 °C with a residence time of 0.5 s (Dharmaraj et al. 2021; Chen et al. 2015). When comparing the vapor residence time, slow pyrolysis holds the vapor within the unit for up to a few minutes, and for fast pyrolysis, the vapor residence time ranges between milliseconds and seconds (Chen et al. 2015). During slow pyrolysis, the formation of solid char is favored (Al-Haj Ibrahim 2020). During fast pyrolysis reaction, bio-oil forms at temperatures above 650 °C, whereas biogas forms at temperatures above 1000 °C. In flash pyrolysis, bio-oil yield reaches up to 70–75% yield. In ultra-rapid pyrolysis, a maximum yield of bio-oil produced can reach up to 90% at temperatures less than 700 °C in addition to char reaching up to more than 10% of the yield (Chen et al. 2015).

Pyrolysis can function either with or without the presence of a catalyst, and the process can be referred to as thermal pyrolysis (non-catalytic pyrolysis) or co-pyrolysis (catalytic pyrolysis), respectively (Purnomo et al. 2021; Lee et al. 2021; Su et al. 2021). The resulting products from the two processes are significantly different, as the presence of a catalyst results in further cracking of tar and solid products, hence lowering the oxygen- and nitrogen-containing compounds (Su et al. 2021). In addition to this, the catalyst acts as a platform to convert the hydrocarbons generated into various useful products such as aromatics, methanol, and bioethanol (Shareefdeen et al. 2015, 2019; Dharmaraj et al. 2021).

There are different types of catalysts used, and the most common ones are divided into two main categories: acid-base metal oxides and transition metal oxides

(Matayeva et al. 2019). The most commonly used acid-base metal oxides are CaO and MgO, whereas the most commonly used transition metal oxides are zeolites, bulk metal oxides, clays, and mesoporous silica-supported metal oxides (Matayeva et al. 2019; Lee et al. 2021). Another commonly used catalyst is the activated carbon which can be extracted from the biochar (Su et al. 2021; Lee et al. 2021; Purnomo et al. 2021).

Lee et al. (2021) observed that the zeolite catalysts were proven to enhance the production of higher desirable aromatic compounds such as benzene, toluene, ethylene, and xylene (BTEX compounds) (Al-Haj Ibrahim 2020; Lee et al. 2021). This is due to the fact that the catalyst induces the reactions such as deoxygenation, cracking of solids, ketonization and aldol condensation, hydro-treating, and aromatization (Matayeva et al. 2019). The deoxygenation reactions are expressed in the form of dehydration, decarbonylation, and decarboxylation reactions, which result in the removal of oxygen in the form of H_2O, CO_2, and CO, respectively. As a result of these reactions, water vapor, carboxyl groups, carbonyl groups, and oxygen are detached from the carbonaceous feed, respectively, which will lead to higher chances of forming the desirable aromatic compounds. Ketonization and aldol condensation reactions demonstrated an ability to transform carboxyl and carbonyl groups into longer carbon chains, which eventually can be converted into diesel and gasoline fuels (Matayeva et al. 2019). Additionally, zeolite catalysts have been proven to have high porosity and acid sites, which favor the production of BTEX compounds within the pyrolytic oil (Lee et al. 2021). There are six common pyrolysis reactors, and they include entrained downflow reactor, rotary kiln reactor, fixed bed reactor, tubular reactor, plasma reactor, and fluidized bed reactor.

Entrained Downflow Pyrolysis Reactor

The entrained downflow reactor is a pyrolytic reactor that deploys flash pyrolysis technique to work on small-sized feed particles of a diameter ranging between 1 and 5 mm, at which the feed is fed from the top of the reactor (Nachenius et al. 2013; Dupont et al. 2008). The feed is subject to free fall with the help of gravity, and a hot gas is fed from the top (Nachenius et al. 2013). Another type of entrained flow pyrolysis was built to utilize sand which was heated using nitrogen gas (an inert gas). As the waste is in contact with the sand, pyrolysis takes place (Stals et al. 2010). Using this method, the pyrolytic gas flows onto the next compartment for the quenching process. Various laboratory experiments were done using an entrained-downflow reactor at the operating temperatures range of 700–1000 °C (Nachenius et al. 2013; Dupont et al. 2008) with the reaction time between 1 s and 3 h (Nachenius et al. 2013; Stals et al. 2010). A main disadvantage is that it is a pilot-scale reactor that works with pretreated feed of a very small size and limited volume of RDF. Another disadvantage is that some of the vapors present get diluted within the hot gas and end up experiencing reduced partial pressure, hence making the collection of liquid post pyrolysis challenging. Additionally, high gas flow rates are required to ensure adequate heat transfer between the feed and the gas (Nachenius et al. 2013).

Rotary Kiln Pyrolysis Reactor

The rotary kiln pyrolysis is a type of slow pyrolysis, and the reactor supports the anaerobic combustion of the waste feedstock, with the help of its rotating structure which is positioned at an incline. Its rotating structure allows for adequate mixing of the feedstock, which enhances the heat transfer and increases the efficiency of the thermal degradation process (Chen et al. 2015). Moreover, the gentle rotations, according to experiments, have been observed to generate smoother surface of the char particles (Babler et al. 2017). Based on various studies done on a pilot scale, it is observed that the operating temperature range is 200–450 °C; however industrial-scale systems operates normally in the range of 500–900 °C (Li et al. 1999; Fantozzi et al. 2007; Ayanoğlu and Yumrutaş 2016). The residence time reaches up to 1 h (Chen et al. 2015). The reactor relies on its walls, which are supplied with an external heating source to pyrolyze the wastes into bio-oil, biogas, and char, while the reactor is rotating at an incline (Chen et al. 2015; Ayanoğlu and Yumrutaş 2016).

The main advantages of using this type of reactor is that it supports a wide variety of feed, and it is commonly used in industrial-scale processes (Kern et al. 2012). Additionally, they do not require significant pretreatment of the waste feed into RDF (Chen et al. 2015). Furthermore, the rotary kiln pyrolyzers are known for their relatively wider feed channel, in which larger volumes of wastes can be fed in a shorter time (Chen et al. 2015). One of the main disadvantages is that the mixing between the resultant flue gas and the solid waste feed is minimized due to gentle mixing which results in reduced oxidation and heat transfer between the two streams (Babler et al. 2017).

Fixed Bed Pyrolysis Reactor

The fixed bed pyrolysis reactor is a cylindrical shaped unit usually made of stainless steel and is connected to a gas preheater, a liquid quencher/condenser, and an ice-cooled liquid storage container (Nurul Islam et al. 2005). The fixed bed pyrolyzer is fed with the waste feed up to a certain level, according to the unit's design recommendation, and the anaerobic thermal degradation takes place as the walls are sufficiently heated. As volatile constituents of the resultant syngas start forming within the unit, gradual pressure starts building up within the reactor; thus the design of the unit should account for the high-pressure gradients (Kandiyoti et al. 2006). Inert gases, including helium or nitrogen, can be purged into the reactor to ensure anaerobic conditions, as well as to ensure that the vapor residence time (VRT) is reduced (Troell et al. 2014; Kandiyoti et al. 2006). Laboratory experiments have been carried out at temperatures ranging from 300 to 600 °C, and the reaction duration was reported as 40–60 min, and the vapor residence time was reported as 3–5 s (Nurul Islam et al. 2005; Asadullah et al. 2007). This process is one of the least efficient pyrolysis reactors when compared to the other reactor types; hence it is not recommended for industrial-scale operations (Chen et al. 2015).

Tubular Pyrolysis Reactor

The tubular pyrolysis reactor is suitable for small- to moderate-sized processes. One of the disadvantages of using this reactor is that pretreatment of the waste feed is essential to avoid clogging of the feed (Chen et al. 2015). Although scaling up of the equipment is not possible for industrial operations, the usage of multiple tubular reactors in parallel can increase the overall capacity (Nachenius et al. 2013). The reactor usually comes in two main forms either as a screw pyrolysis reactor, which is referred to as the auger reactor, or as a tubular rectilinear reactor (Nachenius et al. 2013; Chen et al. 2015). The screw pyrolyzer is the most commonly used one, and it has a maximum capacity of 5000–6000 tonnes of waste/year. It consists of a rotary screw that is in constant motion while transferring the feed into the reactor. It is a fast pyrolysis process; however it operates at much lower temperatures (Nachenius et al. 2013).

There are three options that enhances heat transfer: increasing the reactor's size, installing a radial mixer, or decreasing the particle size by converting it into RDF. The ideal method would be converting the waste into RDF. When dealing with RDF, the movement of the wastes within the screw is facilitated as it acquires a smoother nature/surface (Nachenius et al. 2013). The common material of the reactor is stainless steel, though specialized alloys were proven to withstand the high pressure (Kandiyoti et al. 2006). The temperature range within the unit can vary, depending on the size of the reactor. In pilot-scale pyrolyzers, the temperature ranges from 200 to 600 °C, whereas the operational temperatures within larger-scale (industrial scale) reactors can go up to 1000 °C (Chen et al. 2012; Zhang et al. 2011; Kandiyoti et al. 2006). According to various laboratory-scale experiments conducted, the internal diameter of a tubular pyrolyzer ranges from 10 to 35 mm, and the length varies from 800 to 1200 mm (Kandiyoti et al. 2006; Zhang et al. 2011; Chen et al. 2012). The pilot-scale experiments reported pyrolysis reaction time as 5 s (Chen et al. 2012). The tubular pyrolyzer requires constant removal of char which minimizes the equipment cleaning costs due to residue buildup (Chen et al. 2015).

Plasma Pyrolysis Reactor

Plasma pyrolysis is a pyrolysis technique that works by decomposing the waste by the help of plasma. The wastes are broken down into a gaseous state due to plasma formed by electric discharge at high temperatures. This is done in the absence of oxygen, and the output of the process usually favors the production of higher syngas content. There are three main types of plasma pyrolysis: high-temperature plasma, low-temperature plasma (also known as thermal plasma), and nonthermal plasma (also known as cold plasma) pyrolysis (Huang and Tang 2007). The most commonly used one is the low-temperature thermal plasma method, and it works with the help of a plasma torch that converts the electrical energy into thermal energy to create sufficient heat required to perform the anaerobic decomposition of the wastes

(Rathna et al. 2018; Huang and Tang 2007). Steam or any inert gas is purged into the plasma pyrolytic chamber in order to ensure anaerobic conditions (Huang and Tang 2007; Dharmaraj et al. 2021; Rathna et al. 2018; Donohue 2003). The efficiency of plasma pyrolysis process can reach up to 95% of waste volume reduction (Dharmaraj et al. 2021). The main disadvantage of using a plasma process is the fact that it operates on extremely high temperatures exceeding 4726.85 °C and the plasma torch has a short life span. Studies have shown that the reactor can also break down feed of low radioactivity and cytotoxic nature (Kerscher et al. 2021).

Fluidized Bed Pyrolysis Reactor

The fluidized bed pyrolysis reactor consists of packing material that is subject to heat by a fluidizing agent (Chen et al. 2015). It is a fast pyrolysis process, and it allows for adequate mixing of feed waste and allows for higher char and tar cracking (Chen et al. 2015). Fluidization enhances the uniform mixing within the fluidizing agent (heated gas) as well as the feed (Mastellone et al. 2002; Yıldız et al. 2019). The reactor consists of packing material, usually sand and a heated fluidizing agent (usually an inert gas) which is fed from the bottom. The most commonly used fluidizing agents include helium, argon, and nitrogen (Liu et al. 2020). The waste is fed from the top (Mastellone et al. 2002). As the thermal decomposition reaction is taking place with sufficient residence time, the waste feed decomposes and converts into pyrolytic vapors, as well as char (Mastellone et al. 2002; Yıldız et al. 2019; Abduhani et al. 2021; Liu et al. 2020; Jeong et al. 2020; Liu et al. 2021). The operating temperature varies due to differences in feed composition, nature, and quantity. One of the main advantages of using this reactor is that it has relatively lower maintenance costs due to the fact that it consists of fixed components, hence minimizing the chances of wearing out quickly (Mastellone et al. 2002; Yıldız et al. 2019). However, the reactor has a risk of de-fluidizing, i.e., the condition at which the bed loses its ability to maintain its fluidized state while the fluidizing agent is fed into the reactor (Mastellone et al. 2002; Zhong et al. 2018).

8.3 Conclusion

Waste-to-energy (WtE) technology is a promising method to eliminate the wastes while making use of it to generate electricity and valuable products. In this chapter, we reviewed the three main WtE processes which are incineration, gasification, and pyrolysis. Different types of reactor configurations used in each type of WtE process are also discussed. All of the WtE processes mainly consist of pretreatment of the waste, thermal degradation, and air pollution control (APC) units to eliminate generated pollutants such as particle emissions ($PM_{2.5,}$ PM_{10}), acidic gases, NO_x emissions, and VOCs. After the flue gas treatment, the generated heat energy is converted through steam engines to generate electricity. Incineration process is the simplest, and it is known to handle a wide variety of feed constituents, and it operates at the highest temperature. Gasification process operates at a larger scale than pyrolysis and operates on partial oxygen feed, and it results in the reduction of feed as well as production of valuable products. Pyrolysis is the most environmentally friendly process due to the fact that it functions at the lowest operating temperatures compared to other WtE processes and it does not require any air feed.

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Chapter 9
Gaseous and Solid Waste Management in Waste-to-Energy Processes

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9.1 Introduction

Waste-to-energy (WtE) plants are used widely across different countries, and they have been portrayed as an effective solution for waste reduction, energy generation from wastes, and useful product formation from unwanted by-products. Thermal energy within the resultant combustion flue gas in WtE is converted into electrical energy which can be a substitute for the depleting fossil fuels including coal, diesel, and natural gas. It is reported that WtE technologies result in 90% waste size reduction, thus leaving 10% as a waste residue (Kumar and Ankaram 2019). Although the resultant waste residue from the WtE processes is insignificant in terms of size, most of it is considered hazardous and poses a threat to the human health and to the environment. Depending on the type of WtE process, different pollutants can be formed, and their quantities can vary; nonetheless, the generated waste residue includes fly and bottom ash, slag, acidic scrubbing liquid, and CO_2.

In general, the three main WtE processes, i.e., incineration, gasification, and pyrolysis, result in the generation of bottom ash and fly ash, as a result of the thermal decomposition process, with incineration process being known for generating the largest quantities of ash, followed by gasification, and lastly pyrolysis (Shareefdeen et al. 2015; Shareefdeen et al. 2019). The generated ash is hazardous, as it consists of dioxins, furans, and heavy metals including mercury, arsenic, barium, nickel, lead, and cadmium (Yashwant 2020; Xu et al. 2018). Fly and bottom ash particle size can range between 10 and 300 microns (Beér 2004). The inhalation of these particles results in varying diseases including respiratory problems, lung cancers, neurological diseases, heart damage, and even mortality (Yashwant 2020). Furthermore, ash results in the contamination of water and in the degradation of the

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air quality (Yashwant 2020). In gasification and pyrolysis WtE processes, the bottom ash that precipitates within the gasifier/pyrolizer can undergo a phase change and melt into a sticky liquid form, depending on the operational conditions and on the type of thermal decomposition chamber used. This sticky substance is referred to as slag (Czop and Łaźniewska-Piekarczyk 2020). The slag is an unwanted by-product, and it may consist of various toxins, dioxins, and heavy metals, and it sticks to the combustion chamber, thus leading to an increased cleaning and maintenance cost. Cleaning slag from combustion chambers has been reported as a challenge due to its sticky nature (Richardson et al. 2015; Arvelakis et al. 2002). Another unwanted by-product that results from WtE processes is the scrubbing liquid that is used for neutralizing acidic gases (Kiang 2018; Macdonald 2007). Scrubbing liquids are usually sprayed or sprinkled onto the acidic scrubber, and they react with the acidic components within the flue gas to neutralize the acidic gases into salts. Thus, liquid-and-solid mixture accumulates into large quantities overtime within the scrubber (Kiang 2018; Macdonald 2007). All three WtE processes generate CO_2 as a by-product, which is a greenhouse gas that significantly contributed toward the global warming effect (Ganopolski 2008). One of the solutions to eliminate CO_2 content is to capture it, by absorbing it into an alkali solvent, thus removing it from the atmosphere (Lee et al. 2004). However, by doing this, the CO_2 content is only displaced into a liquid rather than being completely eliminated. This creates a large quantity of liquid waste over time that will need to be addressed.

In addition to several air pollutants, WtE processes also generate several hazardous solid and liquid pollutants as well. The objective of this chapter is to present pollution control methods used in the elimination of solid particles, acid gases, NOx gases, and volatile organic compounds (VOCs) as well as to present methods to produce useful products from the unwanted by-products generated within the main three WtE processes.

9.2 Major Air Pollution Control (APC) Units in WtE Plants

This section presents major APC units used in WtE plants along with the pollutant elimination processes taking place within each unit.

9.2.1 Electrostatic Precipitator (ESP)

The electrostatic precipitator (ESP) is the first APC unit that is usually equipped within a WtE process, post combustion. This is due to the fact that it works on eliminating the largest-sized particles that escape from the combustion chamber. As a result of combustion, pollutants of various particle sizes, termed as particulate matter (PM), are generated. The ESP targets capturing particles of 10–300 microns (μm) (Beér 2004). There are two main types of ESP units: dry ESP and wet ESP. The wet ESP has been disregarded due to the fact that it results in passing a liquid to absorb the collected particles, which leads to the loss of ready fly ash which is a useful raw material for cement industry, as well as WtE process, as discussed in detail within Sect. 9.3. Hence, the focus will only highlight the functionality of a dry ESP.

The ESP is composed of several electrodes, which are referred to as plates. The plates are split into two main types: one is a discharge electrode, and the other is a collection electrode (Monfort et al. 2014). Within the ESP, a high voltage, ranging from 40 to 120 Kv, is applied with the help of external energy sources, which induces a magnetic field effect and causes the flowing particulates within the flue gas to acquire a charge (Monfort et al. 2014). The effect of creating a magnetic field is termed as the corona effect (Finlayson-Pitts and Pitts 2000). As the neutrally charged flue gas enters the unit, the large-sized particles acquire the charge from the magnetic field and deposit on the collection plates, due to the grounding effect (Beér 2004; Monfort et al. 2014). In order to remove the accumulated particles from the collection plates, a hammer-like structure is used to vibrate the collection plates, and this effect is referred to as the rapping effect (Monfort et al. 2014; Weiner and Matthews 2003). The operating temperature of an ESP ranges from 130 to 150 °C, and the efficiency ranges from 70 to 80% and can reach up to 95% under certain conditions, which mostly depends on the particle size within the flue gas, the rapping system's efficiency and frequency, the corona effect, and the collection plates' efficiency (Jena et al. 2019).

9.2.2 Baghouse Filter

Baghouse filter, also referred to as fabric filter or bag filter, collects smaller-sized particles that managed to escape the ESP unit and the combustion chamber (Shareefdeen et al. 2015). The baghouse filters remove particles of a diameter size ranging from a few sub-microns to 10 μm or PM_{10} (US EPA 1998; Hutten 2007). In addition to the removal of fly ash and other particulates, pollutants such as mercury, dioxins, furans, etc. can be captured if baghouse filters are fed with activated carbon (Shareefdeen et al. 2015). The baghouse filter is shaped as a cylindrical container made of several rows of filter bags that physically trap the particulates under the effect of pressure difference between the flue gas and the filters. As the flue gas passes, a layer of particulates, referred to as "filter cake," accumulates and forms on the front side of the filters facing the flue gas (Hutten 2007; US EPA 1998). The heavier particles fall off under the effect of gravity, whereas the smaller ones get trapped within the filters (Shah 2017). The flue gas is usually fed from the bottom of the unit, and the larger particles accumulate around the surface of the filter, thus forming the filter cake which contributes toward a higher efficiency by trapping particulate matter of various sizes (US EPA 1998; Shah 2017). The main factor that affects the filtration process within the unit is the gas-to-cloth ratio, i.e., the ratio of the volumetric flow rate of flue gas flowing per one area of fabric (US EPA 1998).

Other factors that affect the formation of a high-quality filter cake is the flue gas velocity, moisture content within the flue gas, concentration of PM, temperature of flue gas, type of filter used (material), cleaning intervals, and cleaning method (US EPA 1998; Shah 2017). Additionally, another important factor that affects the performance of a baghouse filter is the differential pressure.

The filter media in a baghouse filter unit are manufactured in different shapes and material, and these include circular, flat, cartridge-shaped, tubular-shaped filters, etc. The filter materials can be chosen based on the inlet flue gas conditions, and they include ceramic fiber, woven fabric, and cartridges (Hutten 2007). Ceramic fibers are recommended for industrial processes with high temperatures reaching up to 1000 °C (Hutten 2007), whereas fabric filters can be ideal for a feed operating at lower temperatures, usually lower than 260 °C (Shah 2017). In order to enhance the efficiency of the filters, a membrane made of lime, calcium carbonate, or ash layer (cake layer) can be applied, and this process is termed as pre-coating or seeding (Shah 2017). The efficiency of a baghouse filter varies from 98 to 99.99% depending on the flue gas composition, operating conditions, and the unit's maintenance (Shah 2017; Shareefdeen et al. 2015; US EPA 1998).

At the end of the process, the filters undergo a cleaning process in order to release the captured particles and filter cake, and this is done in three main methods: high pressure reverse (pulse) jet, low pressure reverse jet, or reverse (mechanical) shaking (Hutten 2007). The high reverse pulse jet is a cleaning method for the filters in a baghouse, in which air is supplied through a venturi nozzle (Hutten 2007) or by the help of a reverse air fan (US EPA 1998). Air is then pumped through the nozzle or the fan into the filters; thus, gently pushing the cake down to the hopper with the support of the gravitational force. The low pulse jet method consumes the lowest energy out of all methods described, and it relies on air being pumped or burst from the top of the filters, hence allowing the cake to drop off the filters into the hopper. The mechanical shaking differs from both high and low pulse jet cleaning techniques, as it is supported by a mechanical shaker that allows the cake to fall off with the help of gravity (Hutten 2007; US EPA 1998). The collected ashes at the bottom of the unit, or the hopper, are then stored and utilized for making products such as cement manufacturing or activated charcoal catalysts (Shen et al. 2011; Pallarés et al. 2018).

9.2.3 Scrubbers for Acid Gas Removal

Following the removal of the particulate matter and fly ash, scrubbers are used for the removal of acidic gases. Acidic gases result in the corrosion of the APC units; therefore, it is important to treat them prior to proceeding with the removal of other pollutants. Acidic scrubbers are mainly used for the removal of acidic gases which include hydrogen sulfide, hydrogen halides, hydrogen chloride, hydrogen bromide, hydrogen fluoride, and sulfur oxides (Rogoff and Screve 2011; Macdonald 2007; Macleod 2018).

Types of Acidic Scrubbers

There are three main types of acidic scrubbers: dry, semidry, and wet scrubbers, and they are distinguished based on the scrubbing agent used in the removal of acidic gases. Wet scrubbers rely on liquid-based materials, whereas dry scrubbers utilize solid sorbents to get rid of the acidic gases (Quina et al. 2008; Kiang 2018). Semidry scrubbers use both liquid and solid materials to remove the unwanted acidic gases (Sparks and Chase 2016). Dry scrubbers use various sorbents including dried limestone, dry hydrated lime, or clay (Kiang 2018; Macdonald 2007; Goodwin 2014). The three main types of acidic scrubbers are discussed in the following subsections.

Dry Scrubbers

Dry scrubbers are mainly manufactured in two designs: either as a circulatory fluidized bed scrubber (also known as the bubbling fluidized bed scrubber) or as a reagent injection system that is injected into the resultant flue gas to neutralize the acidic gases (Kiang 2018). The fluidized bed scrubbers are initially supplied with the scrubbing reagent, at which the flue gas is passed on to chemically react and neutralize into salts. The direct reagent injection is generally done in a duct transporting the flue gas into other APC units, or in an individual chamber to react and neutralize the acidic components within the flue gas. The fluidized bed scrubber is known for higher efficiency compared to direct reagent injection systems (Kiang 2018).

Semidry Scrubbers

Semidry scrubbers incorporate both a dry and a solid scrubbing agent that react with different acidic components. They consume wet slurry solutions as an initial step to neutralize the acids through acid-base neutralization, and consequently, the flue gas undergoes dry scrubbing. The first step ensures that the acidic gases are absorbed and neutralized by the liquid through a spray dryer, whereas the second step utilizes filters to physically remove the formed salts, the ash solids, and additional alkali particles from the flue gas (Sparks and Chase 2016).

Wet Scrubbers

Wet scrubbers use materials including lime slurry, hydrated lime, limestone, sodium-based sorbent, potassium-based sorbent, calcium-based sorbent, magnesium-based sorbent, seawater, or ammonia (Miller 2005). The pH of a hydrated lime ($Ca(OH)_2$) is equivalent to 12.4, and it is known for its excellent acid neutralization ability (National Lime Association 2007). The acidic scrubber works on dissolving the gaseous contaminants into the scrubbing liquid's stream, up to an efficiency exceeding 90% and depending on the pollutant being removed (US EPA 2021). Usually, the sorbent must be of an alkaline nature to be able to dissolve the acidic gaseous components and to convert them into salts within the exit flue gas stream (Rogoff and Screve 2011). The main factors that affect a scrubbing agent are the concentrations of acidic particles within the flue gas, the droplet size (in the case of a liquid scrubber), the type of scrubber, the solubility properties of the scrubbing agent, the flue gas speed, and the rate of mass transfer (Cheremisinoff and Rosenfeld 2010; Sjoholm et al. 2001). The main disadvantage that accompanies wet scrubbers is the high pressure drop that results within the unit (Cheremisinoff and Rosenfeld 2010). In order to maximize the range of pollutants captured, acidic scrubbing can be done with the help of activated carbon in order to extract the heavy metals and dioxins from the flue gas in addition to the treatment of acidic gases (Sparks and Chase 2016; Goodwin 2014; Using Lime for Flue Gas Treatment 2003). The heavy metals that can be extracted include mercury, zinc, nickel, chromium, lead, and cadmium, and the extraction efficiency ranges between 50.6 and 90%, depending on the heavy metal, according to a study conducted by Karnib et al. (2014). A dry scrubber with hydrated lime and activated carbon feed can result in an HCl neutralization of 99% and a 95% reduction of SO_x and HF (Sorrels 2021; Ropp 2013).

Scrubber Configurations

There are three main configurations of acid scrubbing towers: packed and plate towers, spray towers, and venturi towers.

Spray Towers

Spray towers consist of sprinklers that spray the scrubbing liquid from the top of the unit, in which it gets in contact with the acidic flue gas particles rising from the bottom of the unit in a cocurrent flow. As the scrubbing liquid is dripped into the unit, it forms bubbles, which capture and absorb the acidic gases. Several sprinklers spray the basic scrubbing liquid as it gets in contact with the acidic components within the flue gas, thus forming a neutralized slurry at the bottom of the unit. A mist collection plate, which is a porous mesh plate, is installed to capture any liquid droplets that get carried away by the flue gas's velocity (Vallero 2008).

Packed and Plate Bed Scrubbers

Packed and plate bed scrubbers are acidic scrubbers that consist of a flue gas inlet, scrubbing reagent sprinklers, packing bed media, and a mist collection plate. The packed bed scrubber can be designed either in a crossflow or a counter flow. The packing materials consist of various shapes including spiral rings, berl saddles, Raschig rings, etc. As the liquid flows down the unit and gets in contact with the packing material, it forms a thin film which absorbs the acidic gas particles within the flue gas. Due to the speed of the flowing flue gas, some wet liquid particles may escape; hence, the mist collection plate is usually installed in order to capture these particles (US EPA n.d.).

Venturi Scrubber

The most commonly used wet scrubber is the venturi scrubber, and it consists of three main sections: converging section, throat, and diverging section (Cheremisinoff and Rosenfeld 2010). Initially, the flue gas enters from the converging section while passing through the throat of the unit, which is where the contact between the scrubbing agent (absorbent) and the flue gas is enhanced due to the constraint in area, hence the increased mixing and velocity of the flue gas and sorbent (Basson and Daavittila 2013; Cheremisinoff and Rosenfeld 2010). The scrubbing agent can either be fed from the converging section or from the side, i.e., from the throat of the unit, and it is usually sprayed into the flue gas (Cheremisinoff and Rosenfeld 2010). The flue gas flow rate is designed between 50 and 100 m/s and up to 122 m/s at the throat of the scrubber, and the pressure drop within the unit is usually between 30 and 100 in. of water (Sjoholm et al. 2001; Santoleri 2003).

9.2.4 Selective Catalytic Reactor (SCR) and Selective Non-Catalytic Reactor (SNCR)

An Overview of SCR and SNCR

After eliminating the acidic gases from the flue gas, the selective catalytic reactor (SCR) is placed to remove mainly the nitrogen oxides (NO_x) present within the flue gas. An SCR works by converting NO_2, N_2O, NO, and dioxins present in fly ash into N_2 and H_2O gases (He et al. 2017; Herrero and Ullah 2020). The majority of the NOx consists of NO_2, due to the fact that the generated N_2O and NO react with oxygen and are converted into NO_2. NO_x reduction is divided into primary and secondary methods based on the type of wastes fed. The primary method deals with homogenous feed, whereas the secondary method deals with heterogeneous ones. There are different types of secondary method reactors that can be equipped to reduce and minimize the dioxin and NO_x levels, and these reactors include selective non-catalytic reactor (SNCR), selective catalytic reactor (SCR) with fixed bed catalytic reactor, and SNCR/SCR with combinations of the methods described. NO_x levels can be affected by the rate of heat removal, the flow velocity, the ratio of fuel/amount of air fed, the temperature, and the composition of the feed.

The secondary reactor can be chosen based on the NO_x concentrations present within the inlet flue gas. For a feed with NO_x concentrations ranging less than

450 mg/Nm^3, the SNCR is recommended; for a feed with 450–600 mg/Nm^3 of NO_x, the SCR/SNCR is more ideal, and for a feed with NOx concentrations exceeding 650 mg/Nm^3, an SCR with a catalytic fixed bed reactor is the best option (Dvořák et al. 2010). When comparing the efficiency of these methods, the efficiency of the SNCR ranges from 40 to 70%, whereas the efficiency of the SCR ranges from 70 to 90% (Dvořák et al. 2010). The main difference between an SCR and an SCNR is that an SCR utilizes catalysts which are either embedded on the walls of the unit or directly fed as catalyst streams into the unit. Another difference between the two types is that an SNCR requires higher operating temperatures, ranging from 930 to 1090 °C, when compared to SCRs. Though SCRs are costlier in comparison to SNCRs, they have a much higher treatment efficiency (He et al. 2017).

Selective Catalytic Reactor (SCR)

SCRs are associated with several disadvantages which can be eliminated using a well-designed process. One of them is that the feed should be preheated before it goes into the reactor and should be maintained at the optimal catalyst's operating temperature. Depending on the type of catalyst, the operational temperature range is usually between 175 and 600 °C (Dvořák et al. 2010). Installing a heat exchanger to heat the flue gas prior to its entry into the unit can solve the problem. Another disadvantage of using an SCR is that catalytic reactors require a clean input stream, i.e., the stream fed should be cleared from particulate matter (PM). Technology advancements combine the baghouse filter with the SCR in one unit, and this is referred to as the SCR with catalytic filtration or the DeDiox system. This system offers 96.6% removal of heavy metals and dioxin collection on the filters, and the efficiency is further enhanced up to 98.8% of dioxin removal with the help of catalytic cracking located on the inner sides of the filters (Dvořák et al. 2010).

SCRs consist of a reacting solvent feed inlet, a catalyst holder, a flue gas inlet, and a clean gas outlet. They may incorporate an additional extension of a baghouse filter system for widening the pollutant-capturing range to include heavy metals and dioxins, as discussed previously. SCRs are fed with the reacting solvent, and they work by reducing the nitrogen oxides coming from the process by converting them into pure nitrogen gas and water vapor. There are many solvents that can be fed to an SCR, and they include pure ammonia, urea, ammonia water (NH_4OH), cyanamide, and nitrolime (Dvořák et al. 2010). The main design parameters of an SCR that affect its NO_x reduction efficiency are the shape of the embedded catalysts, the type of catalyst used, and the type of solvent fed to the reactor. All these parameters will have a different NOx reduction efficiency. An ammonia SCR operates at a temperature range between 290 and 400 °C, which is considered within the low operational range (He et al. 2017). Urea is also commonly used as a reducing agent to eliminate NO_x; however, studies have shown that it generates CO_2 besides the desired N_2 and H_2O products (He et al. 2017).

Ammonia SCRs require an over-stoichiometric ratio (1.1 mol NH_3: 1 mol NO) in order to prevent the formation of side reactions and unwanted products including ammonium hydrogen sulfate (NH_4HSO_4) and ammonium sulfate ($(NH_4)_2SO_4$), which can form as a result of the presence of trace amounts of SO_3 and SO_2 (Majewski 2005; Miller 2011; Okubo and Kuwahara 2020). Both SO_3 and SO_2 can react with O_2 feed and water vapor, present within the flue gas as a result of combustion, to form ammonium hydrogen sulfate and ammonium sulfate. These by-products cause catalytic fouling due to their acidic nature and due to their ability to bind to the catalyst's surface. Moreover, at temperatures below 200 °C, studies have proven that the NH_3 reagent favors the reaction with acidic gases as well as nitrogen dioxide (NO_2), hence decreasing the NO_x conversion efficiency (Dvořák et al. 2010; Majewski 2005). In addition to this, as NH_3 reacts with NO_2, it forms an explosive compound known as ammonium nitrate, which is also known to result in the deactivation of the catalysts (Majewski 2005). Hence it is highly important to maintain SCR's operating temperature above 200 °C and near or at the optimum chosen catalyst's activation temperature. Furthermore, another disadvantage of using ammonia as a reducing agent is that it reacts with NOx and forms a side product N_2O which is considered toxic. However, N_2O reacts with the ammonia and consumes more of it (i.e., ammonia feed), thus increasing the cost of solvent feed (Dvořák et al. 2010).

Catalysts in SCR

There are ample catalysts that can be used to speed up the reduction reaction in an SCR, and these include Pt/x-Al_2O_3, V_2O_5/TiO_2, zeolites, and Ph_2O_3/CeO_2 (Dvořák et al. 2010; Yang et al. 2021). V_2O_5-WO_3/TiO_2 does not require much preheating (Yang et al. 2021; Majewski 2005). The main active catalyst that is most commonly used is V_2O_5 which is usually placed on porous support materials (Yang et al. 2021). These material come in different shapes including honeycomb, plate, and corrugated plate structures (Yang et al. 2021; Miller 2011). The difference between these porous mesh structures is the mesh size, as well as pore shape; accordingly, they support different types of catalysts. The pores of the honeycomb-type support are either shaped as multiple hexagons, circles, or rectangles. In other support structures, stainless steel is pressed against a metal mesh where the catalysts (mainly V_2O_5 ad TiO_2) are placed (Miller 2011; Yang et al. 2021). The honeycomb holders support homogeneous catalysts including combinations of WO_3, TiO_2, and V_2O_5 (Yang et al. 2021; Miller 2011). Lastly, corrugated plate holders are fortified with glass fiber that utilizes TiO_2 as a base compound and is then coated with V_2O5, WO_3, and other substances in order to limit the corrosion of the catalyst (Yang et al. 2021). There are various ways to prevent and decrease the fouling and poisoning of the catalyst, and these include the following:

- Keep the temperature at nearly 300 °C. If the temperature falls below 250 °C, the ammonia will react with the trace amounts of SO_x that are passed on from the acidic scrubber. If the temperature falls below 200 °C, ammonia will react with nitrate. Both of these compounds can cause catalytic poisoning (Dvořák et al. 2010; Majewski 2005).

- Ensure the over-stoichiometric ratio in the SCR, thus preventing the generation of toxic material (Majewski 2005; Yang et al. 2021).
- Install acidic scrubbers prior to SCRs to ensure the maximum reduction in the amount of acidic gases and alkali metals (Dvořák et al. 2010).
- Ensure well mixing of the ammonia feed with the flue gas (Dvořák et al. 2010).

Limitations of SCR

The limitation associated with an ammonia SCR is that an excess-stoichiometric ratio is required for the DeNox process to occur, as described earlier. Additionally, several side reactions take place within the unit. These side reactions are not harmful; however, they increase the need for supplying more of the solvent (ammonia) which will increase the overall cost of the process. In addition to that, temperature control is required to keep the SCR set to the optimum catalyst temperature (equivalent to 300 °C for V_2O_5-WO_3/TiO_2 catalysts). Another limitation is that the catalysts can become coated with heavy metals and other substances, with respect to time, causing them to become poisoned. Poisoning of the catalyst occurs when sulfur, calcium, or sodium content is introduced to the unit and catalysts' surface (Dvořák et al. 2010). Finally, the cost of the catalyst and the ammonia feed/SCR is considered high when compared to an SNCR.

9.2.5 Removal of Volatile Organic Compounds (VOCs)

Methods to Remove VOCs

VOCs come in different forms, and the most common ones are aldehydes, ketones, ethers, alcohols, halogenated compounds, and aromatic compounds (Kamal et al. 2016). These compounds extend to a very wide range of molecules that include but are not limited to the following: chlorobenzenes, chlorophenols, polyaromatic hydrocarbons (PAH), benzene, toluene, and hydrocarbons varying from methane (CH_4) to pentane (C_5H_{12}). The main methods to treat VOCs include absorption, biological treatment, adsorption, thermal oxidation, chemical scrubbing, catalytic oxidation, and condensation (Shareefdeen 2019). Thermal oxidation ensures up to 99% VOC removal; however, it operates at very high temperatures exceeding 1000 °C; thus the operational cost is very high as compared to other technologies (Kamal et al. 2016; Shareefdeen 2019). It also results in high amounts of CO_2 generation as a result of the combustion process (Shareefdeen 2019). Chemical scrubbing, adsorption, condensation, and absorption processes result in transferring the gaseous VOCs into other phases (Shareefdeen 2019; Kamal et al. 2016). Biological VOC treatment methods utilize microbes to covert VOCs into harmless products, and they mainly include bio-scrubbing, bio-trickling filtration, and biofiltration (Shareefdeen 2019).

Catalytic Oxidizers

Catalytic oxidizers operate at lower temperatures (250–500 °C) when compared to thermal oxidizers (Woodard and Curran Inc. 2006; Kamal et al. 2016). The efficiency of a catalytic oxidizer reaches up to 95% (Sorrels 2017). Catalytic oxidizers consist of a flue gas inlet, a clean gas outlet, a flame generator (preheat burner), an oxygen/air stream inlet, and a catalyst bed (Sorrels 2017; Woodard, and Curran, Inc. 2006). The flue gas carrying the VOCs enters the unit at which it is subject to heat from the preheating flame, and then the VOC molecules reach the catalyst's active surface and react to form CO_2 and H_2O (Sorrels 2017).

Catalyst in Catalytic Oxidizer

There are two main types of catalysts that can be incorporated within the unit, and these include metal-supported catalysts and metal oxide-supported catalysts. Metal-supported catalysts are more expensive than the metal oxide-based catalysts; however, they demonstrate a higher efficiency due to their higher durability. Metal-supported catalysts are either mixed with oxygen or used as noble metals such as platinum, ruthenium, silver, gold, palladium, etc. Metal oxide-based catalysts include manganese oxide, copper oxide, zinc oxide, aluminum oxide, cerium oxide, cobalt oxide, nickel oxide, and lanthanum oxide (Guo et al. 2021).

Chromium oxide catalysts are known to treat halogenated compounds; however, they are also known for their toxicity, thus disposing the catalyst with regular wastes after use is a problem. Cobalt oxides are known to treat acetylene, ethyl acetate, propylene, propane, and 1,2-dichloroethane. Manganese oxide catalysts are low-cost catalysts that are known to target propane, benzene, acetone, ethanol, toluene, n-hexane and NO_x. Titanium oxide catalysts are known for their stability and wide VOC range treatment. Vanadium oxide catalysts are mostly used to treat NO_x; hence, they are not ideal for VOC treatment; however, they can also treat polyaromatic hydrocarbons. Cerium oxide catalysts are expensive, as cerium is a rare metal. Hence, they are not ideal for treating chlorinated VOCs. Copper oxides are ideal to treat methane, ethanol, acetaldehyde, and carbon monoxide (The CMM Group 2021). These catalysts are either supported on a substrate or simply, unsupported (Sorrels 2017).

As a part of reducing the operational cost, catalysts can undergo a process, referred to as catalyst regeneration, at which the catalyst is restored to its original condition. The regeneration can be done by physical, thermal, or chemical treatment. The physical treatment relies on the utilization of external sources to physically or manually remove the adhered pollutants by subjecting the catalyst either to pressurized air or water to remove the pollutant. Thermal treatment subjects the catalyst's surface to elevated temperatures that causes the adhered molecules to drop. Chemical treatment relies on the utilization of acids or bases to remove the adhered molecules by reacting with them, and this method is considered highly effective. The catalyst life prior to its loss of performance varies but generally ranges between 4 and 16 years; however, frequent cleaning of the catalyst can extend its lifetime (Sorrels 2017).

Factors that Affect the Catalytic Process

The factors that affect the VOC removal in a catalytic oxidizer include the amount of oxygen, VOC composition, flow rate of flue gas, type of catalyst, and operating temperature (Shareefdeen 2019; Ashish et al. 2019). Oxygen balance is considered an important factor that ensures complete combustion and limits the production of any harmful materials in the process (Ashish et al. 2019). One of the main disadvantages of catalytic oxidation is that the catalysts can be deactivated due their exposure to acidic gases (Sorrels 2017); however, placing an acidic scrubber prior to the catalytic oxidizer in the process avoids this problem. Selecting the right catalyst is a challenge because different catalysts eliminate different types of VOCs, as discussed previously (Guo et al. 2021). Additionally, fluctuations within the flow rates lead to the variation in VOC concentration levels. Lastly, changes in the type of feed, the presence of larger molecular size VOCs in the flue gas, etc. also affect the VOC degradation efficiency (Guo et al. 2021; Sorrels 2017).

9.3 Placement of APC Units

In general, all the pollutants emitted as a result of WtE process have deteriorating health effects including respiratory diseases, cardiovascular diseases, and cancer (De Gisi et al. 2018). For this reason, flue gas treatment prior to its release into the atmosphere is a requirement by all international environmental agencies. In this section, arrangements of APC units in the three main WtE processes, namely, incineration, gasification, and pyrolysis, are discussed.

9.3.1 APC Units in Combustion Process

Process Overview

Generally, an incineration process consists of four main feed streams including waste, ammonia, air, hydrated lime and activated carbon feed, and oxygen feed. The main unit operations consist of pretreatment units, an incinerator, air pollution control units (APC units), ash collection drums, a steam turbine, a boiler, a generator, and oxidation chambers. These APC units consist of an electrostatic precipitator (ESP), a baghouse filter, a hydrated lime and activated carbon dry scrubber, a selective catalytic reactor (SCR), and a catalytic oxidizer. Initially, the waste feed undergoes pretreatment in order to convert it into RDF. The next step is transferring the RDF blocks into the incineration chamber. In order for the incineration process to take place, oxygen or air is pumped into the incinerator to react with the waste. The resulting exit stream comprises of tar or fly ash, heavy metals, bottom ash settling at the bottom of the incinerator, and a hot gas stream filled with large particles. The process is demonstrated in Fig. 9.1 which is based on many references (Ma et al. 2020; Auzmendi-Murua and Bozzelli 2016; Sorrels 2021; Ropp 2013; Guo et al. 2018; Pallarés et al. 2018; Colomba 2015; Stantec 2011; Vehlow 2015).

Removal of Air Pollutants

- The resulting gas is sent to an ESP, which works on collecting the large-sized particles that escaped the combustion chamber. The exit stream will only contain the gaseous air pollutants and acidic gases, in addition to smaller-sized particulates.
- This contaminated stream is then fed to a baghouse filter where the smaller particles, sized 10 microns or less, that escaped the ESP are captured.
- The resulting exit stream consists of acidic gases, SO_x, NO_x, VOCs, and trace amounts of particulates. The exit stream is passed on to the hydrated lime and activated carbon dry scrubber. The hydrated lime works on eliminating the acidic gases including HCl, HF, and the SO_x gases. In a dry scrubber, hydrated lime is injected directly in the duct leading to the scrubbing chamber. Consequently, the basic hydrated lime neutralizes the acidic gases and turns them into H_2O and salts including CaF_2 and $CaSO_3$ (Kiang 2018; Tillman 2018). Additionally, activated carbon can be fed along with the hydrated lime for absorbing the dioxins, furans, mercury, nickel, and heavy metals present within the flue gas (Tillman 2018).
- The resulting stream is sent to the ammonia SCR for NO_x removal with the presence of oxygen or air. The ammonia reacts with the oxygen under the presence of a catalyst (V_2O_5/TiO_2 in this case), to convert the NO, NO_2, and N_2O into N_2 and H_2 gases. An ammonia SCR can also be used to capture the dioxins that escaped both the baghouse unit and the ESP unit, in addition to the NO_x reduction. The scrubber should be placed before the SCR due to the fact that large amounts of SO_x will lead to catalytic fouling in a very short time (Dvořák et al. 2010).
- The resulting NO_x and dioxin-free stream is sent to a catalytic oxidizer in order to convert the VOCs present in the flue gas into CO_2 and H_2O.
- The clean gas is now composed of N_2, H_2O vapor, CO_2, and trace amounts of pollutants. This stream is sent to a cooler/heat exchanger to condense the steam vapor and separate it from the CO_2 gas.

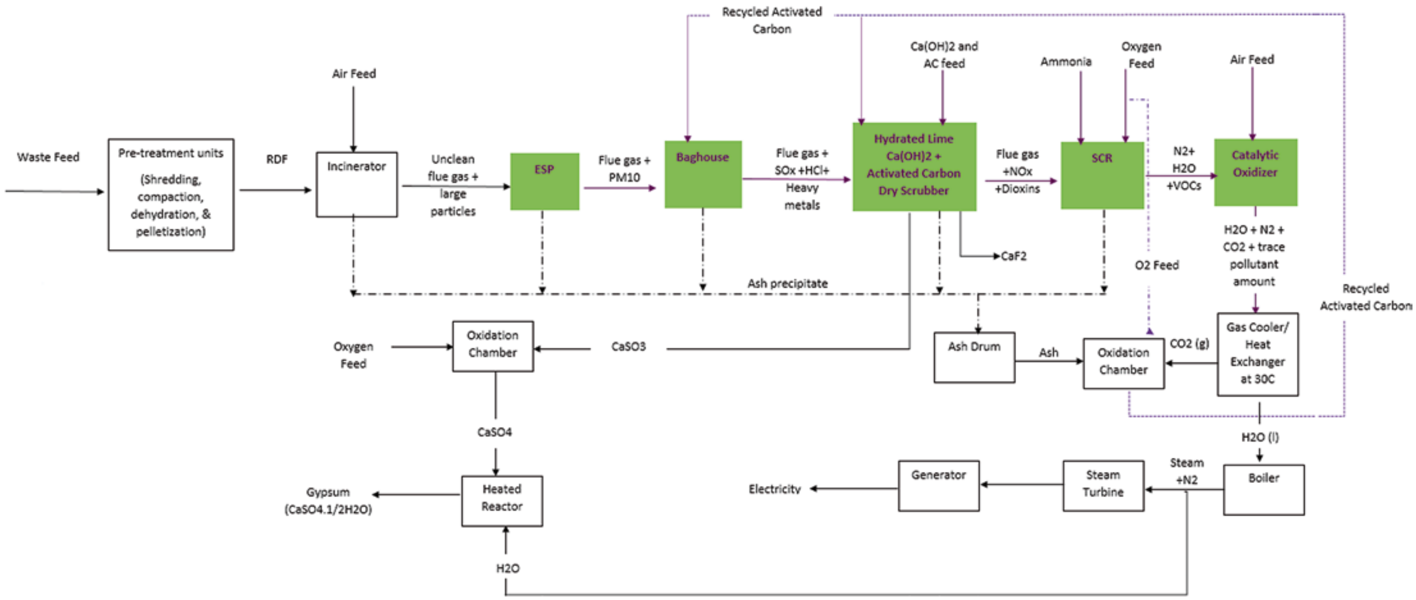

Fig. 9.1 Incineration waste-to-energy (WtE) process with APC units

Power Generation

Converting the thermal energy from combustion into electrical energy can be done in three main methods: a gas turbine, an engine, or a steam cycle (Seo et al. 2018; Shareefdeen et al. 2015). The gas turbine results in a net electrical energy efficiency of 60%; however, pollutants such as tar, chlorine, sulfur, alkali metals, etc. may damage the gas turbine. Thus, treating the flue gas is essential prior to feeding into the gas turbine for electricity generation. Instead of a gas turbine, engines can also be used with a supply of diesel or gasoline for ignition purposes. The net electrical energy efficiency of an engine is about 25%. Engine is considered more sustainable than a gas turbine because of higher resistance to pollutants within the flue gas. Lastly, the steam cycle is the simplest of all methods, and it is known to have the lowest net electrical energy efficiency reaching up to 23%, and it is supported by a boiler, present as a part of its design. The main advantage for using it besides its simplicity is that it does not require flue gas treatment in order to generate the electricity. The main disadvantage associated with it is that HCl present in an untreated flue gas is shown to result in the corrosion of the tube feeding into the turbine (Seo et al. 2018). By utilizing a steam cycle for pyrolysis and gasification, the net efficiency output can be achieved up to 27.8% (Dong et al. 2020). The generated electricity can be used in order to power up process units. Only 20% of the total generated energy is used to power up the equipment, internally within the process, and the remaining gets distributed to electricity grids (Dong et al. 2020).

Managing Generated Solid Wastes

One of the methods to manage solid waste (i.e., ash) is to collect it in a storage drum and to send it to a cement factory. Not only does this help in shifting toward greener concrete and greener buildings, but also it has been proven to enhance the properties of cement, due to the fact that it increases its yield stress (Shen et al. 2011). Furthermore, fly ash can be reacted with the generated CO_2 gas, under oxygen supply, in order to activate the carbon content and convert it to activated charcoal (AC) (Pallarés et al. 2018). This can be done after conducting a magnetic separation on the adsorbed to extract the heavy metals from the fly ash (Han et al. 2007). Calcium fluoride (CaF_2) and calcium sulfite ($CaSO_3$) are generated as by-product wastes due to the reaction between the hydrated lime ($Ca(OH)_2$) and SO_x and HF gases, respectively (Sorrels 2021; Ropp 2013). CaF_2 is a valuable compound that can be extracted and used in several applications including metal production, optical lens manufacturing, health applications, etc. (Ropp 2013). $CaSO_3$ can also be extracted and reacted with excess oxygen to produce $CaSO_4$ that can be converted to a valuable product known as gypsum ($CaSO_4.1/2H_2O$) (Guo et al. 2018).

9.3.2 APC Units in Gasification Process

The gasification WtE process is similar to the incineration WtE process in terms of APC units and energy generation. Thus, this section only highlights the differences between the gasification and incineration WtE processes. The process is demonstrated in Fig. 9.2 which is based on many references (Auzmendi-Murua and Bozzelli 2016; Czop and Łaźniewska-Piekarczyk 2020; Holmgren et al. 2012; Lv et al. 2019; Küngas 2020; Sorrels 2021; Ropp 2013; Guo et al. 2018; Colomba 2015; Stantec 2011; Vehlow 2015; Choy et al. 2004). In a gasification WtE process, after the waste feed is converted into RDF, it is directed to the gasifier where it is subject to a gasifying agent (i.e., steam). The RDF is thermally degraded into polluted synthetic gas (syngas), fly ash within the flue gas, and slag (molten bottom ash).

Prior to undergoing the APC, the syngas is subject to quenching, in order to lower its temperature and condense some VOCs into useful liquids, and to minimize the possibility of formation of undesired products. Subsequently, similar to incineration WtE process, the syngas is then directed to the ESP, followed by the baghouse, followed by the hydrated lime and activated carbon dry scrubber, followed by the ammonia SCR, and finally followed by the catalytic oxidizer. Besides waste reduction and electricity generation, gasification is also known to generate useful products such as methanol. In order to produce methanol, H_2:CO ratio should be maintained at a value of nearly 2, and the removal of CO_2 is the first step in methanol synthesis process (Holmgren et al. 2012; Küngas 2020). Methanol then can be converted to ethylene, butene, propylene, etc. (Holmgren et al. 2012). CO_2 vapors can be reduced into CO and O_2, by passing them into a solid oxide electrolyzer cell (SOEC) (Küngas 2020). The SOEC is an electrochemical cell that functions with the help of metal electrodes, a solvent, and a catalyst (Küngas 2020). This ensures that the necessary CO feed is produced and is ready to be fed into the water-gas shift (WGS) reactor, which ensures that the ideal H_2:CO ratio is met, with the help of H_2 feed (Holmgren et al. 2012). Consequently, the exit stream consists of CO_2, which can be recycled back to the SOEC, as well as methanol, which should be fed into a methanol to olefin reactor (MTO). The MTO reactor should be supplied with a catalyst to speed up the conversion reaction of methanol to olefin products (Holmgren et al. 2012; Lv et al. 2019). Lastly, the MTO reactor exit stream should undergo multiple distillation/fractionation processes in order to separate into butene, propene, and ethylene (Holmgren et al. 2012).

Unlike the incinerator, a gasifier is known to generate slag, which is the liquid form of ash. Although slag is a harmful waste by-product, it can be extracted from the gasifier and sent to a cement and mortar industry. An experimental study conducted by Czop and Łaźniewska-Piekarczyk (2020) demonstrated that the MSW combustion slag meets the requirements of the crushed and granulated furnace slag that can act as a concrete additive. Crushed and granulated furnace slag is widely used in soil stabilization, corrosion resistant applications, etc. (Slag Cement Information Sheet Index 2021).

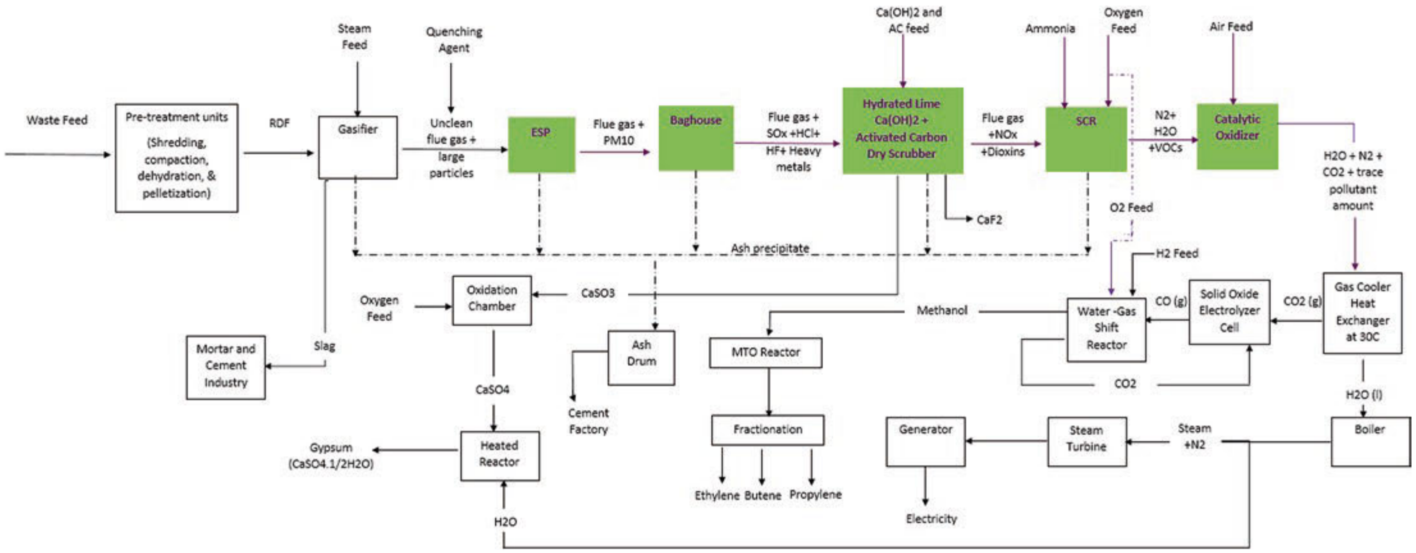

Fig. 9.2 Gasification waste-to-energy (WtE) process with APC units

9.3.3 APC Units in Pyrolysis Process

The pyrolysis process is demonstrated in Fig. 9.3 which is based on many references (Kabir et al. 2015; Auzmendi-Murua and Bozzelli 2016; Lee et al. 2021; Czop and Łaźniewska-Piekarczyk 2020; Sorrels 2021; Ropp 2013; Guo et al. 2018; Pallarés et al. 2018; Colomba 2015; Stantec 2011; Vehlow 2015). The waste feed undergoes pretreatment and is converted to RDF before feeding into the pyrolizer. After the pyrolysis reaction is complete, the resultant syngas is immediately quenched using a quenching agent to condense the condensable vapors into liquid, which is known as the pyrolytic oil. Pyrolytic oil can be distilled for further separation into individual BTEX compounds, i.e., benzene, toluene, ethylene, and xylene. BTEX are valuable and used as raw materials in various industries. Following the quenching process, non-condensable gases will remain in their vapor phase, and these gases are sent to the APC units for further treatment as follows: the ESP, followed by the baghouse, followed by the hydrated lime and activated carbon dry scrubber, followed by the ammonia SCR, followed by the catalytic oxidizer. Another quenching process is suggested to allow the steam to separate from the CO_2 gas. Similar to the gasification WtE process, pyrolysis also results in the production of the harmful by-product, slag, which can be extracted from the pyrolizer and sent to a cement and mortar industry. Furthermore, similar to the other two WtE processes, and after the activated carbon generation process, the resultant AC can be recycled back to the pyrolizer to be used as a catalyst (Lee et al. 2021).

9.4 Conclusion

In this chapter, we discussed management and control methods of gaseous and solid wastes that are generated in the three main WtE processes, namely, incineration, gasification, and pyrolysis. All of the WtE processes consist of pretreatment of the waste, followed by thermal degradation and pollutant abatement. The air pollution control (APC) units in general are arranged in WtE plants as follows: the ESP (which eliminates larger particles), baghouse filter (which captures PM_{10} and below), hydrated lime and activated carbon dry scrubber (which neutralizes acidic gases), ammonia SCR (which reduces the NOx), and catalytic oxidizer (which oxidizes VOCs). The differences in APC methods in each of the WtE processes is also reviewed. Furthermore, WtE processes also generate different types of solid wastes depending on the selected WtE process. The solid waste slag, formed in pyrolysis and gasification processes can be used in mortar and cement industries, and the $CaSO_3$ formed in the acid scrubbing unit can be converted to a more valuable product, such as gypsum. Similarly, the produced ash can be turned into activated charcoal that can be a good absorbent to remove VOCs generated within the WtE process. An efficient design of a WtE plant enables substantial waste reduction and energy generation in addition to generating valuable by-products.

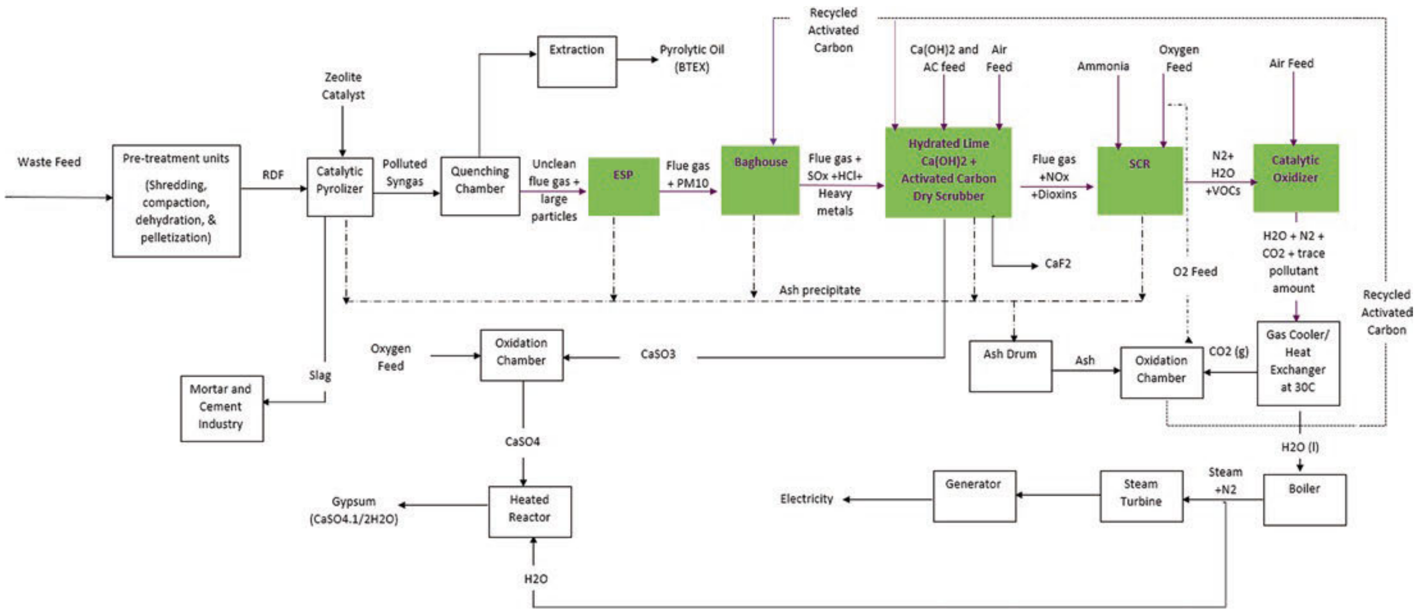

Fig. 9.3 Pyrolysis waste-to-energy (WtE) process with APC units

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Chapter 10
Advances in Hazardous Waste Treatment Methods

Victoria Corbasson, Clara Castro-Vaquero, Zack Clifford, Zarook Shareefdeen, and Ali Elkamel

10.1 Introduction

Hazardous waste is defined as waste which is harmful to the human or to the environment (EPA 2020). This definition is specific to wastes which are flammable, corrosive, or inherently toxic (Government of Canada 2017). Flammable waste poses a fire hazard, and corrosive waste can damage materials and living cells, while the effects of toxic waste on biological organisms can include but are not limited to causing cancer, death, illness, or mutations. Hazardous waste is produced from many sources including from industry and household items; however, the majority of the hazardous wastes are produced from industry. More specifically this can include chemical wastes, batteries, electronic devices, cleansers, and pesticides. Hazardous waste can take the form of either solids, liquids, or gases.

Improper or inefficient hazardous waste disposal poses a threat to the environment, human, and all other organisms which live within it. Hazardous waste can lead to the pollution of groundwater, surface water, and land. In order to combat the harmful effects of hazardous waste on the environment, the government puts in place laws and regulations regarding the transportation, disposal, and treatment of hazardous waste. The Canadian Environmental Protection Act, 1999 (CEPA 1999), affects the transportation of hazardous waste and aims to modernize hazardous waste management (Government of Canada 2017). Once hazardous waste has been produced, it must be transported either for disposal or for treatment. Most of the

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transportation of hazardous waste is done via trucks (Nathanson 2020). Once it has been transported to a treatment facility, the treatment process can proceed.

The four steps for dealing with waste are source reduction, recycling, treatment, and disposal. The first two fall under the category of waste minimization, whereas the last two should be completed when there is no chance of recovery of useful components from the waste. Hazardous waste comes from two types of sources: on a continuous basis and from an intermittent basis from facilities. The treatment of hazardous waste is an important component of dealing with waste as it will always exist. The purpose of treating waste is to modify so that it can be safely disposed. This chapter presents the current and advanced hazardous waste treatment methods used in the industry.

10.2 Key Technologies

Hazardous waste treatment methods can be categorized into three different types which include physical, chemical, and biological (Wang et al. 2019). They can be used for solid, liquid, or gaseous treatment. Some of these technologies, however, can be applied to multiple types of waste. For example, adsorption can be used toward the treatment of liquid and gaseous waste, and plasma can be used to treat solid and gaseous waste. Some key technologies are discussed in the section.

10.2.1 Waste Treatment Methods for Liquid Waste

Many modern operations, from household to industrial, involve the processing and use of liquids. Even industries which still require the use of water for purposes such as cleaning or cooling. In either case, a stream of liquid hazardous waste is generated which must be treated before it can be safely released to the environment or city water treatment facilities. For example, in the oil and gas industry, three to ten barrels of wastewater are produced for every barrel of oil (Fakhrul-Razi et al. 2009). Some of the key toxic compounds requiring treatment include polycyclic aromatic hydrocarbons, crude oil, diesel, pesticides, pharmaceuticals, and synthetic dyes to name a few.

There are many treatment approaches in current use and also under development. These treatment methods can be further categorized based upon how they remove contaminants from the waste streams. Physical waste treatment methods include adsorption, sand filtration, membrane technology, and cyclone separation. Chemical waste treatment methods include Fenton oxidation and ozone treatment, using reactions to convert high-risk hazardous chemicals into safer compounds such as carbon dioxide and water. Finally, biological treatment methods, including lagooning and biological aerated filters, rely on a biological agent such as bacteria or fungi to convert hazardous chemicals into safer ones through metabolic processes.

Adsorption

Adsorption is a commonly used method to remove contaminants from water. The water is passed through a packed bed of adsorbent material where the harmful chemicals adsorb onto, leaving behind a clean water stream. This technique can be applied to other phases of waste, although for this section the focus is on systems employing solid adsorbent for the purpose of removing hazardous materials from the liquid phase. The choice of adsorbent is key to an effective treatment system. It is desirable to have a material with high performance and low cost. The performance depends on the nature of the material and properties such as the porosity of the material. As such a common choice is through the use of activated carbon, a material made by treating charcoal to create a carbon powder with exceptionally high porosity and surface area. The small pores give lots of sites for chemicals to adsorb onto resulting in good performance as an adsorbent. One study (Demirbas 2011) reports the use of agricultural by-products as a possible adsorbent since materials such as coconut or corn husks are readily available for an almost negligible price from nearby farms or agricultural processing facilities.

Sand Filtration

Sand filtration is a physical treatment method commonly used for treating wastewater. Typically, sand filtration is used to reduce suspended materials and bacteria from water but can also be used for treating sewage water, whereby ammonia and nitrates can be decomposed into nitrogen gas (Sand Filter 2020). The main advantage of the sand filter is its simplicity and abundance of the filter medium availability. Unfortunately, the sand filter is not able to chemically convert compounds but simply separate it, meaning that the filter material must be replaced and the chemicals need further processing. Depending on the industry, it is possible to use the filtered contaminants back in the production process. For example, this is seen in conjunction with the Fenton process, discussed later, which requires a reaction creating an iron rich by-product while decomposing other hazardous chemicals. The iron can be filtered out using a sand filter and regenerated by reaction with sulfates or some other materials.

Membrane Technology

Membrane separation can be used to decontaminate wastewater and recover process chemicals. Membrane separation uses membranes with pore sizes which are small enough to filter out the particles which are unwanted/hazardous. Different types of membranes include reverse osmosis membranes, ultrafiltration membranes, nanofiltration membranes, microporous filters, and conventional particle filters. Each of these filters/membranes have different application. As such, the key to a successful treatment is a thorough understanding of the chemicals to be treated and selecting the correct combination of membranes. By selecting an appropriate combination, contaminants can be removed and separated in stages, allowing the cleaned water stream to pass through.

One of the most commonly used membrane technologies is reverse osmosis. This membrane allows only water to pass through and works by using osmotic pressure. When a stream of high contaminant concentration is placed on one side of the membrane, and fresh water on the other, the natural osmotic pressure drives the water to move toward the side of high concentration to dilute it (refer to Fig. 10.1). By applying pressure to the high concentration side in excess of the natural osmotic pressure, osmosis occurs in reverse. This means that the freshwater in the contaminated stream is driven through the membrane, leaving the contaminants separated on the other side. The membrane required for this separation is relatively fine and delicate, so it is crucial that the waste stream be pre-treated using either a coarser membrane or some other filtration mechanism to remove the large particles first.

Fenton Process

The Fenton process is a chemical treatment method used for liquid waste. This process relies on the use of the hydroxyl radical to initiate a chain reaction with the chemical waste to break down compounds such as benzene or other hydrocarbons and aromatics. The result is that the waste compounds are chemically converted into those which are safer to be released such as carbon dioxide and water (Xu et al. 2020). This is a major advantage over many of the other methods as the hazard is eliminated rather than just separated out for further treatment.

The Fenton process is carried out through the reaction of hydrogen peroxide with ferrous salts to produce the hydroxyl radical. This radical then reacts with the hazardous organic compounds to oxidize and break them into safer or less toxic byproducts. A side reaction can also take place, whereby the Fe^{2+} is oxidized into Fe^{3+} by the hydroxyl radicals. This side reaction is minimized by running the Fenton process at a pH of less than 3 (Xu et al. 2020). Finally, the Fe^{2+} can be regenerated through reaction with radicalized alkyl (R) groups produced during oxidation, which can help to minimize the iron consumption. The traditional chemical reaction mechanism of the Fenton process is as follows:

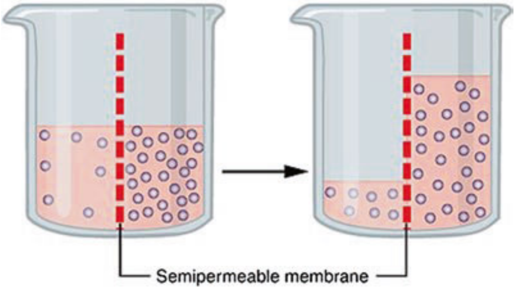

Fig. 10.1 Osmosis effect (Osmosis 2021)

$$Fe^{2+} + \mathrm{H_2O_2} \rightarrow Fe^{3+} + \bullet OH + OH^- \tag{10.1}$$

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^- \tag{10.2}$$

$$RH + \bullet OH \rightarrow \mathrm{H_2O} + \mathrm{R} \rightarrow \text{further oxidation} \tag{10.3}$$

$$\mathrm{R}\bullet + Fe^{3+} \rightarrow Fe^{2+} + \mathrm{R}^+ \tag{10.4}$$

Unfortunately, in addition to the hydroxyl radicals, this process accumulates Fe^{3+} ions, leaving an iron-rich sludge phase which must undergo further processing. The iron is commonly removed using the previously mentioned sand filtration method, allowing it to be recovered for future waste treatment use after regenerating the iron into a salt (Lenntech Water Treatment Solutions 2020).

Another advancement in the Fenton treatment process is the photo-Fenton process. By introducing UV radiation into the process, the conversion rate from Fe^{3+} to Fe^{2+} can be enhanced. This step limits the rate at which waste can be treated; thus the photo-Fenton process offers a higher treatment throughput compared to the regular Fenton process. In addition to increasing the rate, the introduction of UV radiation has the secondary effect of decreasing the catalyst dosage which reduces the accumulation of iron into the sludge by-product, helping improve the largest drawback of Fenton process (Xu et al. 2020). Unfortunately, the photo-Fenton method is currently prohibitively costly.

Ozone-Based Technology

Ozone treatment is a chemical method which relies on the use of free radicals to engage in reactions with the hazardous waste to break these compounds down into safer ones. The process is similar to the Fenton process except instead of requiring a ferrous salt to initiate and catalyze the radical production; ozone is able to react directly producing radicals (Pryor 1994). This offers a cleaner overall treatment solution as the by-product seen within the Fenton process is not incurred here, eliminating a further step. This technology is very promising as it chemically converts the hazardous chemicals and does not have the same by-product issues seen in many other chemical treatment methods.

Lagooning

Lagooning is a biological treatment method, relying on the use of a biological agent such as bacteria to break down hazardous waste materials during the metabolic process (refer to Fig. 10.2). This method is commonly applied in industries which discharge nitrogen-containing compounds such as ammonia and have nearby land to deal with treating the water. For example, mining, oil processing, and metal finishing industries often utilize this method. When the nitrogenous compounds are

Fig. 10.2 A lagoon used for biological treatment of wastewater (Facultative Lagoon 2021)

introduced into the bacteria-filled lagoon, the bacteria begin to metabolize the compounds, using them as nutrients for growth.

This method is convenient and reasonably inexpensive, as it requires only the bacteria culture and a location large enough to place a lagoon in, however it is not without drawbacks – the largest being the possibility of chemical leaching. Since these lagoons are frequently placed directly in the ground without any barrier, the hazardous waste is introduced into an environment where it can escape into the soil through leaching. This can be prevented by lining the lagoon with an impermeable layer, though this is often not cost-effective. Additionally, there is less control with this method as it is an open batch process by which environmental factors can affect the components in the lagoon and the rate of metabolic reactions.

Biological Aerated Filter

The biological aerated filter, or BAF, is another biological treatment method developed to address the technical drawbacks of other methods. By immobilizing the bacteria onto filter materials, the waste stream can be contacted with the bacteria in a more controlled manner. Additionally, the size of the filtration unit when compared to the required size for a more standard lagoon treatment is a major advantage for industrial sites where space is of a concern. Furthermore, the issue of leaching seen with the more standard lagooning biological treatment is eliminated here as the BAF is a piece of process equipment which can be connected into existing process piping systems, ensuring no accidental release of hazardous materials. Further developments into biological treatment include the investigation of the potential for other biological agents such as fungi to be used in place of bacteria. Fakhrul-Razi et al. (2009) report 94% treatment efficiency in the removal of oil content by using a BAF, which is comparable to the results seen using lagooning but without any of the aforementioned risks posed to the environment.

10.2.2 Waste Treatment Methods for Gaseous Waste

Volatile organic compounds (VOCs) are considered to be a gaseous hazardous waste or hazardous air pollutants (HAPs) which fits into the toxic category. Some examples of VOCs include acetone, benzene, formaldehyde, heptane, hexane, and more. They are also dangerous due to their ability to damage the ozone layer and produce a smog when they react with nitric oxides. VOCs come from many sources, and 25% of VOC production comes from human activity. This includes cooking, smoking, the use of fossil fuels, and industrial processes which are the main source. Some methods for treating them include (1) incineration, (2) photocatalysis, (3) nonthermal plasma, (4) biological abatement, (5) adsorption, (6) liquid solvent absorption, and (7) membrane separation. The first four methods are considered to be destructive technologies, and the last three are considered to be recycling technologies which are elaborated below.

Adsorption

Adsorption is the process of when particles from a gas or liquid adhere onto a surface. Adsorption is a method which has high efficiencies depending on the chosen adsorbent and is cheap, and stable. Gas adsorption is a mass transfer process of when an adsorbate (gas) is attracted to an adsorbent (solid material). The process occurs in three steps: the adsorbate diffuses near the adsorbent, diffuses into the pores of the adsorbent, and adsorbs to the surface of the pore wall. There are two types of adsorption: physisorption and chemisorption. For physisorption the gas molecule is attracted by weak van der Waals forces. For chemisorption the gas molecule forms a chemical bond with the surface which is stronger than van der Waals forces. Typically for more adsorption to occur, a larger surface area is needed. Activated carbons are commonly used to adsorb VOCs.

Liquid Solvent Absorption (Scrubbing)

Liquid solvent absorption is also known as scrubbing. It can be used to remove VOCs by contacting them with a suitable liquid which dissolves the VOCs into the liquid. This method of removal is considered to be a mass transfer process. The gas absorption takes place through a stagnant or nondiffusing liquid. Just as with adsorption, absorption has two types: physical and chemical absorption. Chemical absorption refers to when there is a reaction occurring alongside the absorption. Liquid solvent absorption is widely used for the capture of VOCs due to its simplicity, low cost, and recyclability.

Membrane Separation

Gas membrane separation is a method in which gases can be separated by membranes. Sometimes these membranes are made of polymers or of ceramic materials. Membrane separation works by allowing smaller particles to pass through the pores of a membrane, while stopping larger particles from passing through. Membranes have been reported to have difficulty with fluctuating concentrations of VOCs in the air.

Photoelectrochemical Oxidation

Photoelectrochemical oxidation (PECO) is a method which can be used to remove allergens from the air (Rao et al. 2018). This process combines the use of a physical filter and a photoelectrochemical reaction in which an organic material is oxidized. The pollutants which can be removed from air by this method includes bacteria, viruses, mold, and VOCs such as benzene or formaldehyde.

Nonthermal Plasma

Nonthermal plasma is a technique which is used to treat air pollution. Plasma, ionized gas, is used for the treatment of VOCs. Nonthermal plasma has also been used to disinfect objects such as food in the food processing industry, and it has application in solid hazardous waste treatment.

Photocatalysis

Photocatalysis is when a photoreaction is enhanced with a catalyst. This is a destructive method which is used for treating VOCs in the air. Photocatalysis is an advanced oxidation process (AOP) which typically uses titanium dioxide as the catalyst for the treatment of VOCs. Titanium dioxide is chosen as the catalyst for its many properties such as its chemical inertness, physical stability, low price, and strong oxidizing abilities. Photocatalysis has also been used in the treatment of liquid waste.

VOC Removal Technologies from Recent Studies

Removal of VOCs using biochar: Zhang et al. (2021) report adsorption using biochar as the adsorbent for the removal of VOCs from the air. Biochar is charcoal produced from pyrolysis of biomaterial in the absence of oxygen. The choice to use biochar is based on the availability, low cost, and high efficiency. Biochar has been used to adsorb VOCs including acetone, toluene, and cyclohexane. According to Zhang et al. (2021), biochar was found to perform better than activated carbon.

Removal of VOCs from indoor air using different adsorbents: Mondal et al. (2021) report a study on the removal of VOCs from indoor air. This study compares different activated carbon-based filters based on their efficiency and surface area. The most efficient material for adsorption was found to be bamboo charcoal at 72.3% efficiency, and the least efficient was phosphoric acid activated carbon at 34.7%. In terms of specific VOCs, steam-based activated pecan shell performed the best for the removal of bromodichloromethane, carbon tetrachloride, trichloroethane, chloroform, and dichloroethane. Coal-based activated carbon performed the best for the removal of benzene from the air. Bamboo-based activated carbons were found to be the best overall with an adsorption efficiency of about 70%. They are found to be chemically stable, readily available, and an inexpensive option in place of other adsorbents.

Removal of VOCs using ionic liquids: Yu et al. (2020) report the use of liquid solvent for the removal of VOCs. This study is related to ionic liquids (ILs) which can be used to efficiently remove toluene from the air. The designed ILs had an absorptivity of up to 99.992% for toluene at ambient conditions. It is suggested that these ILs will also have high absorption efficiencies for other VOCs such as benzene, ethylbenzene, and xylene. The performance of the ILs did not decrease with the reuse of the ILs, suggesting great recyclability.

Removal of VOCs using microbubbles: Sekiguchi et al. (2020) report a study on the use of microbubbles (MB) for absorbing toluene in water. The capture efficiency was compared between bubbles of different magnitudes. These include microbubbles, millimeter-order bubbles, and centimeter-order bubbles. It was found that, using a starting concentration of 40 ppm toluene, the capture efficiency was highest for the microbubbles and lowest for the centimeter-order bubbles. This difference is thought to be due to the difference in the rising speed of the bubbles; a lower speed resulted in a higher efficiency. The study also looked at the effects that different oily substances may have on the capture efficiency including rapeseed oil, mineral oil, silicone oil, and oleic acid. Table 10.1 lists comparative results reported by Sekiguchi et al. (2020).

Removal of VOCs using membrane technology: Rolewicz-Kalińska et al. (2021) report a study on the use of membrane separation technology for the removal of VOC, H_2S, and NH_3 at three different plants: municipal solid waste treatment plant, a food industry, and a wastewater treatment plant. The type of filter used was a two-stage membrane filter consisting of a filter bed with membrane fabric. The effectiveness of the system was measured based on removal efficiency and elimination

Table 10.1 Absorption of toluene in water with different oils (Sekiguchi et al. 2020)

	Absorption efficiency (at 24 h)
Rapeseed oil	100%
Mineral oil	97%
Silicone oil	87.1%
Oleic acid	84.8%

capacity. Rolewicz-Kalińska et al. (2021) report high removal of VOCs ranging from 89% to 98%.

If VOC removal methods result in hazardous solid wastes, there are technologies to convert them into inert material which can be safely disposed in a landfill or returned into its life cycle or reused. The technologies such as thermal plasma or accelerated carbon treatment can alter the hazardous nature of a material or reduce toxicity levels. In selecting the right technology for VOC removal, it is also important to examine the associated costs along with the removal efficiency of each technology. Often two dissimilar technologies may not be directly compared as one measured the performance based on elimination capacity and the other measured the performance based on efficiency. Thus, it is important to include different parameters in technology comparison before selecting the optimum method for VOC removal application of interest.

10.2.3 Treatment Methods for Solid Waste

There are many methods available for the treatment of solid waste including plasma technology and accelerated carbon treatment. Waste management and minimization as well as recycling methods are also very effective ways of dealing with solid waste.

Waste Management

Waste management is described as the collection, transport, processing, recycling or disposal, and monitoring of waste materials. Its purpose is to provide sanitary living environments, reducing the amount of wastes produced, and encouraging reusing instead of disposing. It is also important to consider local facts such as waste characteristics, seasonal variations, social aspects, and cultural attitudes as well as having awareness of possible resource limitations. To be able to use waste management to the best of its abilities, it is important to develop waste and recycling plans prior to the start of any projects in order to sustain environmental, economic, and social development principles.

One of the main strategies that can be used to minimize landfill waste is recycling. There are many types of recycling including physical repurposing, biological reprocessing, and energy recovery. Resources can be recovered from solid wastes and reduce the amount of waste discharged into the environment. Although the common methods to deal with solid wastes are landfilling and incineration, a better way to deal with municipal solid waste is composting which is a natural biological process.

It is also important to properly manage hazardous waste, as it can be deadly and cause harm to humans, animals, and the environment. It is important to establish proper waste management practices to avoid loss of resources and energy (Demibas 2011). When it come specifically to hazardous solid waste management, it is important to ensure safe, efficient, and economical collection, transportation, treatment, and disposal. The idea for the treatment of hazardous waste is to modify the physical and chemical properties of the waste to become suitable for disposal.

Some of the technologies used to treat hazardous waste include acid-base neutralization, incineration, and chemical fixation/solidification. These technologies are characterized by the efficiency in treating specific waste types, waste residue gratification factor, and costs and risks associated with them. The methods used in the disposal of hazardous waste depend on the type of waste that needs to be treated. Proper hazardous waste treatment and disposal needs to be planned to protect people and the environment from any harmful effects. Options for disposal include deep well disposal, solidification and stabilization, incineration, ocean dumping, sanitary landfill, and land burial. Usually, the choice of disposal is based on the evaluation of economics and potential pollution risks. Overall, hazardous waste treatments are expensive; it is more economically viable to reduce wastes in general, which includes the waste minimization concept and simple waste reduction systems (Misra and Pandey 2005).

Thermal Plasma Technology

Plasma technology is used to destroy the organic fraction of the hazardous wastes, and it converts the inorganic fraction to inert silicon slag or glass that can later be reused or placed in a landfill. Plasma is the fourth state of matter which consists of a mixture of electrons, ions, and neutral particles. Overall, it is electronically neutral with the degree of ionization controlled by mostly temperature. Plasma technology creates and sustains an electrical arc of passage of electrical currents through a gas. The plasma production methods used to treat hazardous waste include the DC plasma torches and the inductively coupled plasma devices.

The main issue with plasma technology is that at high process temperatures some metals vaporize and are carried out through the process with halogens and other acid gasses. The acid gas output can be reduced, and most of the gas will have to be recycled, reprocessed, or disposed. The process requires a gas abatement technique for remedial treatment. The types of hazardous wastes that can be treated by plasma technology include residues from waste-to-energy process, asbestos-containing residues, healthcare waste, waste from steelmaking, electroplating waste, aluminum dross, and carbon- and chlorine-containing wastes. The technical feasibility of plasma technology has been demonstrated for many types of hazardous waste, but it is unclear that that the treatment is economically viable in a large scale. There is still a remaining area of growth for plasma technology, and with the avoidance of landfill charges, the recycling of vitrified product and production of syngas can improve commercial viability for plasma technology (Gomez et al. 2009).

There are many different types of plasma technology including plasma pyrolysis, plasma gasification, and plasma compaction. The method of treatment depends on the type of waste. Plasma pyrolysis is used for organic hazardous waste, while plasma gasification and compaction are used for inorganic materials. Plasma pyrolysis works by thermally breaking down chemical components of the hazardous waste without oxidation (refer to Fig. 10.3). Plasma gasification uses the incomplete oxidation of organic components of the hazardous waste. This process produces gases that can be used for generation of hydrogen and later used for gas engines to generate electric power. Plasma compaction and vitrification gasify the organic material and melt inorganic materials. The most widely accepted treatment method is the vitrification of incinerator ash which can be immobilized by plasma treatments. Plasma treatment can be the final stage of treatments for many hazardous waste treatment remains as it will turn the toxic compound inert and safe for disposal (Heberlein and Murphy 2008).

Treatment of Electronic and Electronic Equipment Waste

Electrical and electronic equipment waste (e-waste) is considered hazardous due to the presence of heavy metals, flame retardants, and other potentially hazardous substances. If not managed properly, the substances present can have significant human

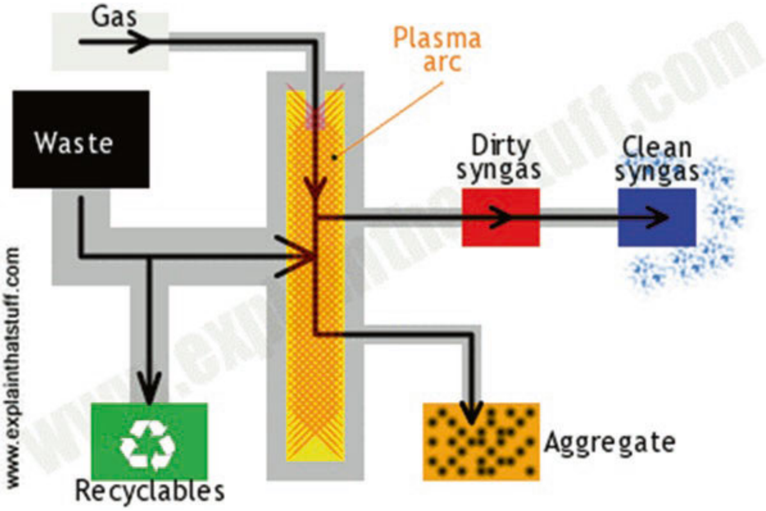

Fig. 10.3 Use of plasma in waste treatment (Plasma recycling 2021)

and environmental health risks. When dealing with e-waste, the major hazards arise with the size reduction, separation, and pyrometallurgical treatment steps. Other end-of-life treatments like incineration and landfilling also add on to the risks of disposing of e-waste due to the emissions of metal fumes as well as leaching in landfills. It is also dangerous to recycle e-waste as the manual disassembly as well as recovering solder and chips from the waste by heating them can be hazardous. Acid extraction of metals, melting of plastics, and burning of plastic and isolate metals are also very hazardous to workers in recycling plants. Therefore, for the safety and minimizing the exposure of these hazardous materials to the workers, it is important to use correct methods to properly recycle e-waste (Tsydenova and Bengtsson 2011). The best way to deal with electric or electronic waste is by implementing recycling stages.

The three main processes are disassembly, upgrading, and refining. The first process of disassembly targets or singles out hazardous or valuable components in the e-waste with recent advancements using robots to complete this task. The second process is upgrading and can use a variety of methods to upgrade the desirable material content. Screening is the first method that can be used to upgrade and works by screening the metals with a rotating trammel (refer to Fig. 10.4). The unit used has a high resistance to blinding and is important when there is a diverse array of particle shapes and sizes present in the e-waste. Other techniques used for screening include shape separation and magnetic separation. Another form of upgrading is using eddy current separation. This method is used by exerting electric conductive particles from repulsive forces that are made from interacting between the alternative magnetic field and eddy currents induced by the magnetic field. Corona electric separation is another screening method caused by a corona charge and differentiated discharge leading to different charges of particles and therefore different forces used to separate the materials. The last method that can be used for screening is triboelectric separation. This method makes a tribocharge with either positive or negative charges of the components that cause different force directions. The last step in the recycling of e-waste is refining which includes recovering materials so they can return to their life cycle (Cui and Forssberg 2003).

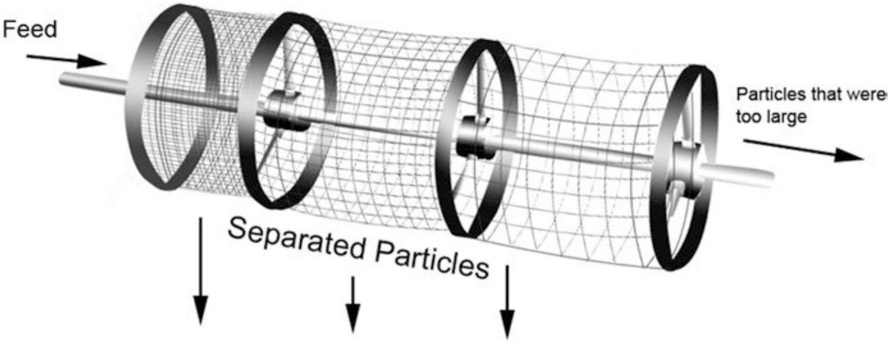

Fig. 10.4 Trommel screen (Trommel 2021)

Accelerated Carbon Treatment

The way this treatment method works is by exposing the waste to pure carbon dioxide gas and is used to treat industrial waste to reduce the toxicity and alleviate logistical and economic issues. The treatment works by placing waste in a pressurized reaction vessel with carbon dioxide gas. Accelerated carbon treatment is known to be effective in reducing the leaching of lead and barium, but there is increased levels of antimony and chromium. All the other metals are left unchanged, but the treatment reduces the corrosive nature of the waste. Through this treatment overall reduction of mobility of some metals is achieved (Gunning et al. 2010).

10.3 Conclusions

In this work, different technologies used in the treatment of liquid, gaseous, and solid hazardous waste are discussed. For liquid waste, there are many options for effective waste treatment depending on the waste stream to be treated. The more cost-effective treatment methods tend to separate waste rather than treat it. However, free radical chemical treatment and biological treatment result in a cleaner overall treatment as they break down the hazardous components into safer ones. Overall, better waste management and elimination at the source is the ideal solution to the problem of hazardous waste. A thorough understanding of the waste stream and a combination of several treatment methods together may offer efficient treatment for hazardous wastes. In future studies, it would be very beneficial for an actual in-depth cost analysis to be performed on implementing the emerging technologies so that a more realistic comparison can be made. While the existing liquid waste treatment technologies have been found to be effective within industry, further research into improving efficiency and reducing risks is always beneficial. There needs to be more innovation in the methods of treating solid waste as well as making the current methods more commercial friendly.

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Chapter 11
Hazardous Waste Transport in the Environment

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11.1 Introduction

Hazardous waste is defined by the US Environmental Protection Agency (EPA) to be any waste that is dangerous or capable of causing a harmful effect on human health or the environment and is generally generated in manufacturing processes (US EPA 2020). Hazardous waste can exist in solid, liquid, or gaseous forms. Waste can be hazardous if it is reactive, infective, radioactive, toxic, corrosive, or ignitable. Some examples of hazardous waste in the environment include heavy metals (e.g., Hg, Pb, Zn, Ni, Mn, etc.), radioactive elements (e.g., Pu), arsenic, cyanide, non-aqueous phase liquids (NAPLs) (e.g., trichloroethylene, TCE), pharmaceuticals, toxic microplastics (MPs), and acidic gases (NO_x, SO_x).

Hazardous waste can originate from numerous places such as electronic products (e-waste), landfill leachate, biomedical, nuclear plants, manufacturing and industrial processes, mining activities, agriculture, fossil fuel burning, wastewater treatment, chemical spills, etc. The proper transport, treatment, storage, and disposal of hazardous wastes are critical for maintaining a safe environment for all. Thus it has compelled governments to regulate hazardous waste and its transport through stringent environmental laws (Nathanson 2020). This chapter examines how hazardous waste is transported through the air, subsurface, and water based on several case studies.

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11.2 Transport of Pollutants in the Air

Chemicals are transported in air through diffusion and convection. Diffusion occurs in gases, liquids, and solids, but the diffusion coefficient in gases is four orders of magnitude greater than in liquids and nine orders of magnitude greater than in solids. Hazardous waste transport through air is much more complex as it includes reactions with water vapor, ozone, volatile organic compounds (VOCs), and other chemicals in the air. While diffusion through gases is the starting point for hazardous pollutants transfer in air, convection also plays a critical role in the transfer of hazardous waste. To accurately understand the complexities of convective mass transfer for real-world applications, a deeper understanding of fluid mechanics and mass transfer is needed. Based on the theory, several air pollution predictive models are developed to evaluate transport of pollutants in the air.

Recommended software tools such as AERMOD, CAL3QHC/CAL3QHCR, CTDMPLUS, OCD, etc. from the US Environmental Protection Agency (EPA) are available to evaluate pollutant dispersion in air. For example, AERMOD modeling system is a steady-state plume model that includes air dispersion based on planetary boundary layer turbulence structure. Concentration predictions can be made through AERMOD which can be applied to both surface and elevated air emission sources and both simple and complex terrains (US Environmental Protection Agency 2017). Figure 11.1 shows a typical concentration profiles predicted by AERMOD. Azlah et al. (2018) applied another important dispersion model, CALPUFF, to predict pollutant concentrations and dispersion of a pollutant known as dimethyl sulphide (DMS) under various atmospheric conditions. Practically modeling software such as these are widely used to understand the transport of hazardous pollutants in air.

11.2.1 Case Studies Related to Pollutants in the Air Phase

In this section several case studies related to pollutants in the air phase are discussed.

Pollutants from Fossil Fuel Combustion

Traffic and transportation emissions are a large source of hazardous waste in the air. The US EPA identified 188 hazardous air pollutants (HAPs) that come from human production (Tchepel et al. 2012). These HAPs are dangerous because of their toxicity and serious negative effects on human health. Some specific HAPs from traffic are formaldehyde, 1,3-butadiene, naphthalene, and particulate matter (Tchepel et al. 2012).

Yang and He (2016) investigated the impact of the fuel cost and demand have on road transport pollution in China. China has seen very fast economic growth in the past three decades. Air pollution has increased and been blamed largely on the

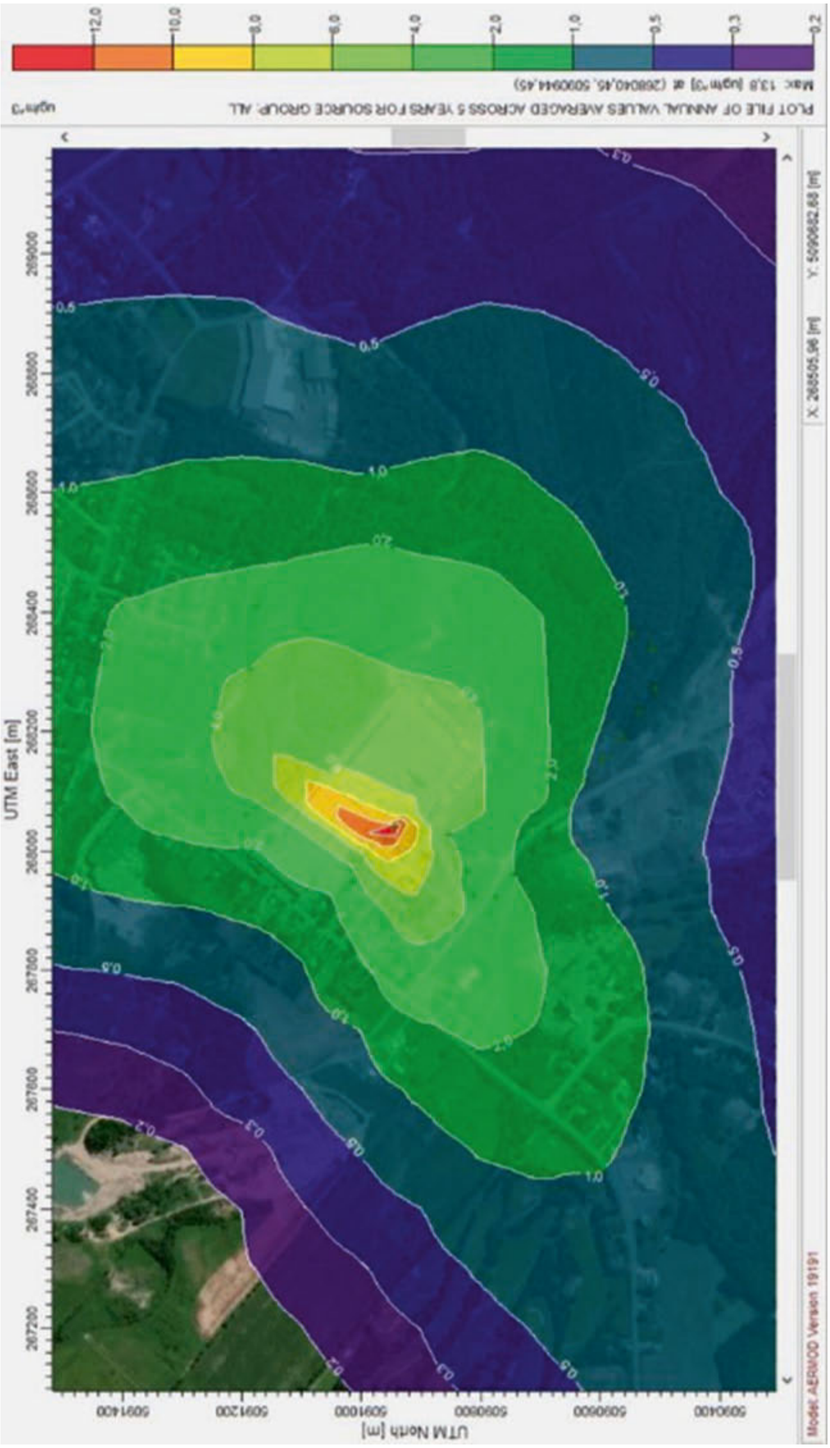

Fig. 11.1 Prediction from concentration profile using AERMOD (Dispersion modeling 2021)

transportation sector (Yang and He 2016). They investigated diesel and gasoline supply and demand between Chinese provinces. The emissions under study were carbon monoxide, nitrogen oxides, and particulate matter smaller than 2.5 microns (CO, NO_x, and $PM_{2.5}$). Their conclusions unsurprisingly found that if fuel prices increases, demand decreases, and resident health improves. Two other commonly discussed air pollutants are NO_x and SO_x. These nitrogen and sulfur oxides come from the combustion of fossil fuels, specifically coal and oil because they have a higher sulfur content. These oxides are responsible for acid rain which has harmful environmental effects as it can lower the pH of soil and groundwater over time and cause aluminum leaching from soil clay particles. Aquatic environments experience the effects of acid rain the most. NO_x and SO_x which are produced through fossil fuel combustion are transported by air currents which can carry the pollution quite far. For example, the pollutants produced in industrialized northeast side of the USA are transported to the North by polar jet stream and into the Eastern part of the Canada and the Maritimes where they precipitate with rain and alter the environment. The mechanism that they are transported also depends on what other chemicals present in the atmosphere and what type of chemical reactions occur (Office of Technology Assessment 1984).

Emissions from Lagoons and Landfills

Hazardous waste comes from many sources including manufacturing industries, hospitals, and laboratories. As these sectors have continued to grow, the amount of waste they produce has followed suite. Industrial manufacturing is the largest producer of toxic waste, and its disposal must be done properly to protect people and the environment. In 1981, the USA produced approximately 264 million metric tons of hazardous waste, and about 80% of these wastes were deposited in lagoons, ponds, pits, landfills, open dumps, and deep well injections (Shen 1985). Of this waste, the US EPA reports 70% were organic compounds that could create toxic emissions or cause air pollution problems when not managed properly (Shen 1985).

Air monitoring is performed to evaluate the emissions coming from the storage facilities, but it is often done only at few specific sampling locations in a large site, and the results can vary based on the procedure followed, meteorological conditions, and who performed the test (Shen 1985). However, spot air sampling was considered the best available technique. Applying emission models for air quality assessments is more accurate but requires more knowledge of the site, specifically the quantity and type of waste deposited. Emission modeling can be faster and cheaper than traditional air concentration measurements; however, models require experimental data for refinement and sufficient input information to be accurate and trustworthy (Shen 1985).

Emissions from Industrial Hazardous Waste Incinerators (IHW)

Hong et al. (2017) performed a life cycle analysis of industrial hazardous waste (IHW) including toxic chemicals, heavy metals, and irradiation substances. China has seen an average annual increase in IHW production of 12.3% each year for the past decade. IHW is less than 1% of the overall waste produced in China, but its harmful nature makes it very disturbing. A final outcome for their work was creating an IHW disposal inventory designed specifically for China. The largest overall consequence of IHW under study was an increased carcinogen risk for people in China. The cause of this was predominantly the consumption of diesel, cement and sodium hydroxide production, transportation, electricity generation stages caused by direct mercury and arsenic emissions, and indirect chromium emission (Hong et al. 2017). In this case study, they concluded that less hazardous waste would be produced in the air by increasing efficiencies, minimizing the use of products that create IHW, developing new air pollutant control systems, improving IHW reuse and recycling technologies, and reducing distances between IHW originators and disposers (Hong et al. 2017).

Polychlorinated Dibenzo-P-Dioxin and Dibenzofuran (PCDD/F) Emissions

Polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) are hazardous compounds emitted from incineration plants. Rivera-Austrui et al. (2011) evaluated the performance of a continuous monitoring system for the analysis of PCDD/Fs from stationary sources at a modern hazardous waste thermal treatment plant. The emissions coming from incineration plants is highly dependent on the configuration of the incineration plant. Incineration can be a source of many hazardous pollutants such as nitrogen oxides, sulfur dioxide, carbon dioxide, hydrogen chloride, particulate matter, and metals (lead, chromium, cadmium, and arsenic) as well as volatile organic compounds (VOCs) (Rivera-Austrui et al. 2011). PCDD/Fs are the focus of their study because of high toxicity and persistence even though they are normally present at low concentrations. Wang et al. (2019) studied PCDD/F formation mechanisms by adding three different precursors to phenol containing raw material and analyzed the flue gas, bottom ash, and fly ash, and three stages in the incineration facility to investigate formation pathways, emission characteristics, and mass balance of PCDD/Fs. This study tracked PCDD/F formation pathways and identified the dominant formation mechanisms by adding precursors to the feed of a full-sized hazardous waste incinerator (HWI). Wang et al. (2019) evaluated the efficiency of the quenching tower in stopping PCDD/F formation.

Emissions from Co-Processing of Hazardous Waste in a Cement Kiln

Zhu et al. in 2019 investigated the use of cement kilns to treat hazardous waste. Their study was on the evolution and transformation of chlorine during co-processing of hazardous waste incineration residue in a cement kiln. If there is too much chlorine in the hazardous waste, it will negatively impact the cement kiln operation and the quality of cement products (Zhu et al. 2019). They studied how chlorine behaved throughout the co-processing and measured it in the flue gas, the clinker, and the fly ash under different environmental conditions. They found that chlorine was primarily contained in the flue gas and clinker. Less than 1% of the chlorine entering the kiln is left in the fly ash (Zhu et al. 2019). They found that with a higher kiln operating temperature, more chlorine was found in the flue gas compared to the clinker but stopped changing once the temperature exceeded 1300 °C. The fly ash contained roughly 0.5% of the inlet chlorine regardless of operating temperature or retention time. They also found a longer retention time was connected to a larger amount of chlorine in the flue gas. There is a dechlorination reaction occurring between hydrochloric acid and calcium oxide to form calcium chloride and water. They also noted that the amount of chlorine fed to the kiln had little effect on how the chlorine portioned in the different outlet streams (Zhu et al. 2019). They conclude, in order to maintain a high-efficiency kiln in this co-process, close regulation of the chlorine entering the cement kiln is needed (Zhu et al. 2019).

Emissions of Heavy Metals from Hazardous Waste Incineration

Chen et al. (2020) studied immobilization of heavy metals in hazardous waste incineration residue using SiO_2–Al_2O_3–Fe_2O_3–CaO glass ceramic, and they explored how hazardous waste incineration residue (HWIR) can be turned into glass ceramics to immobilize the hazardous waste. The HWIR investigated in this study contained heavy metals: zinc, copper, and chromium. The melting-sintering process of making the glass ceramic physically immobilized the heavy metals. The glass ceramic is formed by heating a raw material until it has melted and is usually done at around 1300–1500 °C. Then this hot material is quenched with water to form an amorphous glass that can have crystallization embedded in its already amorphous matrix through a heat treatment process (Chen et al. 2020). HWIR is a good raw material for a SiO_2–Al_2O_3–Fe_2O_3–CaO glass ceramic because it already contains the necessary building components for the structure. This study used 100% HWIR as feed material to increase efficiency and decrease the cost of the process.

The physical encapsulation and the ion exchange are the primary ways the heavy metals were immobilized (Chen et al. 2020). The safety and stability of the samples were evaluated through leaching experiments using the toxicity characteristic leaching procedure (TCLP). X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, field emission scanning electron microscopy (FE-SEM) with energy dispersive spectrometry (EDS), and heavy metal morphological analysis are used to determine how well the heavy metals were contained (Chen et al. 2020). Chen et al. (2020) created 78 samples and found that the immobilization reduced the leaching of the heavy metals by 99%, well below the US EPA limit. The study adjusted four parameters to create varied glass ceramic materials but found that crystallization temperature and heat treatment had the largest impact. The optimal operating parameters were crystallization temperature and time of 1080 °C and 1 h, respectively, and a nucleation temperature and time of 760 °C and 1 h, respectively (Chen et al. 2020).

11.3 Transport of Hazardous Waste Through Surface Water

The transport of hazardous waste through surface water concerns the pollution of any water found above ground, which includes oceans, seas, rivers, streams, lakes, wetlands, and man-made reservoirs and waterways. Toxic contaminants from the hazardous waste can enter surface waters through a variety of means, from both point and nonpoint sources. Waste can be discharged directly into a water body, thus releasing the contaminants, or they may travel through land surface runoff and leachate from subsurface, or even be deposited by the atmosphere via the water cycle. The contaminants may also manifest themselves differently in the water. It is possible that they can be dissolved directly into the water, but, more commonly, they tend to be attached to carrying particles such as sediment, silt, sand, dust, and organic matter (National Research Council 2000).

In natural surface waters, the subsequent transport and travel of the contaminants depend largely on the movement patterns of the water, although advection and dispersion are the main factors. Tides, currents, and elevation changes carry water bulk to different geographical areas and thus the contaminants with it. It follows that a river or stream will have a much higher velocity and flux of water volume than when compared to a more stationary body of water, such as a lake or even an ocean. Simultaneously, a small stream does not have the same dispersion power as a vast ocean does. Within a control volume, water can also experience thermal stratification, eddies, turbidity, and sediment disturbances that will push around the contaminants (Vallero 2014). These effects are more prominent in water bodies such as estuaries, where it may be more difficult to describe or model the water movement. The physical and chemical processes through which contaminants may be exchanged between dissolved phases and particulate matter include adsorption and desorption, precipitation and dissolution, and different types of degradation.

11.3.1 Major Surface Water Pollutants

In this section, some of the major pollutants found in the surface water are discussed.

Oil Spills

A common example of hazardous marine waste is the infamous and unfortunately regular occurrences of oil spills in the oceans, coming from off-shore rigs or from cargo ships. Oil spills encompass more than just crude oil; gasoline, diesel, kerosene, and intermediate oils, all adversely affect the marine environment and are considered hazardous. The spills can happen through ship collision, wrecking, pipeline bursting, refinery operations, pipeline vandalism, sabotage, and other criminal activity, or just during normal ship maintenance like tank cleaning (Balogun et al. 2021).

When oil leaks into water, it spreads out in a thin, continuous layer and undergoes processes known collectively as weathering. These processes include spreading, evaporation, entrainment, dissolution, biodegradation, oxidation, and sedimentation. It is even possible that the oil may emulsify with the water, although this depends on the properties of the type of oil in question. The reason oil will spread outward from its source point in surface waters is a result of gravity and surface tension forces. On top of this, there is the regular dispersion and advection that water exhibits as a fluid. Oil spills threaten marine life and their ecosystems by blocking out sunlight and preventing oxygen diffusion to water below the surface. Birds, fish, and mammals can ingest oil, which has acute and chronic toxic effects on their organs. The spill will coat any surface it comes into contact to, which is dangerous to coastlines, where plant life is abundant.

Pharmaceutical Waste

Pharmaceutical waste is also becoming increasingly concentrated in drinking water, surface water, wastewater, sediments, and biota. Pharmaceutical drugs are designed to induce a biological response in a targeted living organism but may have unintended side effects when not regulated properly, such as when released into open water. The agricultural industry, due to its size, plays a role in contributing pharmaceutical waste: runoff from livestock farms, crop fields, and aquaculture facilities might all contain some sort of drug enhancement for their particular product (Khan et al. 2020). The pharmaceutical contaminants are transported through water channels that come into contact with aquatic life, which can then absorb the microscopic compounds. As with other toxic waste, pharmaceuticals face breakdown processes such as biodegradation, photodegradation, and sorption into sediments, which result in equally toxic transformation products. The rate and extent of these processes depend on the water temperature, pH, irradiation, redox conditions, depth, organic carbon content, and microbe population, but they also depend on the specific compound's solubility, vapor pressure, and lipophilicity. Pharmaceutical compounds are attracted to matter suspended in the water such as soil, sediments, dust, particles, and colloids, which then act as transporting vessels. Clay minerals, organic particles, metal oxides, and biocolloids like bacteria, protozoans, and viruses are all examples of colloids, which are distinguished as particularly strong sorbents. In this act of sorption, the pharmaceutical contaminants then lose their ability to degrade.

The consequences of pharmaceutical compounds being released unregulated into surface water are dire for aquatic biota. Khan et al. (2020) detailed conclusive evidence that many compounds have toxic effects on the marine environment. For instance, during wastewater treatment, the antiviral drug acyclovir is shown to produce toxic by-products that were found to inhibit the growth of green algae and decrease the reproduction of a microscopic crustacean by 40% (Khan et al. 2020).

Increased toxicity to green algae is observed when cephalosporin antibiotics undergo photolysis to form their resulting transformation products. The anticonvulsant drug carbamazepine does not even need to break down to pose a persistent toxicity risk to aquatic life including fish, bacteria, and algae. Unfortunately, the effects of pharmaceuticals in aquatic environments on aquatic life tend to be chronic rather than acute due to the bioaccumulation of the compounds, and that the organisms will live their whole life surrounded by it. Biota can inhale, ingest, and metabolize pharmaceutical compounds and their derivatives but have limited ability to dispel or excrete the toxins, which results in bioaccumulation and possibly fatality. At a concentration of just 5 μg/L, the drug diclofenac caused gill alterations and renal lesions in rainbow trout (Khan et al. 2020). Pharmaceutical toxins can have such obvious physical symptoms but may also manifest in more elusive ways by damaging organism or cell DNA or changing reproduction patterns.

Micro- and Nanoplastics

A persistent form of hazardous solid waste in water bodies is micro- and nanoplastics. As indicated by the name, these are microscopically sized particles of any plastic or polymer that are insoluble in water; they can be made of polyethylene (PE), polypropylene (PP), polystyrene (PS), nylon (PA), thermoplastic polyester (PET), polyvinyl chloride (PVC), and many more (Zhang et al. 2018). They can also form from liquid solvents, paints, coatings, and adhesives drying up.

Most microplastics are collected by runoff and running water such as rivers and streams and end up in the ocean, where they will be transported by ocean currents. Oxidative degeneration, friction, and biodegradation will alter the size and shape of microplastics from their original form and will cause them to break into even smaller pieces which can then become even more difficult to clean up from marine and terrestrial systems. This is what makes microplastics such an offensive form of hazardous waste. Microplastics will only sink to accumulate in the sediment if their density is higher than that of water; otherwise they will float and be subject to the various methods of degradation.

In a body of water, tidal fronts, currents, and flowrates will all affect the distribution patterns of the microplastics, as explained previously. Unfortunately, microplastics are excellent vehicles for contaminant transport as they are strong sinks for absorption. The chemicals that may latch onto the solid microplastics are persistent organic pollutants (POPs) such as DDT and heavy metals like zinc and lead. It is also notable that higher concentrations of microplastics have been observed in areas of high levels of industrial and harbor activity, most likely due to high turbidity of the shallow water and high volume of industrial material and waste exchange.

As with pharmaceutical toxins, aquatic organisms swallowing microplastics could face severe digestive tract damage from ingesting too many particles over a period of time. Their digestive organs may be blocked or negatively affected in their ability to digest nutrients or produce energy; nanoplastics may even be transported directly into individual cells if they are small enough (Zhang et al. 2018). Zhang et al. (2018) have explained that microplastics ingested by fish can alter gene expression and hormone function, shown specifically in a Japanese fish known as medaka. They comment that much research is still to be explored on the specific interactions and effects of different types of plastics on aquatic biota, largely due to the current lack of analysis methods that can be applied in an underwater environment. However, it is known that microplastics are found in a majority of trophic levels of the food chain in the marine environment. This implies that not only can microplastics infiltrate almost any organism's body but that they can move through the food chain over time as one organism is ingested by another; thus, so microplastics bioaccumulate in the same way as pharmaceutical compounds.

11.3.2 Case Studies Related to the Transport of Pollutants in the Surface Water

In this section several case studies related to transport of pollutants in the surface water are discussed.

Prediction of Oil Spill

In 2018, Chiu et al. (2018) developed a model using radar technology, hydrodynamic data, and correlations to simulate the trajectory of an oil spill in Taiwan. Opting to use an X-band radar, a type of remote sensing tool on ships for detecting wave characteristics, they were able to detect oil slicks due to their lower radar echo intensity compared to the surrounding oil-free water (Chiu et al. 2018).

They also chose to implement the semi-implicit cross-scale hydro-science integrated system model, SCHISM, to simulate water elevations and currents by considering diffusion and advection of the water, ocean currents, surface winds, surface, and water temperatures in order to improve their model's accuracy. They used the X-band radar to initially detect and monitor the simulated oil spill in the early stages and then used SCHISM to predict water surface elevation and velocity to obtain the necessary hydrodynamic properties. Finally, they used a Lagrangian particle-tracking method to predict the trajectory of the oil spreading.

The authors applied their model to the TS Taipei shipwreck in Taiwan in 2016. The ship ran over shallow ground and cracked its hull, which eventually split the ship in half and released 50 tons of fuel oil into the water off the Shimen Coast. The authors had observational data from the event to which they could compare their simulation's results, as well as nearby tide stations that provided water elevation data that they could also validate their predictions with. Their final results showed that their simulated data was very similar to observed circumstances from the real oil spill, but the affected coastline stretch was shorter than the observed. This was attributed to the lack of wind speed and direction data that could be obtained during a forecast simulation. Chiu et al. (2018) concluded that their model could be very useful in the prediction and forecasting of future oil spills as it could facilitate a more immediate emergency response and mitigate harmful environmental impacts.

Cyanide Toxic Contaminant Transport

The development of a model for toxic contaminant transport in a water body using the lattice Boltzmann method (LBM) and accelerated it with a 2D graphics processing unit (GPU) was achieved by Wang et al. (2018). Their objective was to ensure that the model accurately represented water and solute movement, that it involved both physical and chemical transportation theories and equations, and that it would be reasonably computationally efficient. They used the Navier-Stokes equations for the fluid mechanics of shallow water, advection-dispersion equations, and mass and momentum conservation laws for both water and solute. They validate their method using two examples of hydrodynamic behavior: first, they simulate the advection-dispersion of a solute in a finite length aquifer, and second, they simulate a constant stream of solute in a rectangular control area. They then apply their model to the Danjiangkou River Reservoir in China.

A dam was built in 1958, then raised to higher height in 2009 to increase the water volume stored and water surface area in order to be able to provide to cities in Northern China such as Beijing (Wang et al. 2018). Water is diverted from southern cities to be used as irrigation and for domestic and industrial use along the middle route of the “South-to-North Water Diversion.” The authors chose this as water body to model obviously for its importance to the distribution of water in China. They modeled a 2-ton release of cyanide in the upper Danjiangkou River, then ran their simulation for 7 days to calculate the cyanide concentration distribution change over a simulated 180 days. Included in these calculations were the velocity vectors of water movement in the region of the Danjiangkou Reservoir at different water depths. They concluded that the most concentrated area was the immediate accident area; then for the first 30–60 days, it would become the region along the bank. Wang et al. (2018) claim that their work is an excellent advancement in pre-warning systems for the severity of toxic waste spillages in important waterways.

Transport of Industrial Wastewater Sludge

In Europe, a key export of Mediterranean countries like Greece, Italy, and Spain is olive oil, which requires a large amount of water to mill and thus also produces a lot of wastewater. Pavlidou et al. (2014) studied the effects of olive oil production and its wastes on surrounding river systems in the Greek region of Messinia. This region is 21% covered by olive trees and is home to 250 olive oil mills, which are only used for 3–4 months of the year (Pavlidou et al. 2014). Although the disposal of untreated olive oil wastewater is illegal in Greece, it is still common practice by many mills, and it’s estimated that 1.4 million tons have been discharged into the rivers of Messinia and the nearby Messiniakos gulf in the last 10 years. To make their analysis, Pavlidou et al. (2014) took samples at multiple points several times a year from the five major Messinian rivers, on the coast of the Messiniakos gulf, and from streams where olive oil wastewaters are directly discharged. They found that the water samples they collected were high in phenolic compounds, which is expected as olive oil does contain phenols, and there was high chemical oxygen demand that indicated that there was a high organic content. It was also observed through other testing that there was increased inorganic nitrogen concentration in the samples collected from the mouth of the rivers and in the gulf. This nutrient concentration can significantly alter the phytoplankton population and thus poses a danger to the balance of the ecosystem and its food web. Moreover, the toxicity of these samples was indicated as a Class V level, which is high, by performing an acute biotoxicity assay using Palaemonidae shrimp. By comparing samples taken at different times during the year, the authors remarked a decline in water quality during the productive season that would not return to acceptable levels until after 5 months later. This case study demonstrates the dangers associated with allowing untreated wastewaters to be discharged to the precious waterways of the Earth.

Illegal Dumping

Not all toxic waste released into water is by accident; illegal dumping is another way by which entities with hazardous waste do not wish to safely treat and then dispose of their waste. One such example is when 500 tons of toxic waste in the form of sludge was brought by a Dutch cargo ship to the port of Abidjan in Côte d'Ivoire and dumped at multiple locations around the city (Dongo et al. 2012).

These locations included waste storage sites, canyons, agricultural land, and water ponds. This waste sludge contained 750.6 g/L of hydrogen sulfide, which is highly toxic and extremely volatile, organic chloride compounds in concentrations greater than 250 g/L and other chemicals such as mercaptan. Dongo et al. (2012) investigated the health effects of this dumping crisis on the surrounding population. Participating households were questioned and examined by qualified physicians 4 months after the illegal dumping took place. The serious widespread health effects included in the population were asthenia, abdominal pain, nausea, rhinitis, and pruritis, as well as 17 deaths.

11.4 Transport Through the Subsurface

The subsurface contains soil and groundwater, both of which transport hazardous waste through the environment. The hydrological cycle helps distribute hazardous waste contaminants from a point or nonpoint source through the subsurface. For instance, hazardous contaminants may infiltrate into the aquifer after rainfall, first passing through the unsaturated zone of soil, also known as the vadose zone, where soil pores are filled with both air and water. A region known as the capillary fringe is located just above the water table, where water is held in pores due to capillary forces and surface tension. When contaminants reach the water table, they can enter the saturated zone where soil pores are water-filled (Bear and Cheng 2010). In the saturated zone, groundwater plays a role in transport and may eventually seep into surface water such as a pond or a river (He et al. 2009). Figure 11.2 illustrates the entire hydrological cycle.

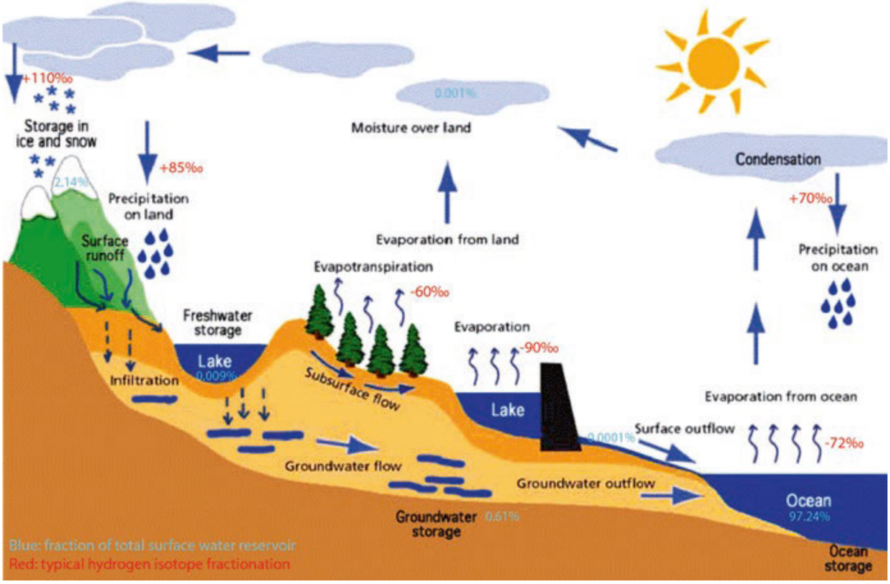

Fig. 11.2 Entire hydrological cycle (Water Cycle 2021)

The flowrate and direction of groundwater in the subsurface are influenced by the hydraulic gradient of the aquifer and the hydraulic conductivity of the soil. The hydraulic gradient is the difference in piezometric hydraulic heads in the saturated zone, while hydraulic conductivity represents the ease with which water flows through a porous matrix. Both of these parameters are included in Darcy's law, which is often used to describe groundwater flow, as shown in Eq. (11.1) (Bear and Cheng 2010).

$$q = \frac{k\left(h_{\text{inflow}} - h_{\text{outflow}}\right)}{L} \tag{11.1}$$

In Darcy's law, q represents the specific discharge of groundwater through porous media (m/s), while h_{inflow} and h_{outflow} represent the piezometric hydraulic heads between two points of groundwater flow over a sloped distance, L. Hydraulic conductivity, k, is measured as distance per unit time (Bear and Cheng 2010).

Hazardous contaminants can have different chemical and physical properties, ultimately affecting how they are transported. The fate of contaminants in the subsurface depends on processes of "transport, storage, and transformation" (Bear and Cheng 2010). Processes of advection, dispersion, diffusion, retardation, and degradation can all control transport (Ya et al. 2018). Additionally, the overall groundwater chemistry, including the solubility and ionic charge of contaminants, is also important (Fig. 11.2).

Contaminant mass flux by advection can simply be described as the mass of a certain contaminant passing through a unit area of the soil matrix while being carried by a fluid phase that occupies the void space at a volumetric fraction, θ, and is described in Eq. (11.2) (Bear and Cheng 2010)

$$J_{\text{adv}} = \theta V c \tag{11.2}$$

The advective flux, J_{adv}, is based on a particular contaminant species and is proportional to the average mass-weighted velocity of the phase, V, and the concentration of the contaminant in the phase, c (Bear and Cheng 2010).

In the subsurface, mass flux by diffusion may represent more than one fluid such as water and air. Hydrodynamic dispersion is also important, as it represents the spreading of a contaminant longitudinally and transversally while dissolved in the fluid phase. Dispersion is caused by the diffusion of molecules across streamlines. Retardation is another important parameter affecting transport, as it describes the adsorption of contaminants onto the solid grains of the soil, which reduces the mean contaminant movement to a retarded velocity. Dispersion and diffusion are both affected by retardation. Finally, the degradation or decay of a contaminant over time will also affect its transport through the subsurface (Bear and Cheng 2010).

There are many transport models that have been developed to simulate hazardous waste transport in the subsurface based on particular contaminants and their transport parameters. For example, the EPA developed a Composite Model for Leachate Migration with Transformation Products (EPACMTP). The EPACMTP simulates saturated zone flow of landfill leachate contaminants in a homogeneous porous medium, by modeling advection, dispersion, diffusion, degradation, and retardation processes that affect transport. Required inputs for the EPACMTP model include the thickness, hydraulic conductivity, and longitudinal dispersion of both the unsaturated zone and the aquifer, as well as the hydraulic gradient, and the concentration of contaminants of interest. It is represented by the following two equations (Ya et al. 2018):

$$\frac{\partial c}{\partial t} = D_L \frac{\partial^2 c}{\partial x^2} - \frac{x}{n}\frac{\partial c}{\partial x} - R\gamma c \tag{11.3}$$

$$D_L = \alpha v + D_m \tag{11.4}$$

The above differential Eq. (11.3) can be solved using the appropriate boundary conditions, and it represents the contaminant concentration, c, as a function time, t, and horizontal distance, x. It includes coefficient of longitudinal dispersion, D_L, which is a function of groundwater velocity, v, the medium's dispersion, α, and the coefficient of molecular diffusion, D_m, as represented by Eq. (11.4). The second term in Eq. (11.3) factors in the effective porosity of the soil, n, while the third term factors in the retardation factor, R, and the decay rate, γ (Ya et al. 2018). The EPACMTP model was developed for landfill leachate transport, but many of the transport parameters it contains apply to other forms of hazardous contaminants in the subsurface.

Landfill leachate is an important source of hazardous waste because it contains toxic contaminants that originate from a landfill after rainfall passes through the waste. Normally landfills are equipped with a geomembrane liner that prevents leachate from leaking and infiltrating into the soil. However, liner defects such as punctures and tears have led to leachate entering the soil and aquatic environments, especially for landfills in developing countries. Over the long-term, landfill equipment is known to further deteriorate, leading to more leakage into the environment. Leachate can contain many different types of pollutants such as various ions, organic and inorganic species, heavy metals, POPs, pharmaceuticals, nanoparticles, and other toxic contaminants. These contaminants can migrate from the landfill site into drinking water wells if not properly managed (Ya et al. 2018).

11.4.1 Major Pollutants in the Subsurface

In this section, some of the major pollutants found in the subsurface are discussed.

Nonaqueous Phase Liquids (NAPLs)

Sometimes in the subsurface, a third phase of fluid can be found, which is known as nonaqueous phase liquids (NAPLs). NAPLs are often considered as hazardous waste with toxic properties that may originate from spills, leaks, or improper waste disposal, primarily from industrial processes. They may be hydrocarbons or organic solvents that are immiscible in water (Bear and Cheng 2010). Some examples include elemental mercury NAPLs which can originate from chlorine production at chlor-alkali plants or TCE NAPLs which may originate from degreasing and dry cleaning activities. NAPLs that are less dense than water are called light nonaqueous phase liquids (LNAPLs), while NAPLs that are more dense than water are called dense nonaqueous phase liquids (DNAPLs) (Bear and Cheng 2010). These two forms of NAPLs are transported differently in the subsurface. DNAPLs can sink through the unsaturated and saturated zones until they reach a layer of impermeable soil, such as clay, where they form pools. The pools can be mobile and move slowly along the clay layer in the direction of a downward slope. Over time, the pools can dissolve in small concentrations into the groundwater. Contrarily, LNAPLs will only sink through the unsaturated zone before forming a floating layer above the water table, which can move with the hydraulic gradient until it eventually becomes immobile due to residual saturation. In the unsaturated zone, both forms of NAPLs may have volatile or soluble components that either diffuse into pore spaces as a gas or as an aqueous solute. Both leave behind ganglia, which are small blobs of NAPL, as they migrate downward through the soil. The extent to which a NAPL travels is also highly influenced by the volume of the spill (Bear and Cheng 2010).

Nuclear Wastes

In addition to NAPLs and landfill leachate, another hazardous waste that is threatening humans and the environment is nuclear waste, which produces actinides as radioactive contaminants. Nuclear waste originates from nuclear power plants or nuclear weapon test sites, where accidents have led to the release of toxic radionuclides into the environment. In the USA, there are 60,000 tons of nuclear waste temporarily stored at nuclear power plants in large aboveground storage facilities. Countries like Russia have started storing liquid nuclear waste deep underground. Toxic radionuclides can take thousands of years to decay and must be isolated from the biosphere. Therefore, it is critical to understand nuclear waste transport mechanisms in the subsurface if storage and testing are taking place underground (Kersting 2013).

A unique transport mechanism that can occur for some radioactive contaminants is transport by sorption onto mobile colloids in the groundwater. For example, plutonium is a highly reactive actinide that can be found in waste originating from nuclear fission in nuclear reactors, and its principal transport mechanism in the subsurface is colloid sorption. Colloids are incredibly small particles that can be organic, inorganic, or microbial in nature and originate from both anthropogenic and natural processes, with sizes ranging from 1 to 1000 nanometers (Kersting 2013). Colloids can also facilitate the transport of plutonium through fractured rocks and soils (Wolfsberg et al. 2017). Plutonium can also travel as an aqueous species or bind to rocks and soil, becoming immobilized. Aqueous species of plutonium in the environment include Pu(III), Pu(IV), Pu(V), and Pu(VI). Pu(V) and Pu(IV) are dominant in a groundwater environment, as Pu(V) is rather soluble, while Pu(IV) is very easily sorbed to colloids. The solubility and ease of transport of plutonium can sometimes be increased when it forms stable complexes with ligands (Kersting 2013). Fractures and cracks in the subsurface are also known to affect contaminant transport of plutonium and other chemicals, as they can promote stronger advection and colloid transport, as well as diffusion from the cracks into the porous matrix.

11.4.2 Case Studies Related to the Transport of Subsurface Pollutants.

In this section, case studies related to transport of subsurface pollutants are discussed.

Nuclear Waste

A recent study by Wolfsberg et al. (2017) examined how plutonium is transported in tuffaceous fractured rocks at the Nevada National Security Site (NNSS) where underground nuclear testing took place. They predicted fracture flow of the radionuclides to be the dominant transport mechanism in the volcanic tuff rocks of the site due to low groundwater velocity and high sorption in the porous matrix.

The authors based on previous experiments conducted by other researchers in the Yucca Flat corrective action unit (CAU) of the NNSS have built an inverse model that predicts the transport of plutonium (Pu) in the tuff rock fractures. Samples were collected from the tuff confining unit and the lower carbonate aquifer. Synthetic groundwater was prepared in the lab to reproduce the same groundwater conditions as in the Yucca Flat. Another radionuclide, tritium, was also measured for comparison purposes. Lab experiments demonstrated that colloid-facilitated transport of plutonium in the groundwater. High- and low-flow experiments were conducted to determine matrix diffusion, sorption, and desorption processes. Pu was also found to sorb onto the fracture surfaces and the soil matrix minerals, after diffusion into pore spaces, causing it to become immobile (Wolfsberg et al. 2017).

The migration of Pu-Colloids was first modeled using a forward advection-dispersion model, which also included diffusion into the porous matrix. Next, an inverse model was applied using the shuffled complex evolution metropolis (SCEM) algorithm to estimate sample-specific radionuclide transport parameters. Parameters such as diffusion and retardation could be estimated using the inverse SCEM algorithm by minimizing an objective function based on multiple experimental data sets. Data sets included the high- and low-flow experiments for both Pu-colloids and tritium. Inversion of multiple experiments helps identify proportionality relationships between the unknown parameters. Modeled breakthrough curves of concentration versus time were fitted to measurement curves using a stepwise procedure. The inversion modeling approach helped to identify the proportional relationships between unknown parameters from multiple experiments, until it could estimate the true transport parameters within a 95% confidence interval (Wolfsberg et al. 2017). The parameters identified in this study and the approaches that were used helped to better understand radionuclide transport in rock fractures.

Landfill Leachate

Ya et al. (2018) evaluated the long-term transport of contaminants originating from the Chang Shou Hazardous Waste Landfill (CSHWL) in Southwestern China. The EPACMTP model was applied to simulate the transport of hazardous contaminants in the subsurface based on advection and attenuation processes. The model only applies to the saturated zone of an unconfined aquifer with uniform thickness and homogeneity, which was applicable to the target aquifer at the site. Experiments identified several heavy metals in the leachate samples, including Zn, Ni, Pb, and Mn. Groundwater flow in the aquifer was calculated using Darcy's law and used in the advection-dispersion analytical solution of the EPACMTP to predict heavy metal concentrations over time and horizontal distance (Ya et al. 2018).

Ya et al. (2018) coupled their EPACMTP model with other models including the Hydrological Evaluation of Landfill Performance (HELP) model and the Degradation Model for Functional Units (DMFU). The HELP model uses the landfill's water budget, such as seasonal precipitation and infiltration, to predict the volume of leachate leaking from the CSHWL. Since the HELP model does not consider the aging process and deterioration of the landfill's geomembrane liner material, the DMFU helps estimate the change in permeability of the liner with time. Defects and failures of other landfill components such as the capping system and the leachate collection and drainage system can also be estimated using the DMFU. Using the three models, the leachate leakage rate and the concentrations of the four heavy metals were modeled over a time period of 1000 years to determine long-term effects. In the long-term, the leakage rate was found to increase dramatically after about 100 years.

Heavy metal concentrations were simulated in a well located 700 m from the landfill site where local villages receive their drinking water and in a monitoring well (point of compliance) located 350 m from the site. Concentrations in both wells spike dramatically in the long-term, resulting in substantial and unacceptable groundwater quality and human health risks predicted by this study. Pb was found to be the highest risk heavy metal, as it exceeded drinking water standard concentrations in both the medium and long term, while also having the highest carcinogenic potential (Ya et al. 2018).

Dense Nonaqueous Phase Liquids

Sweijen et al. (2014) examined the transport behavior of an elemental mercury DNAPL through the subsurface near a former chlor-alkali plant in the Netherlands. At the time of the study, the authors pointed out that transport behavior of elemental mercury through aquifers was limited. The major purpose of the study was to characterize mercury DNAPL distribution with depth in the saturated zone based on field data and a two-phase flow modeling approach. In the field approach, a cone penetration test (CPT) was conducted. The CPT probe was penetrated into the subsurface to a depth of 9 m and capable of capturing high-resolution images of bright silvery mercury ganglia; it also helped determine the lithology of the soil. Images from the CPT were used to measure mercury pore saturation based on a ratio of image pixels. The results were later compared to the modeling approach (Sweijen et al. 2014).

The Subsurface Transport Over Multiple Phases (STOMP) model was used to model multiphase flow in the subsurface. It is based on Darcy's law and uses the Newton-Raphson iteration method for numerical integration of differential equations. Capillary-saturation behavior was simulated using a van Genuchten model. The mercury DNAPL transport was modeled and compared to the transport of a PCE DNAPL, which is much less dense than mercury. Both DNAPLs' ability to infiltrate the soil was highly dependent on capillary pressures and interfacial tension with water in the void spaces. Both mercury DNAPL and PCE DNAPLs were modeled in homogeneous saturated soil and later in heterogeneous saturated soil. The mercury DNAPL was able to infiltrate the loam layer and reach a depth of over 20 m, while the PCE DNAPL could only infiltrate part of the loam (Sweijen et al.

2014). The results of the STOMP models were relatively consistent with the field observations from the CPT images. This study demonstrated that mercury is capable of penetrating great depths largely due to its high surface tension and density. Additionally, its transport through the subsurface can be very different from other common DNAPLs such as PCE (Sweijen et al. 2014).

Another more recent case study by Ayral-Çınar and Demond (2020) reports transport of PCE and TCE DNAPLs through clayey lenses and layers, by focusing on mass accumulation through diffusion. While DNAPLs normally form pools on low permeability clay layers in the subsurface, they can also diffuse into clay pores and accumulate mass. When the pools eventually migrate downslope, the contaminant mass can be "back-diffused" into the groundwater from the clay. Despite diffusive transport thought to be the dominant mechanism of mass transfer to clays, other mechanisms such as advection may also occur due to cracks in the clay. Cracks are often overlooked, as clay is normally assumed to be uniform; however, cracks in clay are important to consider when evaluating the mass accumulation of DNAPL contamination, especially since cracks can significantly increase the hydraulic conductivity and advection capabilities within clay. Ayral-Çınar and Demond (2020) modeled three scenarios of TCE mass storage in clay. The first scenario assumed diffusion from the pool was the sole transport mechanism, the second assumed cracks were present with diffusion occurring from the cracks, and the third simply assumed DNAPL was present in the cracks. Results showed that masses calculated from the diffusion-only scenarios were much lower than those calculated from field observations. As a result, the authors concluded that other transport mechanisms must be occurring in addition to diffusion, such as advection into cracks and DNAPL storage in the cracks (Ayral-Çınar and Demond 2020).

Electronic Waste (E-Waste)

Zhao et al. (2019) found high concentrations of heavy metals in rice paddy soils in Wenling City, Southeastern China, where 30 villages are involved in unauthorized e-waste handling. Proper management and disposal of e-waste continues to be a great challenge worldwide, with approximately 42 million tons of e-waste being generated per year on a global scale. China is known to process millions of tons of illegal e-waste, imported annually from developed countries, at low-cost labor. There are many informal e-waste dismantling sites in southeastern China that are driven by economic profits. The e-waste being processed contains potentially hazardous materials (PHM), such as heavy metals (Cd, Cu, Pb, Zn, Ni) that can contaminate the subsurface around these sites. PHM accumulation in agricultural soils is known to have significant ecological and human health impacts (Zhao et al. 2019).

In the selected study site area, paddy soils are the dominant soil type. There is a very low hydraulic gradient in Wenling City, so horizontal groundwater transport is very slow, and vertical infiltration transport is much more dominant. Zhao et al. (2019) collected 90 topsoil samples (20 cm depth), 10 soil profile samples (down to a depth of 1 m), and 8 groundwater samples from the shallow unconfined aquifer.

PHM concentrations in each sample were determined from laboratory analyses. A pollution assessment index and ecological risk assessment were calculated based on measured concentrations. To assess the spatial variations of contamination, a spatial autocorrelation tool called Moran's I was used along with geostatistical analysis software programs (Zhao et al. 2019).

Zhao et al. (2019) compared the concentrations of PHM in the topsoil samples collected from Wenling City to control samples taken from another rice production region in Zhejiang Province. They found that PHM concentrations were much higher in the topsoil from the study area. Additionally, the Moran's I tool showed a strong spatial correlation between the high-concentration clusters of PHM and e-waste dismantling areas. Most PHM concentrations in the study area were higher in shallower layers of the soil and lower in deeper layers. However, the concentration of Ni was fairly consistent along the soil profile. The authors concluded that much of Ni is derived from underlying parent material rather than e-waste. The authors found that Cd posed the greatest ecological risk, as its soil concentration was above environmental standards and 20 times higher than the control samples. Additionally, the Cd concentration in the groundwater samples was much higher than the Chinese safe drinking water standard. As a result, this study showed the threat of PHM contamination in Wenling City and other e-waste processing areas (Zhao et al. 2019).

Pharmaceuticals

Biel-Maeso et al. (2018) monitored pharmaceutically active compound (PhAC) accumulation in a garden adjacent to a wastewater treatment plant (WWTP) in Jerez de la Frontera, Spain, where effluent water is used for irrigation of the garden. Reclaimed wastewater has become a popular water source for irrigation purposes in dry regions due to water scarcity concerns. However, wastewater can contain PhACs which are considered contaminants of emerging concern (CECs), and they can have ecotoxicological risks. Many pharmaceuticals are ionizable in the subsurface, and their transport depends highly on the moisture content, hydraulic conductivity, and pH of the soil, as well as climatic factors such as precipitation and temperature (Biel-Maeso et al. 2018).

Over a period of 2 years, Biel-Maeso et al. (2018) collected influent and effluent wastewater samples, as well as soil samples from the garden. In the soil samples, the most predominant PhACs were anti-inflammatories and analgesics. They sampled soils every season in 2014 and 2015 to determine vertical distributions in the vadose zone down to a 3 m depth. The results showed that PhAC accumulation was greater in the winter compared to the summer, even though more irrigation occurs in the summer. The lower concentrations in the summer can be explained due to higher microbial activity in the summer months with warmer temperatures causing microbes to degrade certain PhACs in the soil. Additionally, certain PhACs can be photodegraded in the summer due to higher solar irradiance (Biel-Maeso et al. 2018). Climate and microbiological factors influence the transport of contaminants such as pharmaceuticals and their accumulation in the subsurface, as some types can be degraded by high solar irradiance or by microbes that are more active in the soil at higher temperatures (Biel-Maeso et al. 2018).

Heavy rainfall caused the rapid infiltration of contaminated water seep into the vadose zone and prevented adsorption in the shallower soil layers. As a result, PhACs were accumulated from 2014 and then transported and evenly distributed through the soil column in 2015 due to heavy rain events (Biel-Maeso et al. 2018). Anti-inflammatories were the PhACs of highest concentration in the soil column. The results also showed that beta-blockers such as nadolol have a limited sorption capacity and are quite mobile in the subsurface, so they can reach the saturated zone. Additionally, PhACs with a negative net charge were less likely to adsorb to clay particles in the soil. Therefore, the vertical transport of PhACs is highly dependent on sorption, temperature, pH, and soil type. Despite PhACs being present in the soil, this study concluded that the environmental risk to terrestrial species in the garden was low (Biel-Maeso et al. 2018).

11.5 Conclusions

Hazardous wastes come from a variety of sources and processes and are harmful to the surrounding environment and to the health of all living organisms. Hazardous wastes are produced continuously by industrial and commercial operations, hand-in-hand with all the products that we use every day. Toxic contaminants can be transported through three main mediums: air, subsurface, and water; each carrying medium has different transport mechanisms. Diffusion, convection, advection, dispersion, dissolution, adsorption, degradation, bioaccumulation, evaporation, radiation, and sedimentation are all examples of transport or transformation processes that contaminants may undergo in air, water, and subsurface.

In this chapter, a number of case studies were reviewed in order to provide insight on real-world applications of hazardous waste transport in all phases. For case studies involving hazardous waste in air, incineration was a focus. Case studies focused on transport through surface water such as oil spills, cyanide release, wastewater discharge, and illegal dumping of sludge. Furthermore, the importance of mathematical modeling and software is discussed, and the models could deliver effective warning systems on the spread of toxic contaminants and highlighted the importance of following environmental regulations and laws. From the case studies involving hazardous waste in the subsurface, the main cases discussed involved nuclear waste, landfill leachate, DNAPLs, e-waste, and pharmaceuticals. The physical and chemical properties of the hazardous wastes, as well as the hydrogeological environment, affect contaminant transport and accumulation in the subsurface. The long-term impacts of various industrial processes that cause air, surface water, soil, and groundwater contamination and transport of hazardous wastes are of global concern and require continuous monitoring.

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Chapter 12
Application of Internet of Things (IoT) in Waste Management

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12.1 Introduction

Successful waste management strategies have become more relevant and critical in the establishment of sustainable cities as the amount of municipal solid waste (MSW) generated follows urbanization, economic, and industrial development trends (Quintili and Castellani 2020). By 2050, it is projected that the world will generate 3.40 billion tons of municipal waste which should be managed effectively as poor or inefficient waste management practices can have significant health, environmental, and economic consequences (Kaza et al. 2018). In addition, the health and standard of living of our communities are impacted by mismanaged waste.

For example, waste collection vehicles often act as a notable source of emissions, which can be exacerbated by poor route planning, and unregulated waste can raise health and comfortability concerns for the public as mismanaged waste can promote the presence of disease-carrying vectors and produce foul odors (Bhada-Tata and Hoornweg 2012). As a whole, waste management is often a very expensive municipal responsibility that on average accounts for roughly 20, 10, and 4% of municipal budgets in low-, middle-, and high-income countries, respectively. Much of these waste management budgets are allocated to operational costs for labor, fuel, and equipment maintenance. To minimize the health, environmental, and economic impact of waste management, local governments must implement improved systems to address current deficiencies in the waste management sector. Such

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improvements include designing efficient collection routes, deploying vehicles only as needed, and adapting to changes in waste production patterns to optimize waste collection (Kaza et al. 2018). To enable such advancements, novel solutions involving garbage bin monitoring have been proposed to ultimately reduce fuel demands and maintenance costs attributed to solid waste collection (Longhi et al. 2012). Another deficiency in the waste management sector is with regard to waste sorting which is considered a critical component of recycling endeavors that can be optimized through automation (de Souza Melaré et al. 2017). The implementation of automated waste sorting techniques is necessary as manual sorting is labor-intensive, time-consuming, and exposes workers to toxic and pathogenic work environments (Gundupalli et al. 2017). Additionally, using innovative monitoring techniques, wastewater management schemes can be improved to reduce the polluting of water bodies. One strategy to address waste collection, waste sorting, and wastewater management concerns is to develop monitoring systems to collect relevant waste-related information which is crucial for taking steps toward an optimized municipal waste management system (Kaza et al. 2018).

The Internet of Things (IoT) is one such innovation that shows potential as a practical solution to the waste management problem by bridging current city infrastructure to the digital realm of the Internet. The Internet of Things (IoT), characterized by its growing popularity and potential in countless fields, is described as the network of interconnected objects that each possess their own unique address (Govinda and Saravanaguru 2016; Perwej et al. 2019). Substantial research has been dedicated towards applying IoT technology to various municipal challenges including waste collection, waste sorting, and wastewater management which are the focuses of this chapter. In this work, we summarize how the sensors and connectivity of IoT are implemented to tackle waste-related issues by introducing the digital world to city infrastructure that may revolutionize the waste management methodology.

12.2 Internet of Things (IoT)

There are three main components of an IoT device: (1) the physical element or object; (2) the smart component which senses, processes, and stores data; and (3) the connectivity component which uses existing networks to share the accumulated data where it can be further used outside of the object itself. Each of these three components build upon each other to collectively improve the capabilities of the original object (Heppelmann and Porter 2014).

IoT is essentially an extension of the classical computer network, enabling the incorporation of sensing, communicating, and computing devices (Idwan et al. 2019). A concrete IoT infrastructure and architectural model is required to truly benefit from the vast amount of data that is collected by IoT devices and sensors (Vahidnia and Dian 2021). An IoT technology stack commonly consists of three core tiers, the first being the device layer that involves hardware (i.e., sensors, actuators, and processors) that can either exist on their own or be added to physical things to improve or manage its functionality. The second tier is the connectivity tier which consists of the communication protocols necessary to connect the thing/device to the cloud. The third layer is sometimes referred to as the cloud layer and is responsible for supplying, managing, and communicating with the connected objects through device communication and management software (Wortmann and Flüchter 2015). An application layer is often also considered as an important component of IoT models as it brings value to the IoT system by using data analytics to analyze and process the data collected by the sensors or through network analytics which monitors the connectivity of the IoT system (Vahidnia and Dian 2021).

In the past, computers were almost completely limited by the attention, time, and accuracy of the humans operating them; however, current technologies such as IoT are equipped to independently monitor and share the evolving nature of an object and its environment which proves to be a valuable tool for automating various processes. Perhaps the most advantageous aspect of smart-connected devices is that they can exist within a network of other devices where each product contributes to the improved functionality of another to create an optimized system (Wortmann and Flüchter 2015). The IoT allows for items that would otherwise be considered “dumb” to be connected and enriched in a smart ecosystem to build domains such as smart homes, buildings, and cities. As urbanization trends continue to grow, the need for effectively managed cities becomes increasingly more apparent. As of 2016, 54% of the world’s population resided in urban areas; however, projections estimate that this number will increase to 68% by 2050 (Ritchie and Roser 2018). Rapid urbanization poses a great threat to already strained municipal systems as the need for efficient management is magnified.

12.3 IoT Technology in Waste Collection

Waste collection is greatly dependent on the income level of nations, for example, low-income countries, with struggling waste management systems, collect roughly only 48% of municipal solid wastes (Kaza et al. 2018). In high-earning countries, waste collection is managed by city authorities through scheduled curbside pickup for residential and commercial areas where the waste can then be transported by trucks to disposal and recycling facilities. Careful consideration is dedicated to planning effective waste collection schedules as early pickup visits before bins are filled results in a waste of fuel, time, and labor, while late pickup visits can result in overflowing waste bins that cause environmental and public health concerns (Ramson and Moni 2017). The struggle of manually monitoring the cleanliness and fill level of waste bins is a labor-intensive and time- and financially consuming process that municipalities can better address using the technologies of today (Vishnu et al. 2021).

IoT technologies show promising aptness as they serve as a tool to automate waste bin monitoring in residential and public spaces to create a more efficient waste management system. Most proposed IoT solutions follow a similar framework to address waste management concerns. The main objective is to collect, share, store, and use garbage bin data to design optimized waste collection routes and schedules depending on the fill and priorities of waste bins. The monitoring of waste bins is achieved through sensors which relay fill status to a central database where relevant municipal authorities can be notified. The analytical information gathered can then be stored and used to perform tasks such as collection scheduling and route planning (Muyunda and Ibrahim 2017). Using the schedules and routes informed by the sensor data, the labor, time, and financial demand of MSW collection can be reduced.

12.3.1 Hardware and Sensors Used in IoT Waste Collection

This section provides an overview of the IoT technology, in particular hardware/sensors, used in addressing waste collection concerns. The device layer of the IoT framework incorporates hardware such as sensors and actuators to perform tasks like gathering information from the environment such as location, temperature, weight, motion, vibration, acceleration, humidity, etc. (Al-Fuqaha et al. 2015). The first step in IoT-based waste collection is the application of sensors to waste bins. Various types of sensors have been proposed to monitor the status of garbage bins, many of which are used in combination with each other. Commonly proposed devices include ultrasonic sensors to measure the fill level of waste bins, load sensors to measure the weight of waste, GPS modules to identify the location of the bin, and gas sensors to monitor emissions from waste (Ravi et al. 2021). In the following section, different sensors used in IoT smart waste bins are discussed.

Ultrasonic Sensors

Based on the principle of ultrasonic wave propagation, ultrasonic sensors are commonly used for automating tasks involving distance measurement, and they have been used by various research groups to monitor waste levels in trash bins (Koval et al. 2016). Ultrasound is generally considered to be sound waves with frequency higher than 20 kHz. Ultrasonic sensors operate by measuring the time taken for ultrasonic pulses to be transmitted and received again by the reflected signals, which allow the distance between the sensor and the object to be determined (Nirde et al. 2017).

Due to the wide range of materials that reflect sound, even materials such as liquids, bulk materials, and transparent objects can be reliably detected independent of the color of the said object. Ultrasonic sensors are also capable of performing in dusty and dirty environments (Koval et al. 2016), making them an optimal choice for garbage bin applications. In the trash bin context, ultrasonic sensors are typically placed at the highest point where accurate measurements can be taken (Nirde et al.

2017). Ultrasonic sensors can be programmed to notify authorities only when a specific garbage level (i.e., 80% fill) has been reached (Ravi et al. 2021) or can provide status updates of “empty,” “full,” or “partially full” depending on waste level values (Idwan et al. 2019). Ultrasonic sensor systems can also be designed to provide real-time information that is readily sent to a central database to trigger necessary action (Vishnu et al. 2021). There are many ultrasonic sensors available that are suitable for waste bin applications due to their measuring range and accuracy. For example, Vishnu et al. (2021) report the use of a MB1010 LV-MaxSonar-EZ ultrasonic sensor in the Public Bin Level Monitoring Unit (PBLMU), as it is small, lightweight, cost-effective, commercially available, and highly accurate with a solid waste detection range of 0–6.45 m. The various ultrasonic sensors are available in the market, and their programmability enables flexibility when designing IoT-based smart waste bins.

Load Sensors

Load sensors have been a common addition in the system designs of various proposed IoT-based garbage bins. Load cells are weight-measuring systems that convey exerted force as an electrical signal (Ishak et al. 2020). Of the many types of load cells, strain gauge-based load cells are mostly used in today’s industry due to their low cost and high accuracy (Hernandez 2006). Acting as the primary sensing component, strain gauges are thin foil resistors attached to an elastic body known as the spring element. According to the deformation of the spring element, the strain gauge resistance changes at an intensity that is proportional to the applied force (Muller et al. 2010). When attached to the bottom of waste bins, load cells are equipped to detect even the smallest changes in weight such as the evaporation of water from waste (Aleyadeh and Taha 2018).

Load cells are often used in combination with ultrasonic sensors to gain an improved understanding of waste bin fill levels. The advantage of using load cells in conjunction with ultrasonic sensors is that they can notify municipal authorities when waste bins reach a threshold weight, allowing for the deployment of waste-collecting vehicles that are most suited to lift said bin. This is particularly important in cases where the bin is considered unfilled based on ultrasonic sensor data but still reaches the lifting limit of waste-collecting vehicles (Ishak et al. 2020). An example of a load cell is presented by Nirde et al. (2017) who report the use of the TAL220 load cell in their proposed monitoring design which is equipped with four strain gauges, composed of an aluminum-alloy, and is capable of reading up to 10 kg (Nirde et al. 2017). The HX711 board is a 24-bit analog-to-digital converter providing a direct interface for load cells to measure weight (Ravi et al. 2021). The rapid response, immunity, reliability, and various other features made HX711 a good choice for waste-bin applications (Ishak et al. 2020).

GPS Module

Global Positioning System (GPS) is a navigation system based on satellites placed in orbits. GPS receivers (or modules) accept the radio signals periodically emitted by the satellites to provide accurate location data (Hannan et al. 2011). The geolocation of each trash bin in an area is required for effective garbage collection. Due to the time-consuming nature of manually recording geolocation data, smart bins can be equipped with GPS modules to automatically collect such data, enabling the identification of moved or stolen bins as well as optimal collection routes (Vishnu et al. 2021). Vishnu et al. (2021) used PAM-7Q GPS antenna modules in their proposed design due to its low power consumption, clear interface, high sensitivity of -161 dBm, and advanced interference suppression allowing for effective performance even in harsh environments (Vishnu et al. 2021). Ravi et al. (2021) reported using the commercially popular, U-blox NEO-6 M GPS module as an economical and high-efficiency addition to their proposed smart bin monitoring design. The information regarding the status of waste bins would become virtually useless if the location of the bin could not be determined; thus, the integration of location identification is a critical component of IoT-based smart bins.

Other Sensors

Many research groups have proposed systems using various other sensors depending on their specific concerns, usually in combination with the sensors discussed in previous sections. For example, Misra et al. proposed a scheme to assess the intensity of biogas produced from waste in combination with an ultrasonic sensor to monitor the fill level. Gases commonly produced from waste decomposition include ammonia (NH_3) and hydrogen sulfide (H_2S) which cause foul smell. The MQ-135 and MQ-136 sensors can detect ammonia and hydrogen sulfide, respectively, and they provide wide detection scope and fast response as well as high sensitivity, stability, and longevity (Misra et al. 2018).

Ali et al. (2020) proposed an alternative prototype system that addressed fire safety concerns as well as the usual waste level monitoring. HC-SR04 ultrasonic sensors were used to define waste status based on three fill levels: empty, half full, and full, while SEN-10245SEN-10,245 load sensors were used to measure the weight of waste within bins. In Ali et al.'s (2020) proposed system, these two sensors were accompanied by SK-026 flame sensors configured to a detection distance of 100–200 cm. To incorporate a prediction system to warn against fires and other unfavorable conditions, the HW-505 temperature and humidity sensors were also integrated into their design (Ali et al. 2020).

Aleyadeh and Taha (2018) report integration of proximity, humidity, and weight sensors into their presented smart bin. Data provided by the proximity sensors about the area surrounding the garbage bin include information such as the accessibility of the bin which could temporarily be unreachable due to parked cars. Humidity sensors monitored the moisture level within waste bins to avoid leakages when too wet or fire hazards when too dry. Overall, implementing sensors into waste bins enables the observation of long-term waste collection trends and predictions of future demands, which allows for optimized systems to be designed to alleviate the financial, environmental, and social impacts of waste collection (Aleyadeh and Taha 2018).

Whether it be related to fill level, weight, location, gas generation, or flame detection, a variety of sensors can be implemented to collect a vast amount of waste-related information. Several proposed sensor systems have contributed to the advancement of waste bin monitoring to improve current waste collection infrastructure.

12.3.2 Communication Networks in IoT of Waste Management Systems

IoT is built upon the concept of using unique addressing schemes to enable the interaction and collaboration of diverse objects such as radio frequency identification (RFID) tags, sensors, actuators, mobile phones, etc., to accomplish different goals (Atzori et al. 2010). The true potential of IoT can be fulfilled when connected objects/devices are able to communicate with one another and connect with other systems (Lee and Lee 2015). This potential can be realized in the context of waste management. To enable the use of the waste data collected from the sensors, the acquired data must be forwarded to a centralized server via a wireless link (Ali et al. 2020). RFID, 3G, GSM, UMTS, Wi-Fi, Bluetooth, etc. are some of the various technologies capable of transferring the data gathered by sensors (Al-Fuqaha et al. 2015).

Information collected by sensors can be remotely shared to notify relevant city officials to take appropriate action. Much consideration has been dedicated to employing the most optimal connectivity techniques for smart waste bins. Vishnu et al. (2021) propose a hybrid IoT architecture to efficiently manage MSW based on the suitable connectivity technology in residential and public areas. A Wi-Fi-based solution was recommended for residential areas since virtually all homes are supplied with wireless Internet connection. Vishnu et al. (2021) suggested that Wi-Fi modules in residential smart bins wirelessly connect to home routers to access cloud servers. This is preferred in the residential context because it reduces additional infrastructure expenses; however, it is not practical for public waste bins that might require data to be transferred over longer distances. For this reason, a long-range-wide-area-network (LoRaWAN) architecture was proposed for monitoring public spaces (Vishnu et al. 2021). Another aspect of connectivity that may require consideration is the choice of microcontroller. Depending on the cost, efficiency, memory, processing, and power consumption requirements, appropriate microcontrollers are selected (Ali et al. 2020). For example, Ali et al. (2020) presented a system consisting of the Arduino servers through a network interface Uno microcontroller, which they report as cost-effective and capable of receiving sensor data and transferring it to servers through a network interface card and internet services.

12.4 IoT Technology in the Sorting of Waste

12.4.1 *Solid Waste Sorting and Separation Methods*

Waste sorting is a key element in a successful waste management system, especially from an environmental protection, public health, and financial viewpoint. To reduce the threat of harmful materials from being introduced to the environment, different materials must be separated and dealt with accordingly. Traditional disposal conventions rely heavily on landfilling, but a commonly adopted method to mitigate the negative impacts of current disposal practices is recycling (Bonello et al. 2017). Recycling is the process of recovering materials after they have entered the waste stream to reuse it for another purpose. This concept is highlighted by the 4R strategy: reduce, reuse, recycle (materials), and recover (energy) (Hopewell et al. 2009).

Municipal solid waste (MSW) often includes organic, recyclable, and electronic materials as well as other forms of waste. Useful recyclable materials such as metal, paper, plastic, and glass are often abundantly found in MSW, and successful waste management practices enable the retrieval of these valuable recyclable materials (Gundupalli et al. 2017). For example, plastic production has notably increased over the last 60 years due to its inexpensive nature, durability, and ability to be molded and used in a variety of applications (Hopewell et al. 2009); however, despite its advantageous functionality, current plastic usage and disposal practices are causing numerous environmental issues. Roughly 7–8% of the world's oil and gas is allotted for plastic production with approximately 3–4% of it used for energy during the manufacturing process (Hopewell et al. 2009). Additionally, most plastic is produced and used in a disposable capacity resulting in plastic products being discarded shortly after being manufactured. Due to the durability of the polymers, plastics can accumulate in landfills and habitats. Recycling is a key method to mitigate plastic-related environmental issues as it reduces plastic generation; thus, fewer fossil fuels are required for production, and plastic dumping is minimized (Hopewell et al. 2009).

Manual sorting of recyclable waste relies on human labor through visual inspection and or physical handling (Bonello et al. 2017). While manual waste sorting is precise, it is a time-consuming process that poses significant risk for workers as they can be exposed to hazardous materials (Paulraj et al. 2016). For these reasons, there is a great demand to find methods of automating solid waste sorting processes. Preliminary sorting of recyclables from nonrecyclable waste, or source segregation, often occurs at the waste collection stage and may not be practiced uniformly at all locations. To improve the efficiency, considerable research has been dedicated to the exploration of automated sorting techniques (Gundupalli et al. 2017).

Currently, material recovery facilities typically extract recyclable materials from domestic waste. Materials such as ferrous and nonferrous metals, plastics, paper, and cardboard are sorted according to plant requirements and then further processed for shipment to relevant markets (Bonello et al. 2017). Research advancements in the field of automated waste sorting are often practiced in developed countries where source segregation is commonly implemented; therefore, most proposed designs are only fit for processing source-segregated MSW (Gundupalli et al. 2017). At waste sorting facilities, source separation and tracking waste diversion can be a complex process. Waste diversion here refers to prevention and reduction of generated waste through source reduction, recycling, reuse, composting, etc. Adopting source-separating practices on site has become a priority for many waste management companies to reduce costs (Al-Masri et al. 2018). Overall, to reduce the impact of incorrect waste disposal, the segregation of waste based on type should be promoted (Sirawattananon et al. 2021).

12.4.2 IoT Technology Application in Solid Waste Sorting

Advances have been made to create public and residential waste stations that include separate bins for recycling, organics, and/or other waste; however, consumer behavior is not always as effective as intended (Sirawattananon et al. 2021). Consequently, the integration of smart technologies such as IoT have been proposed to tackle waste sorting challenges. Such mechanisms have been proposed to allow for users such as waste management companies to monitor recycling behavior or violations, in real-time by analyzing recycling patterns during disposal. For example, to improve recycling and disposal practices for waste management systems, Al-Masri et al. (2018) reported a serverless IoT framework called the Recycle.io. Recycle.io leverages IoT techniques to transform garbage and recycling bins into smart ones capable of monitoring waste violations in real time to create an enhanced source separation process that may assist waste management and environmental protection agencies by preserving resources and discerning perceived costs of disposal operations. Recycling.io is composed of multiple smart recycling bins (SRB) and smart organic bins (SOB), each possessing a Raspberry Pi (small and economical computer) with camera modules and ultrasonic sensors which work together to send data to an analytical unit that examines whether the waste is considered a violation. An example of a violation would be if nonrecyclable waste was added to the SRB. All of this is processed locally, and then a summary is sent to a cloud-based application that establishes a dashboard to oversee the IoT smart bins. The summary usually consists of a snapshot, as proof of the breach, as well as the location, data, and time of it. Al-Masri et al. (2018) report using an Azure IoT Hub to control and maintain their smart bins and to promote interaction between the cloud and edge devices. Application of the edge devices to analyze and process serves as a good tool to limit network traffic, improve processing times, enhance performance (i.e., reduce latency), and lessen costs related to operations of the smart devices (Al-Masri et al. 2018).

Raj et al. (2020) reports an IoT-enabled waste sorting prototype that uses various IoT-connected devices to exchange resources in a flexible way to solve waste separation concerns. The proposed system consists of a metal, nonbiodegradable, and moisture bin. The scheme incorporates metal, IR, and moisture sensors to identify metal, dry nonbiodegradable, and wet waste, respectively. The separation of these three types of waste is executed in steps using DC motors and conveyors to smoothly pass the waste through the system. In the first stage, metal waste is extracted using magnets and collected in the metal bin where metal sensors are present. The second stage separates the dry nonbiodegradable waste using medium-speed blowers which allows low-density waste such as paper and plastic to be collected into the duct and placed in the appropriate bin where IR sensors are present. The final stage is to place the remaining wet waste into the moisture sensor-equipped bin. The data received by each sensor is stored by the IoT module and sent to the cloud server using Wi-Fi for further processing. Based on their analysis, Raj et al. (2020) report an accuracy of 95, 85, and 82% for detecting metal, paper, and wet waste, respectively (Raj et al. 2020).

12.4.3 Combined IoT Technology and Artificial Intelligence (AI) in Solid Waste Sorting

Significant research has also gone into combining IoT with other technologies such as artificial intelligence (AI) to address waste sorting concerns. Machine learning (ML) refers to a critical application of AI that enables a system to learn and automatically make refined decisions based on experience without being explicitly programmed to do so. A significant subset of ML is deep learning which has an important class called the convolutional neural network (CNN) which is generally used for image classification. Image classification refers to the process of accepting an input image and returning an output of the class that the image belongs to (Rahman et al. 2020).

Rahman et al. (2020) proposed a smart system that blends IoT and deep learning paradigms to intelligently classify bio and non-bio waste. Their system consists of a camera module responsible for capturing waste images and sending them to the microcontroller where they can then be fed to a trained CNN model. By extracting features from images, the CNN can classify images with high accuracy. Based on the CNN analysis, the servo motor is instructed to put the waste in the appropriate bin. The model consists of two categories: indigestible and digestible waste. The indigestible waste category is further divided into subcategories, namely, cardboard, glass, metal, paper, and plastic, while all digestible waste is grouped together as trash. An overall classification accuracy of 95.3% was reported. Rahman et al. (2020) also integrated ultrasonic and load sensors that send data to an android application via Bluetooth or Internet connection to provide collection and cleanup insight.

12.5 IoT Technology in the Management of Wastewater

12.5.1 Wastewater Management

As urbanization trends continue to rise worldwide, effective environmental safety management becomes increasingly more vital, one area of concern being wastewater management. Pollution of surface water, soil, and groundwater are all consequences of discharging untreated or partially treated wastewater into the environment. In general, discharging untreated wastewater poses a great threat to human and environmental health as it can cause outbreaks of food-, water-, and vector-borne diseases and can devastate ecosystems. Evaluating and reporting the pollutants released to the environment is necessary so that the problem can be fully defined and the success of policies can be assessed (WWAP 2017).

In terms of wastewater management, generally, corrective action is significantly more expensive than preventative operations. For decades, wastewater treatment facilities have faced notable difficulties regarding the detection and separation of discarded chemicals and hazardous materials such as paints and battery waste (Kalirajan et al. 2021). The composition of municipal wastewater is very diverse, reflecting the domestic, commercial, and institutional sources of water that supply municipal wastewater. While domestic sources do not normally contribute to the hazardous substances found in wastewater, there are recent concerns regarding medications that can be found in low concentrations resulting in many long-term consequences (WWAP 2017). Water pollution associated with agriculture also contributes to hazardous substances found in wastewater. Agricultural water pollutants include organic matter, pathogens, metals, fertilizers, and other agrochemicals as well as livestock-related pollutants such as antibiotics, vaccines, growth promoters, and hormones (WWAP 2017). Industrial wastewater can also contain toxic materials which present a considerable threat to human health and the environment. Small- and medium-sized enterprises typically release their wastewater into municipal systems or directly into the environment and usually must meet regulations to avoid fines; however, in some cases, it may be financially more favorable for industries to pay the fines than to invest in proper treatment facilities (WWAP 2017). One promising strategy to address wastewater management issues is to implement on-site systems that can efficiently and effectively monitor and or recycle wastewater.

12.5.2 IoT Technology in Wastewater Management

To address concerns related to wastewater management, IoT schemes have been considered. The goal of the IoT systems is to ensure that hazardous materials are not introduced to dumping sites by notifying users to extract such materials from wastewater before it is dumped. Resource recovery depends on the separation of waste materials which is a labor-intensive process. Businesses commonly rely on surveys and questionnaires to examine source separation intentions; however, this is a subjective and unreliable system (Kalirajan et al. 2021). The continuous monitoring of water becomes increasingly more relevant as water bodies continue to become polluted by industries (Rekha et al. 2020). For this reason, real-time wastewater monitoring via IoT technologies proves to be a promising smart solution.

For example, Kalirajan et al. (2021) have proposed a system that provides real-time information on waste violations and recycling practices to waste management organizations by using IoT technologies. Their scheme integrates turbidity, temperature, and pH sensors into the design to collect and feed relevant data to the server. When the sensor data violates accepted values, notifications are sent to the user, and the wastewater is redirected to the recycling pit where it may be treated. This process of monitoring and redirecting will continue until waste levels are in accordance with the values set by the user so that the unsafe wastewater will not pollute dumping sites (Kalirajan et al. 2021).

With the rise of cities depending on distant and/or alternative sources of water to satisfy growing demands, reclaiming water presents an opportunity. One promising solution to address this issue is to utilize water recycling, especially in an industrial context. Generally, reusing water at the point of production is economically more viable especially when treating water according to fit-for-purpose standards (WWAP 2017). Kalirajan et al. (2021) note that their wastewater monitoring system can also perform a cost-effective recycling as the tested water can also be redirected or reused by the factory. The collection of wastewater violations in real time can prove to be a valuable tool for waste management and environmental protection agencies as it is a cost-effective option for recycling and eliminating hazardous waste dumping (Kalirajan et al. 2021).

Rekha et al. (2020) propose an IoT system that uses various sensors to monitor the quality of wastewater for agricultural uses. Their objective is to use the IoT system to detect parameters such as pH, turbidity, temperature, biochemical oxygen demand (BOD), and total dissolved solids (TDS) to evaluate the quality of the water. Deviations from predetermined threshold values may indicate the presence of chemical spills, plant treatment issues, or complications with supply pipes which can severely impact soil quality and crop cultivation. When abnormal levels are detected, an alert message is triggered so that relevant government authorities may take corrective action (Rekha et al. 2020).

The release of inadequately treated wastewater can reduce water quality which can be harmful to human health, disrupt ecosystems, and could potentially disrupt economic activities that use water (i.e., industrial production, agriculture, fisheries, aquaculture, and tourism) (WWAP 2017). Technologies such as IoT have been studied to mitigate these negative outcomes. Whether intended to assist in wastewater recycling or notifying authorities to either treat wastewater or investigate potential complications, the sensing and connecting capabilities of IoT can be utilized to improve upon current wastewater management systems to ultimately reduce the impact of poor wastewater management.

12.6 Conclusion

The Internet of Things (IoT) is a notable technology that researchers are exploring to address waste management difficulties. With many aspects of waste management operating inefficiently, significant research has been devoted toward optimizing current systems to protect public health, environmental, and financial interests. Research groups have presented novel methods to gather waste bin data critical for designing efficient waste collection systems using IoT schemes equipped with sensing hardware. Such IoT-based schemes commonly incorporate ultrasonic, load, and GPS sensors/modules to collect waste fill level, waste weight, and waste bin location, respectively. This type of data is crucial to understand the status of waste bins so that suitable collection instructions may be sent to ensure waste bins are being emptied at the most appropriate time using efficient collection routes. Some other notable sensors used in proposed IoT-enabled smart bins include gas, flame, humidity, temperature, and proximity sensors that offer additional data to prompt collection based on aspects that may impact public hygiene and safety. IoT techniques have also been applied to the field of waste sorting which is another essential area of waste management. Research has shown that optimizations in the field of waste separation can be realized by IoT's sensing and connecting abilities which enable accurate sorting of waste and notifies users of violations to improve waste separation practices. Such advancements promote recycling endeavors by recovering valuable materials such as cardboard, glass, metal, paper, and plastic which would otherwise be directed to landfills. The applicability of IoT in waste management is further established in wastewater management. Proposed IoT schemes for wastewater management convey that wastewater can be efficiently monitored using IoT. Such monitoring allows for authorities to know when wastewater is undertreated so that the most appropriate corrective action may be taken to prevent harmful pollutants from entering the environment. Overall, IoT enables the collection of real-time data, connects involved devices in a meaningful way that promotes optimizations in the field of waste management, and provides municipalities the necessary tools to solve waste management challenges.

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Chapter 13
Hazardous Petroleum Wastes and Treatment Technologies

Ajay Singh and Bill Mullin

13.1 Introduction

Crude petroleum oil is a complex mixture of four broad hydrocarbon fractions known as saturates, aromatics, resins, and asphaltenes (SARA) consisting of both organic and inorganic compounds. Saturated hydrocarbons (alkanes) can range from methane to compounds with carbon chain lengths of 40 or more, which occur as straight-chain or branched-chain compounds. The aromatic fraction contains ringed hydrocarbons, including benzene, multi-ring polycyclic aromatic structures of nitrogen, sulfur, and oxygen derivatives of hydrocarbons (Salanitro 2001; Scullion 2006). Asphaltene group is the most recalcitrant fraction in crude oil containing higher hydrocarbons formed by cross-linking of nitrogen, sulfur, and oxygen.

A large volume of hazardous petroleum wastes are generated during oil production, recovery, and spills during transportation and refining (Table 13.1) and are potential sources of pollution and pose serious threats to the environment (Van Hamme et al. 2003; Marques et al. 2011; Caliman et al. 2011; Safdari et al. 2018). Most of the petroleum hydrocarbon waste (~80%) generated within a refinery is reused, reclaimed, or recycled with the remaining (20%) disposed of by acceptable methods (Asim et al. 2021). Of the various physical, chemical, and biological technologies available for cleaning of hydrocarbon and heavy metal contaminations, bioremediation methods using microorganisms and plants are considered efficient and less expensive.

Despite the fact that hydrocarbons are toxic compounds and may have negative impact on the environment, they could be utilized as a substrate by naturally present living organisms in the environment. Since a variety of microorganisms have the

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Table 13.1 Hazardous wastes

Petroleum hazardous wastes	Other hazardous wastes/compounds
API separator sludge	Pesticides
Dissolved air floatation (DAF) floats/oily sludge	Halogenated organics
Slop oil emulsion solids	Chlorinated solvents, PCBs
Tank bottoms oily sludges	Azo dyes
Waste oil and solvents, petrochemical waste	Explosives, nitroaromatic compound-contaminated soil
Exploration and production (E&P) oily sludges, drilling muds	Electronic waste
Soil contaminated with oily sludge	Heavy metal-contaminated soil
Pond sediments	Volatile organic compound (VOC) emissions

ability to utilize hydrocarbons as an energy source, their application in bioremediation processes is a natural consequence.

Among saturated hydrocarbons, *n*-alkanes are generally considered to be readily degradable components of crude oil. *n*-Alkanes are divided into three groups: lower alkanes (C_8–C_{16}), medium alkanes (C_{17}–C_{28}), and higher alkanes, ($>C_{28}$), based on the chain length. Although most of the microorganisms show satisfactory growth and faster degradation of *n*-alkanes up to C_{16} carbon chain length, biodegradation of *n*-alkanes with carbon chain length from C_8 to C_{16} is generally favored due to their increased solubility. The resins and asphaltene are generally considered to be recalcitrant to biodegradation (Van Hamme et al. 2003).

Microorganisms and their enzymes have extensively been studied in petroleum contamination, bioremediation, and upgradation of crude oil and its products (Monticello 2000; Singh et al. 2006; Sen 2008; Huang et al. 2010; Glick 2010; Varjani and Upasani 2019). Biological catalysts operate in a wide range of environmental conditions and contribute to the reduced energy costs and desirable products with low carbon footprint. Biotechnological processes have become complementary to the development of new petroleum refining processes while managing environmentally safe remediation and disposal practices during the last two decades (Kilbane 2006; Ward et al. 2009; Voordouw 2011; Xu et al. 2018).

This chapter provides an overview of various (see Table 13.2) potential physicochemical and biological treatment technologies and recent advances of biological processes in remediation of contaminated soil and oil sludge during oil recovery, processing, and distribution of petroleum, as well as upgrading of petroleum oil.

13.2 Petroleum Contaminant Biodegradability and Toxicity

Crude oil contains thousands of different hydrocarbon compounds as follows: (a) alkanes (decane, hexadecane, etc.), (b) iso- or branched-chain alkanes (pristane, phytane, etc.), (c) cycloalkanes (cyclohexane, decalin, etc.), (d) mono-aromatics

Table 13.2 Current petroleum waste treatment technologies

Treatment	Technology
Physical	Centrifuge, filter press
	Oxidation
	Microwave
	Electrokinetic
	Ultrasonic
	Freeze-thaw
Thermal	Incinerator
	Thermal desorber
	Coker
	Pyrolysis
	Cement kiln
Chemical	Soil washing—surfactant, biosurfactant, hot water
	Solvent extraction
	Froth floatation/dissolved air floatation
	Solidification and stabilization
	Chemical oxidation
Biological	Bioreactors
	Landfarming
	Bioaugmentation and biostimulation
	Engineered biopiles and composting
	Monitored natural attenuation
	Bioventing and biosparging
	Biosouring biocontrol
	Biofiltration
	Phytoremediation
Biorefining and upgrading	Microbial enhanced oil recovery (MEOR)
	Biodemulsification
	Biodesulfurization, biodenitrogenation, biodemetallation
	Biocatalysis and biotransformation
	Biological/synthetic nanoparticles for biotransformation

BTEX (benzene, toluene, ethylbenzene, xylenes etc.), (e) polynuclear aromatic hydrocarbons (PAHs) (naphthalene, phenanthrene, pyrene, benzo(a)pyrene, etc.), and (f) heterocyclic or polar compounds that contain nitrogen, sulfur, or oxygen (resins, asphaltenes, etc.). Light crude oils with high API gravity generally contain more mono-aromatics and fewer heterocyclic compounds than heavy viscous crude oils of low API gravity. The biodegradability of petroleum contaminants depends on the type of hydrocarbons present in a particular oily waste or sludge. The following sequence represents the order of decreasing biodegradability:

$$n-\text{alkanes} > \text{branched}-\text{chain alkanes} > \text{branched alkenes} > \text{low}-\text{molecular}-\text{weight}\,n-\\ \text{alkyl aromatics} > \text{monoaromatics} > \text{cyclic alkanes} > \text{polynuclear aromatics} > \text{asphaltenes}$$

Effectiveness of bioremediation processes, considering low-cost options to the physical and chemical methods for degradation of oils and the recognition that microbes in soil could degrade and transform many chemicals that are polluting soil environment, has triggered systematic studies worldwide (Lawniczak et al. 2020). While many organic chemicals are biodegradable by microbes present in the environment, other natural or synthetic chemical structures exhibit resistance to biodegradation and tend to persist in the environment for long periods of time. Microbial transformation of organic pollutants is mediated primarily by enzyme-catalyzed reactions but often with the support of other cell components or associated with cell surfaces, surfactants, chelators, vesicles, and organelles.

A major concern regarding petroleum hydrocarbon contamination of the environment relates to contaminant toxicity. Many recalcitrant chemicals are toxic to higher life forms and/or are known carcinogens, pose a threat to human and animal health, and are classified as hazardous by national regulatory agencies. Toxicity concerns do not just relate to the toxicities of the original chemicals. There have been many examples where parent chemical contaminant gets chemically or biochemically transformed into catabolites, which are as much as or more toxic than the parent compound. Furthermore, the presence of strong chemical oxidizing or reducing agents can also give rise to conversions of the contaminants to more toxic products. Thus, in heavily contaminated media, and due to the toxicity of the medium, it may often hinder the application and implementation of appropriate remediation strategies.

The extent of toxicity of a contaminant cannot be simply related to its concentration in the contaminated medium, because the actual toxicity may be reduced or eliminated by the sorption of the contaminant to either soil particles, organic matter, or biological cells. However, the presence of other toxic components already in the contaminated medium produced by the microbes already present could enhance toxicity. For example, a hydrophobic contaminant, with a tendency to sorb to soil, might become mobilized and solubilized by the presence of lipids or surfactants and possibly become more toxic to the living organisms in the soil.

13.3 Physical and Chemical Methods for Petroleum Sludge Treatment Oil Recovery

Recovering, recycling, and reprocessing of petroleum sludges with high oil and low solids have also been one of the major alternative methods to manage oily sludges. It is an important step by the petroleum industry toward energy recovery and reduces the volume of hazardous oily waste. In the USA, 80% of oily waste generated at the refinery are recycled, while the other 20% are effectively treated and disposed as per approved methods (Singh et al. 2009).

The centrifugation treatment process involves mixing the polymers with the petroleum sludge in a pre-treatment tank. During the centrifugation process, the water is separated from the oil, and the oil is then separated from the solids and residual water to recover the oil using gravimetric separators. All the separated water and solids are further treated in accordance with the local environmental standards.

Sludge pyrolysis is thermal decomposition of organic materials at high temperatures (500–1000 °C) in an inert environment. Low-molecular-weight hydrocarbons are produced during pyrolysis. The end product is always char, liquid, and gases. About 80% of total organic carbon in oily sludge can be converted into usable hydrocarbons. The recovered oil shares similar qualities and properties with low-grade petroleum distillates from refineries. However, pyrolysis is an expensive process and can be limited by various factors, such as temperature, and sludge characteristics.

The microwave radiation process involves the application of microwave frequency ranging from 900 to 2450 MHz to demulsify the mixture of oil and water. The denser hydrocarbons can be broken into lighter hydrocarbons by rapid temperature increase. Microwave irradiation performance can be limited by factors such as microwave power, microwave duration, surfactant, pH, salt, and some properties of the sludge (Johnson and Affam 2019). Compared to other techniques that involves heating, microwave irradiation can rapidly raise the energy of molecules resulting in higher and energy-efficient reaction rates within a very short period of time. However, its application at commercial scale is limited due to high equipment and operating costs.

The electrokinetic method is the process of using direct current of low intensity across a pair of electrodes resulting in the movement of electrons from the lower concentration region to the higher concentration region through the permeable liquid phase medium. Various factors such as pH, electrical potential, resistance, and spacing of the electrodes can affect the performance of the electrokinetic method. Although the electrokinetic process for oil recovery from petroleum sludge requires less energy compared to other recovery methods such as centrifugation and pyrolysis, the electrokinetic process studies have only been carried out at the laboratory level.

The ultrasonic irradiation process utilizes ultrasonic waves to generate compression and rarefactions in the treatment chamber, effectively separating solid-liquid in high-concentration suspensions, by decreasing the stability of oil-water emulsions with oil recovery of 50–80%. Ultrasonic treatment is a highly efficient method without environmental pollution (green treatment) that can be carried out in a very short time. The process is costly, and factors including initial oil content, water content, presence of surfactant, treatment time, treatment frequency, temperature, particle size of solids, salinity, sonication power and intensity can limit its performance.

The solvent extraction process utilizes a solvent to extract oil from sludges, which is then separated from the solvent through a distillation process of the mixture. Turpentine, methyl ethyl ketone (MEK) and liquefied petroleum gas condensate (LPGC) are considered good extraction solvents. Various solvents such as naphtha cut, toluene, n-heptane, kerosene cut, methylene dichloride, hexane, xylene, and ethylene dichloride can be used for oil extraction from petroleum sludges. Hexane, toluene and xylene are better extractant solvents that can provide >75% oil recovery from oily sludges. However, when used in a large-scale extraction, low efficiency and high variability have been reported (Johnson & Affam 2019).

The surfactant enhanced oil recovery (EOR) is the process of removing organic pollutants from solid media through the application of surface-active chemicals. Surfactants are amphiphilic compounds containing both hydrophobic groups and have the ability to lower surface tension or interfacial tension between different types of liquids or liquids and solids, thus facilitate removal of hydrocarbons from the solids. Examples of surfactants used in oily sludge treatment include Tween 80, Triton X-100, and sodium dodecyl sulphate (SDS) (Singh et al. 2007; Ward et al. 2011).

The froth flotation method achieves the capturing of oil droplets/small solids through the use of air bubbles in aqueous slurry where they are then floated and collected in a froth layer. In this process, oily sludge slurry is prepared by adding a specified amount of water, and air is injected to form fine bubbles. The mixture of air bubbles and the oil droplets floats to the water surface where the accumulated oil (~55%) can be collected and separated. The froth floatation process can be impacted by the properties of oily sludge, treatment time, temperature, pH, salinity, air bubble size, and presence of surfactant.

After all the useful oil and hydrocarbons are recovered, the residual waste requires a safe disposal method, such as incineration, oxidation, solidification and stabilization, solvent extraction, and biodegradation. Incineration is the process by which oily waste undergoes combustion in the presence of abundant air and auxiliary fuel. The rotary kiln (combustion temperature 980–1200 °C) and fluidized bed (combustion temperature 730–760 °C) are two major incinerator types. The solidification and stabilization process utilizes binders and cement to encapsulate and seal the waste material with an aim to prevent the waste leaching into the environment. Of all the binders, hydraulic cements are the most widely used. Portland cement is often used as a source of alkalinity and calcium to activate pozzolanic reactions in fly ash. Through physical or chemical means, the stabilized product may become an eco-friendly construction material or can be safely disposed into a nonhazardous landfill. Oxidation treatments use chemical reactive agents to oxidize/degrade organic contaminants in oily waste to carbon dioxide and water and convert into nonhazardous materials. Various oxidation reagents such as ultrasonic irradiation, ozone, Fenton's reagent, supercritical water oxidation (SCWO), wet air oxidation (WAO), hypochlorite, and persulfate can be utilized in this waste treatment process. However, some of these methods are not feasible for full-scale applications due to the requirements of large amount of chemical, equipment, high energy consumption, and invariable high cost of operation.

13.4 Biodegradation and Bioremediation

Biological remediation technologies utilize microorganisms or plants to clean up contaminated sites and treat oily sludges. Since most of the petroleum hydrocarbons are biodegradable and hydrocarbon-degrading microbes are ubiquitous, bioremediation methods offer an effective technology for the treatment of petroleum contaminants compared to physicochemical methods (Ward and Singh 2004).

Mixed populations with broad metabolic capabilities are required to increase the rate and extent of complex hydrocarbon degradation since the individual microorganism can metabolize only a limited range of hydrocarbon substrates (Ward et al. 2003). Cooperation of multiple members of the microbial community is required to degrade complex molecules where some organisms would be able to produce growth factors and degradative enzymes, whereas others can produce biosurfactants to enhance solubilization of hydrophobic hydrocarbons (Van Hamme et al. 2003). In the natural environment, organic compounds including hydrocarbons are degraded by a diverse group of microorganisms. The natural process is affected by various factors: physical, chemical, and biological (Singh and Ward 2009; Roy et al. 2018).

Bioremediation of petroleum-contaminated sites typically involves a landfarming process, which is a cost-effective method of treating biodegradable petroleum products in the soil. The contaminated soil is augmented with nutrients and periodically tilled and irrigated to stimulate the natural microbial population that degrades the contaminants over a long period of time, usually 6-–24 months (Ward and Singh 2004; Ortega et al. 2018; Lee et al. 2018). However, it is difficult to reduce hydrocarbon concentration by more than 80–85% in the contaminated soil, particularly, persistent hydrocarbons like high-molecular-weight polycyclic aromatic hydrocarbons, which may not be adequate to meet regulatory standards in some countries (Salanitro 2001; Hejazi and Husain 2004; Singh et al. 2011).

Engineered biopiles or composting involves mixing of contaminated soil with organic materials such as straw, wood chips, etc. to improve soil aeration, and placing the mixture in piles or windrows to support growth of hydrocarbon-degrading microorganisms. Long treatment times in landfarming or composting methods is generally due to the lack of control of parameters affecting microbial activity such as moisture, oxygen, temperature, pH, and mixing. Contained slurry bioreactors are designed for accelerated hydrocarbon degradation, providing greater control of operational parameters such as pH, temperature, oxygen, moisture, mixing, and bioavailability of nutrients to promote desirable microbial populations, growth, and hydrocarbon-degrading activity (Singh et al. 2007).

Bioremediation processes are enhanced by biostimulation (addition of nutrients and oxygen to stimulate the indigenous microbial population) and bioaugmentation (inoculation of enriched mixed bacterial consortia) or a combination of both (Xu and Lub 2010; Singh et al. 2011; Tao et al. 2019). Addition of soil amendments such as coconut, charcoal, cellulose, straw, soybean hulls, humic acid fraction of the composted soil, saw dust, wood ash, oat, root exudates, root debris, poultry litter, coir pith, and rhamnolipid surfactant has been found to enhance the biodegradation process (Miya and Firestone 2001; Rahman et al. 2002; Tao et al. 2019). A variety of food-grade organic substrates such as vegetable oil, sucrose esters of fatty acids, and whey were found to support long-term bioremediation processes (Pannu et al. 2003; Yap et al. 2010; Jonsson and Östberg 2011). The best approach for bioremediation is when bioaugmentation is performed by inoculating microorganisms preselected from the same contaminated site and providing appropriately designed nutrients based on the nature of the contaminant and nutritional condition of the site (Singh and Ward 2009; Ros et al. 2010; Tyagi et al. 2011).

A range of physical, chemical, or biological parameters affect bioremediation of petroleum contaminants. Weathering, sorption, evaporation or volatilization, leaching, and photooxidation processes may affect the removal of certain hydrocarbon compounds during bioremediation resulting in overestimation of the extent of biodegradation (Huesemann 1995; Salanitro 2001; Mphekgo et al. 2004; Safdari et al. 2018). Hydrocarbon biodegradation can occur over a wide pH and temperature range. The optimum pH for petroleum bioremediation in soil ranges from 6.0 to 8.0. The biodegradation rate generally increases from the psychrophilic to mesophilic temperatures. The optimum temperature for biodegradation has been reported in the range of 25–40 °C (Van Hamme et al. 2003). Biodegradation of hydrocarbons in oily sludge was found optimal at C:N and C:P ratios of 60:1 and 800:1, respectively (Dibble and Bartha 1979). To maintain metabolic activities of microbial cells, the oxygen supply rate must match the overall oxygen consumption rate. Hydrocarbon bioavailability and degradation can be improved by addition of chemical surfactants and biosurfactants. Biosurfactants are generally a more environmentally friendly alternative to synthetic surfactants because of their higher biodegradability and lower toxicity potential.

Phytoremediation methods involve some specific plants and their rhizospheric microorganisms by either providing favorable conditions for contaminant degradation by plant root colonizing microbes or accessing contaminants through the plant roots (Macek et al. 2008; Singh and Ward 2009). Soil phytoremediation methods include phytostabilization, phytostimulation, phytotransformation, and phytoextraction. Decaying biomass and plant root exudates provide nutrients and stimulate co-metabolic transformations of organic contaminants. Microbial-assisted phytoremediation technology has gained a lot more attention with much better understanding of the contribution of bacteria in phytoremediation and the efficacy of these approaches in the removal of petroleum products and PAHs (Ward and Singh 2004; Glick 2010).

Soil bioremediation success depends on various environmental, nutritional, and operational factors. The effectiveness of a biological process depends on the success in identifying the rate-limiting factors which must be optimized in order to achieve maximum treatment benefits. Poorly designed or engineered systems are likely to fail to achieve the desired treatment end points and do not meet required local regulatory treatment criteria. We have advanced our knowledge regarding the mechanisms of biodegradation of petroleum hydrocarbons. A number of hydrocarbon-degrading strains have been isolated and characterized using advanced molecular techniques in the last two decades to help in developing practical soil bioremediation strategies.

13.5 Biorefining of Petroleum Oil

Expensive hydrotreatment processes using high temperature and pressure are generally used to remove sulfur and nitrogen compounds from petroleum that are undesirable in the final refined product. Advanced molecular techniques have made possible in the discovery of engineering biocatalysts (both microbes and enzymes) that are suitable for oil biorefining and recovery processes. The focus of this section is the biorefining processes using biocatalysts (microbes and enzymes) to improve oil quality.

Removal of sulfur from crude oil requires costly and extreme conditions using processes such as hydrodesulfurization (HDS) because most of the sulfur is contained in condensed thiophenes in crude oil. Major microbial species known for biodesulfurization (BDS) activity include *Agrobacterium*, *Gordona*, *Klebsiella*, *Rhodococcus*, *Mycobacterium*, *Nocardia*, *Paenibacillus*, and *Xanthomonas* that are capable of selective desulfurization of organic sulfur (Kilbane 2006; Boniek et al. 2015). Application of extracellular peroxidases with a distillation step has also been proposed as attractive biocatalysts for petroleum desulfurization (Ayala et al. 2007). Peroxidase treatment combined with a distillation step has been evaluated to reduce the sulfur content of straight run diesel fuel from 1.6 to 0.27% in a reaction system of an aqueous medium with a low percentage of water-miscible organic solvent. Nitrogenous compounds in crude oil consist of pyrroles, indoles, and carbazole, which can be toxic and mutagenic compounds, and a potent inhibitor of hydrodesulfurization processes. Some species of *Alcaligenes*, *Bacillus*, *Beijerinckia*, *Burkholderia*, *Comamonas*, *Mycobacterium*, *Pseudomonas*, *Serratia*, and *Xanthomonas* can utilize these compounds (Fetzner 1998; Bai et al. 2010). Denitrogenation and desulfurization processes should be integrated from a practical perspective. An efficient biodenitrogenation and biodesulfurization process requires the removal of nitrogen and sulfur via a specific enzymatic reaction of the C–N and C–S bonds, respectively. However, C–C bonds should not be attacked, thereby preserving the fuel value of the residual products.

Novel biocatalysts have been obtained, and process improvements by rational and random mutagenesis further broaden the scope for application of biotechnology in the fine chemical industry. Biotransformation of petroleum compounds into novel high-value chemicals using the unique regio- and stereospecificity properties of enzymes and their capacities to catalyze reactions in nonaqueous media can be exploited (Holland 2000). Enantiospecific conversions of petrochemical substrates and their derivatives can be achieved by stereoselective biocatalytic hydroxylation reactions using cytochrome p450-dependent monooxygenases, dioxygenases, lipoxygenases, and peroxidases (Kikuchi et al. 1999).

Oilfield emulsions, both oil-in-water and water-in-oil, are formed at various stages of exploration, production, oil recovery, and processing and represent a major problem for the petroleum industry. North American producers estimate that as much as 2% of their oil production ends up as an emulsion during production and pipeline transport, which translates into millions of dollars in lost revenue and potential environmental damage (Becker 1997). Traditional de-emulsification methods to recover oil include centrifugation, heat treatment, electrical treatment, and chemicals containing soap, fatty acids, and long-chain alcohols. However, physicochemical de-emulsification processes are capital intensive, and emulsions often generated at the wellhead have to be transported to central processing facilities.

Since biological processes can be carried out at non-extreme conditions, an effective microbial de-emulsification process could be used directly to treat emulsions at the wellhead, thus saving on transport and high capital equipment costs. Microbial species of *Nocardia*, *Corynebacterium*, *Rhodococcus*, *Bacillus*, *Micrococcus*, *Torulopsis*, *Acinetobacter*, species of *Alteromonas*, *Rhodococcus*, *Aeromonas*, and some mixed bacterial cultures are known to have de-emulsification properties (Das 2001; Nadarajah et al. 2002a, b; Huang et al. 2012). The source of carbon used in growth medium significantly impacts the biodemulsifying properties of the bacteria and cultures grown on petroleum fraction as compared to biodemulsifying properties of cultures grown on carbohydrate sources. Microorganisms exploit the hydrophobic cell surfaces and dual hydrophobic/hydrophilic nature of biosurfactants to displace the emulsifiers that are present at the oil-water interface. Some biologically produced agents such as acetoin, polysaccharides, glycolipids, glycoproteins, phospholipids, and rhamnolipids exhibit de-emulsification properties (Singh et al. 2007; Onaizi 2021). Bacterial surfaces contain proteins and peptides, and polysaccharides, as well as lipids and lipopolysaccharides facilitating biodemulsification processes with field emulsions.

Residual oil in oil wells is often located in areas inaccessible to fluids used for flooding, and usually more than two-thirds of the oil in the reservoir is left unrecovered after primary and secondary extraction (Brown 2010). Sometimes high oil viscosity may also result in incomplete recovery. Conventional EOR methods make use of chemicals (solvents, polymers, surfactants), injected gases (CO_2, N_2, flue gas), and thermal methods (steam flood, hot water) to extract remaining oil (Sen 2008). The microbial enhanced oil recovery (MEOR) utilizes solvents, gases, organic acids, polymers, and biosurfactants produced by microbes to aid in the extraction of unrecovered oil and considered more economical and environmentally friendly compared to conventional EOR (Lazar et al. 2007; Khire 2010). The microbial flooding process is generally used where bacteria and nutrients are injected into a reservoir from an injector, and a normal water flooding operation is then resumed. Bacteria are carried deep into the reservoir with injected water. While being transported inside the reservoir, bacteria produce bioproducts or plug the high permeability zones that improve the recovery of oil. Among the proposed MEOR mechanisms, selective plugging and some biosurfactants are believed to be the main contributors to better recovery. Although there has been only a limited number of studies on using MEOR for oil extraction from oil sands, MEOR has potential for use in oil recovery from oil sands, especially processes focusing on decreasing the viscosity of oil and reducing the interfacial tension between oil and water interfaces (Harner et al. 2011).

Biological souring is the consequence of secondary oil recovery, during waterflooding operations by injecting water (or seawater) down a hole to repressurize the reservoir after natural pressure is lost during primary recovery and to sweep the oil toward production wells (Barton and Fauque 2009). Biological souring requires the simultaneous presence of viable bacteria, sulfate, carbon and energy sources, nutrients, and suitable temperature. Many of these components can be present in the water used for secondary recovery; thus, the water source can play a key role in souring. Readily metabolized carbon sources, volatile fatty acids (acetate, butyrate, and propionate), and labile hydrocarbons such as alkanes and monoaromatics (toluene) are frequently present in the injection water used for water flooding, thus providing carbon sources for SRBs (Grigoryan and Voordouw 2008). With increasing experience and the advent of more accessible molecular methods to characterize microbial communities and their activities, it seems probable that better control of microbial souring will be achieved in the future.

Bionanotechnology is an emerging area that involves physics, chemistry, engineering, and biology disciplines. It has revolutionized different industries with a variety of products designed for applications in material and consumer goods, electronics, transportation, food, cosmetics, pharmaceutical, biomedical energy, and the environment (Serrano et al. 2009; Vikesland and Wigginton 2010). Nanotechnology uses nanoparticles (1–100 nm) produced in the form of metals, metal oxides, semiconductors, polymers, carbon materials, organics or biological, and morphological forms such as spheres, cylinders, disks, platelets, hollow spheres, and tubes. Microorganisms naturally produce colloidal nanoparticles from metal oxides and silicates. These naturally produced particles play an important role in the transport, fate, transformation, and bioavailability of environmentally relevant substances (Theron et al. 2008). There are a limited number of studies done for applications of bionanotechnology in the petroleum industry. Most experiments using nanoparticles at the lab scale have been conducted in small reactors. More data is required on life cycle analysis and effectiveness of these techniques in the field.

13.6 Conclusions

There is a natural link between petroleum hydrocarbons and microorganisms that have been evolved during millions of years of interactions. A large number of bacterial species with petroleum hydrocarbon-degrading ability have been exploited and applied in bioremediation using single or mixed cultures. The ability to degrade hydrocarbons is widespread by microbial populations. Biostimulation using nutrients and surfactants significantly improve hydrocarbon removal in oily waste treatment. Novel and biocompatible surfactants need to be developed to enhance contact between bacteria and hydrocarbons. Using high-throughput screening, vast resources of novel petroleum hydrocarbon-degrading bacteria needs to be further explored. Advances in biomolecular, metabolic, and protein engineering sciences and developments will result in the creation of powerful biocatalysts for applications such as enhanced oil recovery from petroleum reservoirs, biodemulsification of oilfield emulsions and slop oils, bioremediation of contaminated sites, biorefining and upgrading of crude oil and petroleum fractions, specific biotransformation of pure hydrocarbon compounds into fine chemicals, etc. In the future, practical biocatalysts with the capability of simultaneous removal of sulfur, nitrogen, and metals from petroleum need to be developed.

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