1

Wastewater Treatment

Oil and gas are major sources of energy and revenue for many countries today, and their production has been described as one of the most important industrial activities in the 21st century therefore obviously waste treatment and disposal assume a greater degree of importance in the petroleum, chemical processing and unconventional oil and gas industries.

Wastewater treatment refers to the treatment of sewage and water used by residences, business, and industry to a sufficient level that it can be safely returned to the environment. It is important to treat wastewater to remove bacteria, pathogens, organic matter, and chemical pollutants that can harm human health, deplete natural oxygen levels in receiving water, and pose risks to animals and wildlife.

Natural water and wastewater are characterized in terms of their physical, chemical, and biological composition. The principal physical properties and the chemical and biological constituents of wastewater and their sources make a lengthy list. Each designated water body should be controlled according to regulations which may be composed of both basic and more detailed numerical criteria, as briefly discussed below.

Basic freedom from pollution. As far as is practically possible, all bodies of water should attain the basic criteria of the Five Freedoms from Pollution:

1. Free from suspended solids or other substances that enter the water as a result of human activity and that will settle to form putrid or otherwise objectionable sludge deposits, or that will adversely affect aquatic life.
2. Free from floating debris, oil, scum, and other floating materials entering the water as a result of human activity in amounts sufficient to be unsightly or cause degradation.
3. Free from materials entering the water as a result of human activity producing color, odor, or other conditions in such a degree as to create a nuisance.
4. Free from substances entering the water as a result of human activity in concentrations that are toxic or harmful to human, animal or aquatic life and/or are rapidly lethal in the mixing zone.
5. Free from nutrients entering the water as a result of human activity in concentrations that create nuisance growths of aquatic weeds and algae.

Waste Management in the Chemical and Petroleum Industries, Second Edition. Alireza Bahadori.

Table 1.1 *Wastewater pollutants and sources.*

Pollution	Sources
Heavy metals	Process wastewater, tankage wastewater discharges, cooling tower blowdown (if chromate-type cooling water treatment chemicals are used)
NH_3, H_2S, trace organics	Process wastewater (particularly from fluid catalytic cracking unit and coker)
Total suspended solids	Process wastewater, cooling tower blowdown, ballast water tank flow drainage and runoff
BOD5, COD, oil	Process wastewater, cooling tower blowdown (if hydrocarbons leak into cooling water system), ballast water, tank flow drainage and runoff
Phenolics	Process wastewater (particularly from fluid catalytic cracking unit)

The water contaminant parameters determined in refinery wastewater include biochemical oxygen demand (BOD), chemical oxygen demand (COD), oil, total suspended solids (TSS), ammonia (NH_3), phenolics, hydrogen sulfide (H_2S), trace organics, and some heavy metals.

Table 1.1 shows the major sources of each of these contaminants. Process wastewater contributes a portion of virtually all of these, while other sources have more specific contaminant discharges.

1.1 Characteristics of Wastewater

A number of chemical and physical characteristics are used to describe wastewater. The most common are the following:

- Total nitrogen (TN) and total phosphorus (TP) are the sums of all forms of nitrogen and phosphorus in the water, respectively.
- BOD is a measure of the amount of unstable organic matter in the water. It measures how much oxygen is required by the available microorganisms to break down the readily available organic matter into simpler forms, such as carbon dioxide, ammonia, and water.
- Fecal microbes (which includes viruses, bacteria, and protozoans) are found in wastewater and may cause disease.
- Suspended solids, biodegradable organics, nutrients, refractory organics, heavy metals, dissolved inorganic solids, and pathogens are the important contaminants which may be found in the oil, gas, and chemical processing industries' wastewater. Table 1.2 presents a list of important wastewater contaminants and the reasons for their importance.

Suspended solids can be removed by physical treatment to some extent. Removal of biodegradable organics, suspended solids, and pathogens is achieved through secondary treatment operation units.

Table 1.3 shows typical waste compounds classified as priority pollutants. The more stringent rules deal with the removal of nutrients and priority pollutants. When wastewater

Table 1.2 *Contaminant importance in wastewater treatment.*

Contaminant	Reason for importance
Physical suspended solids	Suspended solids are important for esthetical reasons and because they can lead to the development of sludge deposits and anaerobic conditions.
Chemical biodegradable organics	Composed principally of proteins, carbohydrates, and fats, biodegradable organics are measured most commonly in terms of BOD and COD. If discharged untreated to the environment, the biological stabilization of these materials can lead to the depletion of natural oxygen resources and the development of septic conditions.
Nutrients	Carbon, nitrogen, and phosphorus are essential nutrients for growth. When discharged to the aquatic environment, these nutrients can lead to the growth of undesirable aquatic life. When discharged in excessive amounts on land, they can also lead to the pollution of groundwater.
Refractory organics	These organics tend to resist conventional biological methods of wastewater treatment. Typical examples include surfactants, phenols, and agricultural pesticides.
Heavy metals	Due to their toxic nature, certain heavy metals can negatively impact upon biological waste treatment processes and stream life.
Dissolved inorganic solids	Inorganic constituents such as calcium, sodium, and sulfate are added to the original domestic water supply as a result of water use and may have to be removed if the wastewater is to be reused.
Biological pathogens	Communicable diseases can be transmitted by the pathogenic organisms in wastewater.

is to be reused, rules normally include requirements for the removal of refractory organics, heavy metals, and in some case dissolved inorganic solids.

Wastewater from the petroleum industry contains organic compounds, phenols, toxic metals, and other pollutants such as iron, dissolved and suspended solids, oil, cyanides, sulfides, and chlorine. In order to reduce these contaminants, an accurate analysis of processes is necessary.

Pollutants or contaminants which enter a body of water can be divided into:

- *degradable (non-conservative) pollutants*: impurities which eventually decompose into harmless substances or which may be removed by treatment methods, e.g. certain organic materials and chemicals, domestic sewage, heat, plant nutrients, most bacteria and viruses, and certain sediments
- *non-degradable (conservative) pollutants*: impurities which persist in the water environment and do not reduce in concentration unless diluted or removed through treatment, e.g. certain organic and inorganic chemicals, salts, and colloidal suspensions
- *hazardous waterborne pollutants*: complex forms of deleterious wastes, including toxic trace metals, and certain inorganic and organic compounds
- *radionuclide pollutants*: materials which have been subjected to a radioactive source.

Table 1.3 *Typical waste compounds classified as priority pollutants.*

Name (formula)	Concern
Non-metals	
Arsenic (As)	Carcinogen and mutagen Long term: sometimes causes fatigue and loss of energy; dermatitis
Selenium (Se)	Long term: red staining of fingers, teeth, and hair; general weakness; depression; irritation of nose and mouth
Metals	
Barium (Ba)	Flammable at room temperature in powder form Long term: increased blood pressure and nerve block
Cadmium (Cd)	Flammable in powder form; toxic by inhalation of dust or fumes; carcinogen; soluble compounds of cadmium are highly toxic Long term: concentrates in the liver, kidneys, pancreas, and thyroid; hypertension suspected effect
Chromium (Cr)	Hexavalent chromium compounds are carcinogenic and corrosive on tissue Long term: skin sensitization and kidney damage
Lead (Pb)	Toxic by ingestion or inhalation of dust or fumes Long term: brain and kidney damage; birth defects
Mercury (Hg)	Highly toxic by skin absorption and inhalation of fume or vapor Long term: toxic to central nervous system; may cause birth defects
Silver (Ag)	Toxic metal Long term: permanent gray discoloration of skin, eyes, and mucus membranes
Organic compounds	
Benzene (C_6H_6)	Carcinogen; highly toxic Flammable, dangerous fire risk
Ethylbenzene ($C_6H_5C_2H_5$)	Toxic by ingestion, inhalation, and skin absorption; irritant to skin and eyes Flammable, dangerous fire risk
Toluene ($C_6H_5CH_3$)	Flammable, dangerous fire risk Toxic by ingestion, inhalation, and skin absorption
Halogenated compounds	
Chlorobenzene (C_6H_5Cl)	Moderate fire risk Avoid inhalation and skin contact
Chloroethene (CH_2CHCl)	An extremely toxic and hazardous material by all avenues of exposure; carcinogen
Dichloromethane (CH_2Cl_2)	Toxic; carcinogen, narcotic
Tetrachloroethene (CCl_2CCl_2)	Irritant to eyes and skin
Pesticides, herbicides, insecticides (pesticides, herbicides, and insecticides are listed by trade name; the compounds listed are also halogenated organic compounds)	
Endrin ($C_{12}H_8OCl_6$)	Toxic by inhalation and skin absorption, carcinogen
Lindane ($C_6H_6Cl_6$)	Toxic by inhalation, ingestion, skin absorption
Methoxychlor [$Cl_3CCH(C_6H_4OCH_3)_2$]	Toxic
Toxaphene ($C_{10}H_{10}Cl_8$)	Toxic by ingestion, inhalation, skin absorption
Silvex [$Cl_3C_6H_2OCH(CH_3)COOH$]	Toxic; use has been restricted

1.1.1 Wastewater Classifications

1.1.1.1 Water Free of Oil and Organic Material

This category includes boiler blowdown, effluent from cooling water and boiler feed water make-up units, rain water from oil free areas, and cooling water which cannot have direct contact with oil.

1.1.1.2 Water Accidentally Contaminated with Oil

This category includes water streams that are normally free of oil, but may contain oil after an accident. These streams comprise rain water from tank farms, pipe alleys and oil-free processing areas, once-through cooling water, etc.

1.1.1.3 Water Continuously Contaminated with Oil but with Soluble Organic Material

This category comprises rain water from oil processing areas, tank drain water, deballasting water, cooling water blowdown, and flushing and cleaning water.

1.1.1.4 Process water

This water is in contact with process streams, originating from steam stripping, crude oil washing, some chemical oil treatment processes, etc. It contains variable amounts of oil and soluble material such as ammonium sulfide, phenols, thiophenols, organic acids, and inorganic salts such as sodium chloride.

1.1.1.5 Sanitary and Domestic Water

The end result of sanitation and domestic water used in the chemical and petroleum industries is classed as wastewater. Relevant to the above-mentioned facts these categories of water may need different treatments and for this reason, water streams are often kept segregated in a modern refinery to reduce the cost of water treatment facilities. However, in the chemical and petroleum industries different processes could cause pollution, which should be treated.

1.1.2 Water Pollution Terminals

Terminals are storage facilities where refined petroleum products are received from either refineries or import facilities. Fuel is distributed from terminals by truck or rail to retailers or bulk users.

Terminals are the points where wholesalers, distributors, retailers, and other end users access petroleum products. All terminals have loading gantries and storage, and can be supplied by pipeline, ship, and in some cases by road transport.

Import terminals, however, are only supplied by pipeline from refineries or ports. Community health and safety issues associated with the operation of terminal facilities may include potential public exposure to spills, fires, and explosions, although the probability of large magnitude events directly associated with storage operations in well designed and managed facilities is usually low. The likelihood of community exposure to chemical hazards may be greater during road, rail, or water transport activities associated with fuel delivery and distribution.

1.1.2.1 Wastewater Pollutant Sources in Oil Terminals

The onshore facilities for most crude terminals will consist of storage tanks and associated equipment for crude oil, ballast water, and sanitary water. Thus, the major environmental concern is contamination of wastewater with oil and the treatment of the ballast and sanitary water prior to discharge. The treating methods for oil-contaminated wastewater include various types of gravity separators. It is most beneficial to segregate the dirty and clean water and thereby minimize the volume of water requiring treatment.

1.1.2.2 Product Terminals

Product terminals typically are separate from a refinery but in some cases may be associated with a refinery. The products typically handled at a terminal include gasoline, diesel, fuel oil, liquefied petroleum gas (LPG), kerosene, aviation gasoline, and jet fuels.

The few environmental concerns encountered in a product terminal are similar to those in a refinery, and the pollution control methods for product terminals are similar to those in a refinery.

1.1.3 Suspended Solids

Typically, suspended solids carry a significant portion of organic material, thus significantly contributing to the organic load of the wastewater (solids can contribute up to 60% of the BOD of a wastewater). Hence, effective solids removal can significantly contribute to wastewater treatment. The widely accepted way of testing a wastewater for suspended solids is to filter the wastewater through a 0.45 μm porosity filter. Anything on the filter after drying at about 103 °C is considered a portion of the suspended solids. Table 1.4 provides another classification system for the solids found in wastewater.

1.1.4 Heavy Metals

Any cation having an atomic mass (weight) greater than 23 (atomic mass of sodium) is considered to be a heavy metal. Motivations for controlling heavy metal concentrations in gas streams are diverse. Some heavy metals are dangerous to health or to the environment (e.g. mercury, cadmium, lead, chromium), some may cause corrosion (e.g. zinc, lead), and some are harmful in other ways (e.g. arsenic may pollute catalysts). Unlike organic pollutants, heavy metals do not decay and thus pose a different kind of challenge for remediation.

Currently, plants or microorganisms are tentatively used to remove some heavy metals such as mercury. Plants which exhibit hyper accumulation can be used to remove

Table 1.4 General classification of wastewater solids.

Particle classification	Particle size (mm)
Dissolved	Less than 10^{-6}
Colloidal	10^{-6} to 10^{-3}
Suspended	Greater than 10^{-3}
Settleable	Greater than 10^{-1}
Supracolloidal	10^{-3} to 10^{-1}

heavy metals from soils by concentrating them in their bio matter. Some treatment of mining tailings has occurred where the vegetation is then incinerated to recover the heavy metals.

1.1.5 Dissolved Inorganic Solids

Total dissolved inorganic solids (TDIS) is a value calculated to assess the actual inorganic salts content of a water or process water.

The following procedure can be used to determine the inorganic dissolved solids in wastewater. A sample of wastewater is filtered through a 0.45 μm filter, the filtrate is collected, then first the water (at 103 °C) and then the organic fraction (at 550 °C) are vaporized from the filtrate. The amount of material left in the vessel after incineration at 550 °C is referred to as the fixed or inorganic dissolved solids level.

1.1.6 Toxic Organic Compounds

Wastewater systems are known to contain toxic metals, organic micro pollutants, and pathogens that may add constraints to their beneficial uses. Environmental risks related to toxic inorganics, dioxins, furans, and pathogens can be controlled by:

(i) selecting a wastewater system having low content of regulated contaminants that respect the local legislation for land application
(ii) application of decontamination process to remove toxic metals
(iii) the necessary step of sterilization for monoculture process that eliminates pathogens.

These toxic organic compounds eventually reach sewage treatment plants and can be concentrated in wastewater systems. Disposal of wastewater systems is one way that these pollutants can be introduced into environment, among others. The presence of toxic organic compounds may add constraints to the ultimate disposal of sludges and/or reduce the possibilities for their beneficial uses.

Tables 1.5 and 1.6 list some organic compounds that are considered toxic and/or carcinogenic.

1.1.7 Surfactants

Surfactants, or surface-active agents, are large organic molecules that are slightly soluble in water and cause foaming in wastewater treatment plants and in the surface water into which the waste effluent is discharged.

The surfactants present in detergent products remain chemically unchanged during the washing process and are discharged down the drain with the dirty washing water. In the vast majority of cases, the drain is connected to a sewer and ultimately to a wastewater treatment plant where the surfactants present in the sewage can be removed by biological and physical-chemical processes.

During aeration of wastewater, surfactants are collected on the surface of the air bubbles and thus create very stable foam. The determination of surfactants is accomplished by measuring the color change in a standard solution of methylene blue active substance (MBAS).

Table 1.5 *Occupational exposure to carcinogenic substances.*

Compound	Site	Comment
Organic substances for which there is wide agreement on carcinogenicity		
4-Aminodiphenyl	Bladder	Contaminant in diphenylamine
Benzidine	Bladder	Ingredient of aniline dyes, plastics, and rubber
Beta-naphthylamine (2-NA)	Bladder	Dye and pesticide ingredient; exposed workers have 30–60 times as much bladder cancer Synonym: 2-naphthylamine
Bis(chloromethyl) ether	Lung	Used in making exchange resins; exposed workers have seven times as much lung cancer
Vinyl chloride	Liver	Angiosarcoma cases among PVC workers
Additional organic substances on USDA-OSHA cancer-causing substances list		
Alpha-naphthylamine (1-NA)	Bladder	Human case implicated; used in making dyes, herbicides, (1-NA) food colors, color film; antioxidant
Ethyleneamine	Unknown	Carcinogenic in animals; used in paper and textile processing and making of herbicides, resins, and rocket and jet fuels
3,3-Dichlorobenzidine	Unknown	Carcinogenic in animal species; exposure accompanies benzidine and beta-naphthylamine
Methyl chloromethyl methyl ether	Unknown	Carcinogenic in animals Synonyms: CMME; BCME contaminants CMME; used in resin making, textiles, and drug production
4,4-Methylene bis (2-chloroaniline)	Unknown	Tumorigenic in rats and mice; skin absorption may be the hazard; curing agent for iso-cyanate polymers Synonym: MOCA

PVC, polyvinyl chloride.

Table 1.6 *Industrial substances suspected of carcinogenic potential for humans.*

Antimony trioxide production
Benzene (skin)
Benzo(a) pyrene
Beryllium
Cadmium oxide production
Chloroform
Chromates of lead and zinc
3,3-Dichlorobenzidine
1,1-Dimethyl hydrazine
Dimethyl sulfate
Dimethylcarbamyl chloride
Epichlorhydrin
Hexamethyl phosphoramide (skin)
Hydrazine
4,4-Methylene bis (2-chloroaniline) (skin)
4,4-Methylene dianiline
Monomethyl hydrazine
Nitrosamines
Propane sulfone
Beta-propiolactone
Vinyl cyclohexene dioxide

1.1.8 Priority Pollutants

Priority pollutants (both inorganic and organic) are selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity. Many organic priority pollutants are also classified as volatile organic compounds (VOCs).

Representative examples of priority pollutants are shown in Table 1.3. Within a wastewater collection and treatment system, organic priority pollutants may be removed, transformed, generated, or simply transported through the system unchanged. Five primary mechanisms are involved: (i) volatilization (also gas stripping), (ii) degradation, (iii) adsorption to particles and sludge, (iv) transporting through the entire system, and (v) generation as result of chlorination or as by-products of the degradation of precursor compounds.

1.1.9 Volatile Organic Compounds

Wastewater is collected and treated in a variety of ways, some of which result in the emission of VOCs from the wastewater to the air. Water may come into direct contact with organic compounds during a variety of different chemical processing steps, thus generating wastewater streams that must be discharged for treatment or disposal. Direct contact wastewater includes:

- water used to wash impurities from organic compound products or reactants
- water used to cool or quench organic compound vapor streams
- condensed steam from jet eductor systems pulling vacuum-on vessels containing organic compounds
- water from raw material and product storage tanks
- water used as a carrier for catalysts and neutralizing agents (e.g. caustic solutions)
- water formed as a by-product during reaction steps.

Direct contact wastewater is also generated when water is used in equipment washes and spill clean-ups. This wastewater is normally more variable in flow rate and concentration than the streams listed above and may be collected in a way that is different from process wastewater. Wastewater streams generated by unintentional contact with organic compounds through equipment leaks are defined as “indirect contact” wastewater. Indirect contact wastewater may become contaminated as a result of leaks from heat exchangers, condensers, and pumps.

Organic compounds that have a boiling point $\leq 100\,^\circ\mathrm{C}$ and/or a vapor pressure of >1 mmHg (or 133.3 Pa) at $25\,^\circ\mathrm{C}$ are generally considered to be VOCs, e.g. vinyl chloride. The release of these compounds in sewers and at treatment plants, especially at the head works, is of particular concern with respect to the health of the collection system and treatment plant workers.

1.2 Treatment Stages

Generally, the terms “preliminary” and “primary” refer to physical unit operations, “secondary” refers to chemical and biological unit processes, and “advanced” or “tertiary” refers to combinations of all three.

Application and definition of the various stages of treatment and methods to perform specific functions are described in the following sections. Figure 1.1 shows a schematic of the wastewater treatment stages.

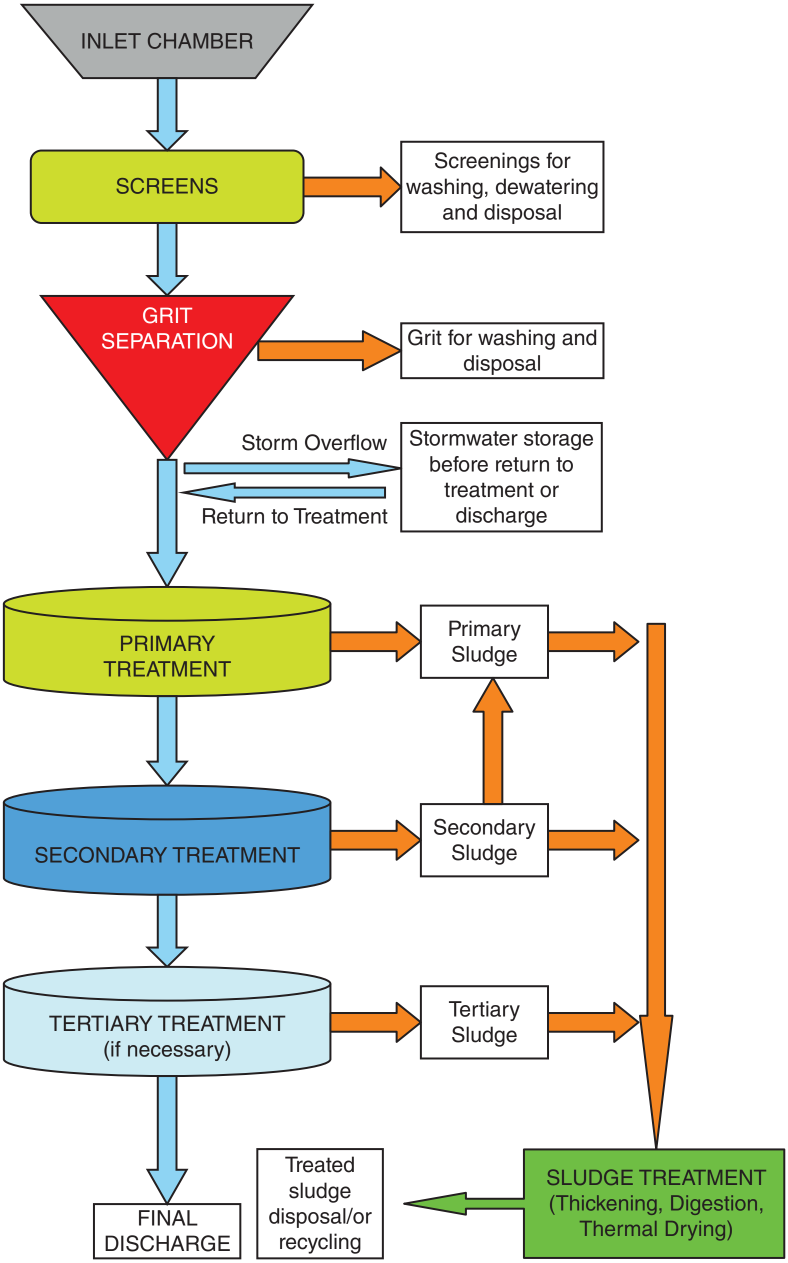

Figure 1.1 *A simplified schematic of the wastewater treatment process.*

Table 1.7 *Typical wastewater qualities.*

Parameter	Unit	Oily wastewater	Stripped sour water	Combined high TDS water (ion exchange waste, boiler blowdown, RO reject)	Cooling tower blowdown
Temperature	°C	30–60	30–35	30–40	—
pH	—	7–8	7–8	7–8	8
TDS	mg/l	150–5000	50–150	500–2500	5000–6000
TSS	mg/l	300–800	10–20	50–100	16 000–19 000
Cl_2 residual	—	—	—	—	0.3–0.5
BOD	mg/l	300–500	100–300	5–150	—
COD	mg/l	300–1200	200–500	100–500	—
TOC	mg/l	—	—	<100	—
Hardness	mg/l as $CaCO_3$	—	—	—	1200–1400
Total alkalinity	mg/l as $CaCO_3$	—	—	—	100–125
Ca^{2+}	mg/l	—	—	—	1000
Cl^-	mg/l	50–2000	—	—	1000–1500
NH_3	mg/l	20–50	40–80	—	<5
Cyanides	mg/l	1–3	—	—	—
Phenols	mg/l	5–20	20–80	—	—
H_2S	mg/l	5–10	10–40	—	—

TDS, total dissolved solids, RO, TSS, TOC.

1.2.1 Sources of Wastewater

Sources of wastewater in the oil, gas, and chemical processing industries include oily wastewater, sour water, stripped sour water, water treatment waste, and blowdown streams (cooling tower, boiler, and gasifier). Each of these sources produces wastewater with slightly different characteristics and treatment requirements.

Table 1.7 shows typical wastewater qualities for some of the wastewater streams in the oil, gas, and chemical processing industries.

1.2.2 Discharge Options and Quality Requirements

Water produced water in oil and gas industry has a complex composition, but its constituents can be broadly classified into organic and inorganic compounds, including dissolved and dispersed oils, grease, heavy metals, radionuclides, treating chemicals, formation solids, salts, dissolved gases, scale products, waxes, microorganisms, and dissolved oxygen.

The following four discharge alternatives are all technically feasible:

- physical and biological treatment followed by discharge to a river
- physical, biological, and chemical treatment followed by discharge to a river
- physical and biological treatment, and recycling with deep well injection, thus no surface discharge
- physical and biological treatment, evaporation, and crystallization, thus no discharge.

The selection of the preferred alternative is a function of the selected process, recycling opportunities, economics, regulatory limitations, and social requirements. Process effects, which relate primarily to dissolved solids concentrations and financial implications, will be examined.

1.2.2.1 Preliminary Wastewater Treatment

Preliminary wastewater treatment is defined as the removal of wastewater constituents that may cause maintenance or operational problems with the treatment operations, processes, and ancillary systems.

Screening and comminution for the removal of debris and rags, grit removal for the elimination of coarse suspended matter that may cause wear or clogging of equipment, and floatation for the removal of large quantities of oil and grease are examples of preliminary operations.

1.2.2.2 Primary Wastewater Treatment

In primary treatment a portion of the suspended solids and organic matter is removed from the wastewater. This removal is usually accomplished with physical operations such as screening and sedimentation.

The effluent from primary treatment will ordinarily contain considerable organic matter and will have a relatively high BOD. The principal function of primary treatment is as a precursor to secondary treatment.

Following primary treatment, the treated water is suitable for use as cooling water and utility water but will require further treatment to be used as boiler feed water.

1.2.2.3 Conventional Secondary Wastewater Treatment

Secondary treatment is directed principally toward the removal of biodegradable organics and suspended solids. Disinfection is frequently included in the definition of conventional secondary treatment.

Conventional secondary treatment is defined as the combination of processes customarily used for the removal of the constituents above and includes biological treatment by activated sludge, fixed film reactors, or lagoon systems and sedimentation.

1.2.2.4 Nutrient Removal or Control

Nutrient removal or control is generally required for:

1) discharge to confined bodies of water where eutrophication may be caused or accelerated
2) discharge to flowing streams where nitrification can tax oxygen resources or where rooted aquatic plants can flourish
3) recharge of groundwater that may be used indirectly for public water supplies.

The nutrients of principal concern are nitrogen and phosphorus, and these may be removed by biological, chemical, or a combination of these processes. In many cases, the nutrient removal processes are coupled with secondary treatment, for example biological denitrification may follow an activated sludge process that produces a nitrified effluent.

1.2.2.5 Advanced Wastewater Treatment/Wastewater Reclamation

Advanced wastewater treatment or tertiary treatment is normally defined as the level of treatment required beyond conventional secondary treatment to remove constituents of concern including nutrients, toxic compounds, and increased amounts of organic material and suspended solids.

In addition to the nutrient removal processes, the unit operations or processes frequently employed in advanced wastewater treatment are chemical coagulation, flocculation, and sedimentation followed by filtration and activated carbon. Less frequently used processes include ion exchange and reverse osmosis for specific ion removal or for reduction of dissolved solids.

Advanced wastewater treatment is also used in a variety of reuse applications where quality water is required, such as for industrial cooling water and groundwater recharge.

1.2.2.6 Toxic Waste Treatment/Specific Contaminant Removal

The removal of toxic substances and specific contaminants is a complex subject and the concentrations of toxic pollutants are usually controlled by pre-treatment prior to discharge to the final treatment system. Many toxic substances, such as heavy metals, are reduced by some form of chemical-physical treatment such as chemical coagulation, flocculation, sedimentation, or filtration.

Some degree of removal is also accomplished by conventional secondary treatment. Wastewater containing volatile organic constituents may be treated by air striping or carbon adsorption. Small concentrations of specific contaminants may be removed by ion exchange. Table 1.8 presents a list of typical pollutants that have an inhibitory effect on the activated-sludge process.

1.2.2.7 Sludge Processing

When a liquid sludge is produced, further treatment may be required to make it suitable for final disposal. Typically, sludges are thickened (dewatered) to reduce the volumes transported off-site for disposal.

Processes for reducing water content include lagooning in drying beds to produce a cake that can be applied to land or incinerated, pressing, where sludge is mechanically filtered, often through cloth screens, to produce a firm cake, and centrifugation where the sludge is thickened by centrifugally separating the solid and liquid. Sludges can be disposed of by liquid injection to land or by disposal in a landfill. For the most part, the methods and systems reported in Table 1.9 are used to process the sludge removed from the liquid portion of the wastewater.

1.3 Effluent Water Pollution Control

Examples of design and procedures which are generally beneficial are as follows:

- recovery of oil spills and hydrocarbons with vacuum trucks to reduce emissions and water effluents
- separation of oily wastes, concentrated wastes, and other process wastes from general effluents for more effective treatment

Table 1.8 *Threshold concentrations of pollutants inhibitory to the activated-sludge process.*

	Concentration (mg/l)	
Pollutant	Carbonaceous removal	Nitrification
Aluminum	15–26	—
Ammonia	480	—
Arsenic	0.10	—
Borate (boron)	0.05–100	—
Cadmium	10–100	—
Calcium	2500	—
Chromium (hexavalent)	1–10	0.25
Chromium (trivalent)	50	—
Copper	1	0.005–0.50
Cyanide	0.1–5	0.34
Iron	1000	—
Manganese	10	—
Magnesium	—	50
Mercury	0.1–5	—
Nickel	1–2.5	0.25
Silver	5	—
Sulfate	—	500
Zinc	0.8–1	
Phenols		
Phenol	200	4–10
Cresol	—	10–16
2,4-Dinitrophenol	—	150

- reduction of shock pollutant loads on treatment facilities through the periodic flushing of process sewers to prevent contaminant build-up and the use of flow and load equalization prior to treatment
- a specialized program for handling oily wastes, sludges, wash water, and other effluents
- maximization of air fan cooling and employing cooling water only for those services in which low process temperatures make air fan cooling impractical or uneconomic
- limiting the amount of water used for process unit washdowns
- converting foul water strippers to reboiler strippers to reduce foul water and recover condensate
- using caustic injection into desalted crude to reduce the amount of NH_3 needed to control corrosion in the crude unit overhead system.

1.3.1 Spill Prevention and Control

Prevention of spills of oil and related petroleum products should be one of the prime objectives of both the design and operation of a proposed facility, and should include, but not be limited to, the siting and design criteria for all facilities, operating procedures, and their periodic review, inspection, and monitoring, personnel training, revision of operating procedures (where required), and redesign (if necessary).

Table 1.9 *Sludge-processing and disposal methods.*

Processing or disposal function	Unit operation, unit process, or treatment method
Preliminary operation	Sludge pumping
	Sludge grinding
	Sludge blending and storage
	Sludge degritting
Thickening	Gravity thickening
	Flotation thickening
	Centrifugation
	Gravity belt thickening
	Rotary drum thickening
Conditioning	Chemical conditioning
	Heat treatment
Disinfection	Pasteurization
	Long-term storage
Dewatering	Vacuum filter
	Centrifuge
	Belt press filter
	Filter press
	Sludge drying beds
	Lagoons
Heat drying	Dryer variations
	Multiple effect evaporator
Thermal reduction	Multiple hearth incineration
	Fluidized bed incineration
	Co-incineration with solid wastes
	Wet air oxidation
	Vertical deep well reactor
Ultimate disposal	Land application
	Distribution and marketing
	Landfill
	Lagooning
	Chemical fixation

Among specific design parameters are impervious dikes around tankage (feedstock and product), containment of storm water from the process area(s), ability to treat contaminated storm water in the wastewater treatment facility, leak detection systems capable of detecting small volume or slow rates of leakage from the pipeline system, and appropriate use of valves to minimize potential spill volumes.

1.3.1.1 Spill Prevention Techniques

Prevention of spills is the first line of defense in protecting life, property, and the environment. Experience has shown that operational or human error and equipment failures are the principal causes of spills. Both of these can be reduced through the involvement and commitment of all staff to spill prevention.

Proper design, inspection, and maintenance of general facilities are of principle importance. Operator capacity is also extremely important and must be periodically tested and upgraded.

Given good equipment, good operators, and good procedures, spills will be reduced. They will not, however, be eliminated.

The difference between a minor event and a catastrophic event depends almost entirely on planning. Such planning includes plant design with spill containment features and alarms, a workable and efficient contingency plan, trained spill control personnel, and adequate spill control equipment.

1.3.1.2 Bulk Storage

Oil storage tank construction and material should be compatible with the oil stored and storage conditions such as pressure, temperature etc.

Impervious secondary containment should be provided for the capacity of the largest single tank plus a sufficient allowance for precipitation and free board.

New metallic tanks buried underground should be protected from corrosion by coatings, cathodic protection, or other effective methods compatible with local soil conditions. The use of non-metallic tanks, if available and practical, should be given consideration.

Above-ground tanks should be subjected to appropriate integrity testing. Appropriate procedures might include hydrostatic testing, visual inspections, or inspection by a system of non-destructive shell thickness gauging.

Plant effluents which are discharged into a watercourse should have disposal facilities that are observed frequently enough to detect any possible system upset that could cause an oil discharge.

1.3.1.3 Facility Drainage

Appropriate containment or diversionary structures should be provided to prevent oil from leaving the property uncontrolled.

1.3.2 Groundwater Pollution Control

Two basic sources of spilled liquid petroleum products are equipment failure and operator error.

- Equipment failure includes corrosion and leaking of both above- and below-ground piping and tanks, valves failure, refinery unit upsets, and sewer and drain leaks. Many of these failures may be avoided through proper inspection and maintenance procedures.
- Operator error includes overfilling tanks and improper alignment of valves and piping. These and other operator errors can best be corrected through developing proven operating procedures, regular training and testing of personnel, and systematic follow-up to assure that procedures are followed.

1.3.2.1 Preventive Measures

The preventive measures to be installed during the construction of a permanent structure must consider the following:

- the type of construction (refinery, storage tank, pipeline, etc.)
- the volume and the nature of the oil likely to pollute the site
- the geology and hydrogeological environment: the nature of the terrain, and the depth, activity, and quality of the aquifer
- the economic environment: proximity to and capacity of water wells and intakes for domestic purposes, risk of pollution of a river, etc.

The preventive system involves four areas: corrosion protection, surface preventive measures, subsurface preventive measures, and monitoring devices to detect and warn of unsuspected pollution not visible from the surface or of a dangerous change in groundwater levels.

Other methods of preventing spilled product from entering the ground and controlling its direction are:

- rendering the soil impermeable where required by means of a concrete paving, a clay or bitumen layer, plastic sheets (PVC sheets covered with gravel, fiberglass reinforced epoxy), and chemical mixed with the soil
- a surface drain system in the plant area carrying all oil and oil-contaminated water to a dirty water sewer, and then to an interceptor or separator, by means of a pipe system with manholes (cast iron, steel, epoxy) and gutters.

1.3.2.2 Types of Devices

- *Trench*

  This system of protection, which is used as a barrier to prevent the horizontal movement of oil, can only be carried out on a practical scale if the water table is situated at a depth of less than about 3–8 m, depending on soil conditions.

  Spread of oil on the groundwater surface is intercepted by digging the trench to about 1 m below the piezometric level. Oil flows onto the water surface, where it can be recovered.
- *Hydrodynamic protection*

  The principle of oil spill control using hydrodynamic methods is to effect a change in the groundwater flow pattern such that the free oil or the contaminated water, as the case may be, can be drawn to a specific control point or points. This can be achieved by discharging or recharging the aquifer, or a combination of both. The success of the method depends on maintaining an artificial gradient in the groundwater surface.
- *Monitoring*

  Groundwater monitoring devices are typically installed to detect and warn of unsuspected contamination not visible from the surface or of a dangerous change in groundwater levels. These devices are installed around petroleum storage areas, waste treatment/disposal facilities (including lagoons, land farms, and landfills), or an entire facility depending on the potential for contamination.

  Care should be taken in choosing monitoring devices to maximize the accuracy and reliability of the system. Monitoring should also be conducted to differentiate between previous and new spills.
- *Mitigation measures*

  After a spill or any contamination is detected, remedial measures such as determination of the extent of contamination (boundaries) and a hydrogeological assessment of the contamination area to determine the corrective action necessary must be conducted. When an appropriate action is determined, steps including recovery of the oil and oily water, and restoration of the site may be instituted.

- *Recovery measures*
  The principal factor to be considered when recovering free oil from the groundwater surface is to employ the natural water gradient or induce one or by increasing an existing gradient by artificial means. By good use and operation of recovery equipment, free oil can be concentrated at a relatively limited number of selected sites and removed. Wells and trenches are typically used for recovering oil and water.

1.4 Treatment Processes

Industrial wastewater treatment processes cover the mechanisms and processes used to treat water that has been contaminated in some way by anthropogenic industrial or commercial activities prior to its release into the environment or its re-use.

Oil, gas, and chemical industries produce some contaminants in wastewater that have to be removed by physical, chemical, and/or biological means. Figure 1.2 shows a schematic of wastewater treatment in the chemical industry.

Unit operations and processes which may be commonly used in wastewater treatment are listed in Table 1.10. The following guidelines should be taken into consideration for the selection of treatment technologies:

a) Technologies should be categorized into those that work, those that have the potential to work, and those that have no place for the particular application.
b) Technologies should be evaluated based on their effectiveness (ability to reliably attain treatment goals), implementability (availability of materials and services), and costs (capital, and operation and maintenance).

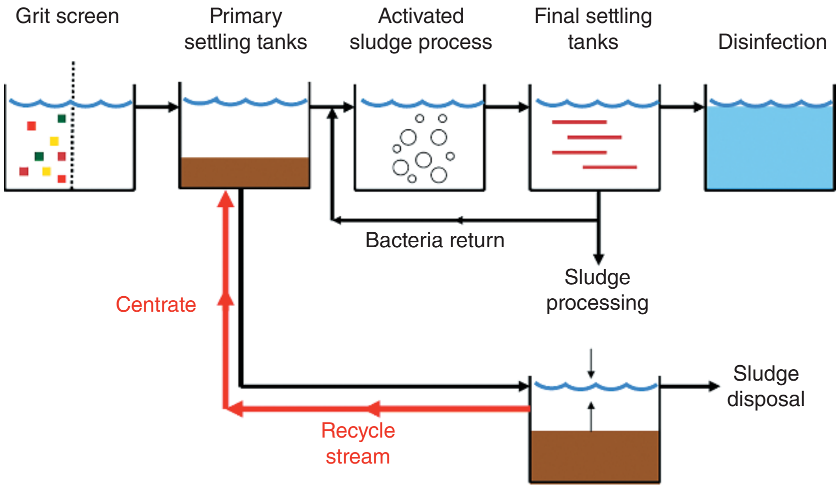

Figure 1.2 A schematic of wastewater treatment. Source: Reproduced with permission, W. Zhou et al., Bioresource Technology 102 (2011) 6909–6919, ©Elsevier 2011.

Table 1.10 *Unit operations, unit processes, and systems for waste-water treatment.*

Contaminant	Unit operation, unit process, or treatment system
Suspended solids	Sedimentation Screening and comminution Filtration Flotation Chemical polymer addition Coagulation/sedimentation
Biodegradable organics	Activated-sludge variations Fixed-film: trickling filters Fixed-film: rotating biological contractors Lagoon and oxidation pond variations Intermittent sand filtration Land treatment systems Physical-chemical systems
Pathogens	Chlorination Hypochlorination Ozonation Land treatment systems
Nutrients	
a) Nitrogen	Suspended-growth nitrification and denitrification variations Fixed-film nitrification and denitrification variations Ammonia stripping Ion exchange Breakpoint chlorination Land treatment systems
b) Phosphorus	Metal salt addition Lime coagulation/sedimentation Biological/chemical phosphorus removal Land treatment systems
c) Nitrogen and phosphorus	Biological nutrient removal Carbon adsorption
Refractory organics	Tertiary ozonation Land treatment systems
Heavy metals	Chemical precipitation Ion exchange Land treatment systems
Dissolved inorganic solids	Ion exchange Reverse osmosis Electrodialysis

c) Viable technologies should be identified for each of the individual wastewater streams. The streams that use the same technologies should be combined to create composite wastewater treatment trains. These wastewater treatment trains should be compared to the current manufacturing and waste treatment practices to identify possible candidates for waste segregation and independent treatment.

d) The level of wastewater treatment and method of effluent discharge should be established to protect the receiving body of water or water table and its usages. The level of treatment of the facility to be designed should be determined by the ability of the receiving water to accept residual wastes and the allocation set up by effluent standards. The degree of treatment can be determined by comparing the influent wastewater characteristics to the required effluent wastewater characteristics. In case of wastewater reuse applications, the quality of water used as make-up will govern the wastewater treatment needed and the degree of reliability required for the treatment processes and operations. The reliability of the proposed treatment processes and operations must be evaluated to provide a continuous supply of water with consistent water quality.

e) All toxic and highly chemically active materials should be treated at the source and not be discharged in any active state into the sewers loading to the waste treatment plant. This may include removal of soluble and insoluble forms of metals such as lead, zinc, copper, or their derivatives and other similarly dangerous classified metals and their by-products. It should be required that highly active metals, including finely divided magnesium or aluminum alloys, should not be discharged in the sewers but be treated and removed by special methods and equipment at the source. It should be required that all highly toxic inorganic chemicals, including cyanides, fluorides, and related objectionable anions, must be treated and removed from the water at or near the source to the degree specified in the code regulations. This includes the chromates and other special complex anion derivatives. Another group for exclusion from discharge of waste in the sewer includes highly active oxidizing agents, particularly peroxides of organic and inorganic structures. This group should also include the exclusion of other powerful oxidizing agents, including of chlorates, perchlorates, nitric acid, and other similar products. The discharge of volatile organic materials into the waste should also be restricted and these materials should be isolated and treated at the source. This restriction is necessary because explosions may occur in sewer systems where volatilization of the organic matter creates an explosive mixture or some other conditions set off chemical reactions. In general all toxic materials, particularly of organics, that are known to be dangerous to plant, animal, or human life should be treated at the source. All solutions containing radioactive products must also be kept isolated and treated at the source.

1.4.1 Wastewater Pollution Oil Terminals

Wastewater from the petroleum industry are numerous and diverse. They can be process water such as crude oil desalting water or sour water from hydrocracking or hydrotreatment processes, general effluents such as drained oily water, washing water or spent caustics. In order to meet quality requirements for wastewater releases, it is necessary to segregate these different types. Common techniques for wastewater treatment in refineries are described here and then best management practices for process wastewater are described.

The largest source of contaminated wastewater at a crude terminal is the ballast water from tankers. The quantity of ballast water requiring treatment depends upon the ship design, operation, and regulations governing the discharge of ballast water. The ship-design parameters include the amount of segregated ballast, the tank dimensions, and the use of onboard oil/water separators. The operating parameters include the type of previous cargo, weather conditions, and tank cleaning operations. Optimizing the design and operation of a tanker can reduce the amount of water requiring treatment.

Ballast water treatment usually consists of settling the ballast in shoreside tankage for periods of 10–24 hours, skimming off any oil, and discharging the water. This simple gravity separation is acceptable in some circumstances. For a better quality effluent physical, chemical, and/or biological methods are necessary.

In some locations where shore space is at a premium off-shore, deballasting facilities in the form of converted redundant tankers are utilized. One method to eliminate contaminated ballast water in tankers is the use of segregated ballast.

1.4.2 Simple Gravity Separation

Oil/water separation is the first step in the general treatment of residual refinery water. Its purpose is to eliminate insoluble hydrocarbons and suspended matters. It is classically carried out by gravity. Several separators are available which can be longitudinal [American Petroleum Institute (API) separators], circular, or lamellar.

These treatment systems rely on gravity difference to separate the oil and water. They are capable of removing the bulk of non-dissolved and non-emulsified oil. Examples these systems include storage and settlement, once through storage with skimming, API separators, corrugated plate interceptors (CPI), and holding basins.

1.4.3 Residual Suspended Matter

If it is necessary to reduce the non-dissolved oil content of the effluent below 25 mg/l, there are several processes available which can be added after the chosen simple gravity system.

These methods will also reduce suspended solids to below approximately 30 mg/l. BOD can also be reduced because of the oil and solids removed. These processes have little effect on soluble oil content.

The physical methods include dissolved air flotation, filtration (using gravity or pressure filters), physical separation plus use of chemicals such as inorganic flocculants, and/or demulsifiers or polyelectrolytes, flocculation/sedimentation, flocculation-dissolved air flotation, and induced air flotation.

1.4.3.1 Combination of Simple Gravity Separation Systems

Various combinations of the above individual treatment steps can be used and such combinations may consist of storage and settlement plus API separators or CPI, storage and settlement plus holding basin, or storage and settlement plus API or CPI plus holding basin.

There are several reasons why a combination of steps is often the best choice of treatment process. First, storage and settlement ahead of a CPI or API will remove crude oil and prevent temporary overloading of the downstream separator.

Second, rather than sizing the CPI or API separator to handle the maximum hourly flow rate, costs can be reduced by having a combination of a settling tank and CPI or API separator, with the tank designed for the maximum flow rate and the separator design to deal with the average flow rate. Third, a CPI or API plus holding basin serves as a guard chamber to finally trap any inadvertent discharge of oil from the settling tank.

1.4.3.2 Physical and Chemical Purification

This step is necessary before biological treatment. This technique associates one chemical reaction with a physical separation. The most commonly used techniques are coagulation, flocculation, air flotation, and filtration. Purification allows elimination of colloidal suspended matters and insoluble hydrocarbons.

1.4.3.3 Biological Treatment

After physical and chemical treatment, dissolved pollutants have still to be removed. These pollutants include soluble hydrocarbons, soluble CODs and BODs, phenols, and nitrogen compounds. They are biodegradable and can be removed with biological treatment techniques such as activated sludge or trickling filters. Biological treatment may in some cases be appropriate for removing dissolved biodegradable materials, which are often in low concentrations in normal ballast water. Typical devices used for biological treatment include activated sludge, trickling filters, rotating discs, and lagoons (aerated or not).

1.4.3.4 Spills

A major environmental concern with terminal operations is oil being spilled and the effects on birds and marine life.

Depending upon the type of terminal (offshore or onshore) and the characteristics of the water (such as currents and proximity to open water), the effects of a spill can vary from insignificant to extremely damaging. For example, an enclosed area such as an inlet from the sea, which has been described as the most productive marine environment, may experience accumulation of oil to unacceptable levels over time.

The oil that is spilled offshore will have less impact on the marine environment than an equivalent oil spill within an inlet from the sea (estuary) for three reasons:

1) There are fewer organisms offshore to be affected.
2) The concentration of toxic compounds within the water column is expected to be less because more dilution water is available offshore.
3) The contact time with marine life will generally be shorter for an offshore spill due to the restricted flushing of the inlet from the sea.

In addition to spilled oil, treated ballast water can also affect marine life in an "enclosed" area. Thus, it may sometimes be best to pipe the treated water to another location where good mixing may occur, thereby protecting the "enclosed" area and minimizing the effects on the marine environment.

Spill contaminant is an important feature of a terminal. The most common types of barrier systems used are floating booms and sorbent ropes. Two less frequently used alternatives are air-bubble barrier systems and enclosed berths.

1.4.4 Selection of Treatment Processes

Removing the all wastewater contaminants will be achieved only through various treatment operation units. Selection of the most appropriate treatment sequences will provide better quality treated wastewater.

Table 1.11 *Selective list of unit processes used for particular waste constituents.*

Unit process	Removal mechanism	Waste constituent
Sedimentation/ flotation	Gravity	Solid phase organics/inorganics
Coagulation/ sedimentation	Particle aggregation/gravity	Solid phase organics/inorganics
	Chemical bonding	Colloidal phase organics/inorganics Colloidal phase inorganics
Biological treatment	Particle aggregation/biological	Solid phase organics/inorganics
	Metabolism/gravity	Colloidal phase organics/inorganics Soluble phase biodegradable organics
Filtration	Entrapment particle aggregation/adsorption	Solid phase organics/inorganics Colloidal phase organics/inorganics
Carbon adsorption	Adsorption	Soluble phase adsorbable organics/inorganics
	Entrapment	Solid phase organics/inorganics
	Particle aggregation/adsorption	Colloidal phase organics/inorganics

The two general categories of treatment are physical/chemical treatment and biological treatment. The essential difference between the capabilities of a physical/chemical process and a biological process is the ability of each to remove certain types of organic materials. Physical/chemical processes are subject to apparent inefficiencies caused by a certain amount of non-adsorbable organics in the wastewater. Biological processes are subject to apparent inefficiencies as a result of non-biodegradable organics in the wastewater. A selective listing of unit processes and the waste constituents for which they are generally applied and/or are effective is shown in Table 1.11.

Deciding on the most applicable process is based on full knowledge of the wastewater conditions and constituents. In general, chemical/physical treatment is a suitable alternative:

- for a waste having a high particulate organic concentration, provided the soluble organic concentration, following chemical coagulation, sedimentation, and filtration, is less than 50 mg/l BOD5
- for wastewater treatment systems where no influent flows will be received for substantial periods of time, for example batch treatment or systems experiencing significant flow variations
- if land space is limited or toxic substances are presented in the raw wastewater.

Care should be exercised in the application of physical/chemical treatment systems on medium to high strength wastes (BOD5 greater than 200 mg/l). For this situation, on-site pilot studies are desirable to determine effluent quality that could be obtained and to ascertain if the biological activity anticipated in the carbon column will be more of a detriment (odor, plugging) than an asset (higher organic removal).

Land application of wastewater is viewed as an alternative to other secondary treatment schemes or as a final add-on step for liquid disposal and convenient water use. Alternative

Table 1.12 *Treatment processes used for the removal of toxic compounds.*

Process	Removal application
Activated-carbon adsorption	Natural and synthetic organic compounds including VOCs, pesticides, PCBs, and heavy metals
Activated-sludge-powdered activated carbon	Heavy metals, ammonia, selected refractory priority pollutants
Air stripping	VOCs and ammonia
Chemical coagulation, sedimentation, and filtration	Heavy metals and PCBs
Chemical oxidation	Ammonia, refractory and toxic halogenated aliphatic and aromatic compounds
Conventional biological treatment (activated-sludge, trickling filter)	Phenols, PCBs, selected hydrogenated hydrocarbons

VOCs, volatile organic compounds; PCBs, polychloro-biphenyls.

land disposal methods include various modes of surface and subsurface percolation and deep well injection. Combined land disposal and wastewater reclamation methods include infiltration-percolation, overland flow, irrigation, and groundwater recharge.

Many treatment methods can be used for the treatment of toxic compounds. Because of the complex nature of toxicity, such treatment methods must consider the specific characteristics of the wastewater and the nature of the toxic compounds. Treatment processes used to remove some specific compounds or groups of compounds are summarized in Table 1.12.

Various combinations of unit operations and processes and their interaction for treatment of refinery wastewater are identified in Table 1.13. A summary of treatment methods for petrochemical wastes is presented in Tables 1.14–1.16. The selection of a process train or alternative process trains should be made on the ability of the individual unit processes to remove specific waste constituents.

1.5 Siting and Design

In previous sections, the sources of pollution and control methods were discussed. In the following pages the general outline of pollutant specific for management in the siting and design of a refinery or terminal will be discussed.

A major design requirement for a refinery or terminal is the need to minimize or eliminate the emission of pollutants to the environment. The methods needed to implement this depend on the types of crude oil processed, the types of products, the availability of water fuel and other utilities, and the agreed pollution parameters.

Safety requirements must also be considered at this stage to ensure that the surrounding population and plant personnel are protected from hazards such as fire, explosion, and toxic chemicals.

The items of concern in the siting and design of a facility are briefly reviewed here with the intention of pointing out potential environmental effects.

Table 1.13 *Refinery treatment sequence options.*

Pre-treatment	Primary treatment	Secondary treatment	Tertiary treatment	
Removal of phenolics, S-, NH_3, RSH, F-, acid, sludge, oil, etc., water reuse; waste equalization	Removal of free oil Suspended solids	**Removal of emulsified oil, suspended and colloidal solids**	**Removal of dissolved organics (variable) produced biological sludge**	
Processes				
Unit separators Steam stripping Fuel gas stripping Air oxidation Neutralization Surge ponds	API separators CPI, PPI separators	Chemical coagulation and air flotation Chemical coagulation and filtration pH control Reduction of intermediate oxygen demand Equalization of wastes	Trickling filter Activated oxidation pond Aerated lagoon Rotating biological contactors	Chemical coagulation and air flotation Chemical coagulation and filtration Carbon adsorption Carbon adsorption
Inhibitory contaminant surge control	↓Sludges	↓Sludges	↓Sludges	↓Sludges

RSH, API, CPI, corrugated plate interceptor; PPI, parallel plate interceptor.

1.5.1 Aquatic Ecosystems

A refinery or terminal siting should take into account potential impacts on aquatic ecosystems. The characterization of aquatic systems in a siting should include the location of spawning areas, feeding zones, commercial fishing areas, sport fishing areas, a description of the benthic populations, and an estimate of primary productivity and its limiting factors.

Design considerations should include the facility's water supply requirements. While water use is usually non-consumptive, attention should be given to the intake and discharge zones.

At refineries or terminals there is always the potential for a release of oil or petroleum products. All facilities should have a spill contingency plan and the basic equipment necessary to clean up a spill.

1.5.2 Terrestrial Ecosystems

Impacts on terrestrial ecosystems from the siting of a refinery or terminal include a reduction or loss in total available habitat, destruction, or modification of food webs, and changes in

Table 1.14 *Summary of physical treatment methods for petrochemical wastes classified by plant product.*

	Physical treatment						
Plant product	Suspended-growth nitrification	Suspended-growth nitrification	Suspended-growth nitrification	Suspended-growth nitrification	Suspended-growth nitrification	Suspended-growth nitrification	Suspended-growth nitrification
General chemicals	✓			✓	✓		
Nylon							✓
Nylon chemical intermediates	✓	✓		✓		✓	
Organic chemicals			✓			✓	
Photochemicals		✓					
Resins					✓		
Rocket fuels			✓				
Synthetic rubber			✓				

Table 1.15 *Summary of chemical and biological treatment methods for petrochemical wastes classified by plant product.*

	Chemical treatment		Biological treatment		
Plant product	pH adjustment	Chemical oxidation	Biological filters	Activated sludge	Lagoons
General chemicals	✓	✓			✓
Nylon			✓		
Nylon chemical intermediates		✓	✓		✓
Organic chemicals	✓				
Oxygenated hydrocarbons				✓	
Photochemicals			✓		
Powders			✓		
Resins			✓		✓
Rocket fuels	✓		✓		
Rubber, textiles, and plastics				✓	

Table 1.16 *Summary of ultimate disposal methods for petrochemical wastes classified by plant product.*

	Ultimate disposal						
Plant product	Controlled dilution to streams and bays	At sea	On land surfaces	Dumping or burial	Deep weles	Incinekation	Salvage
Nylon			✓		✓	✓	✓
Nylon chemical intermediates	✓					✓	
Synthetic rubber	✓					✓	

populations. Another concern in the siting should be the sensitivity of plants and animals to pollutants.

1.5.3 Wetland Ecosystems

Where the water table is at, near, or above the land surface for a significant part of most years, the hydrologic regime is such that aquatic or hydrophytic vegetation is usually established, although tidal flats may be non-vegetated. Because wetlands are water systems, any alteration affecting the quality of water in a small area is transmitted to other areas, magnifying potential impacts.

Wetlands may be altered directly by filling, dredging, draining, or creating impoundments. Indirectly, alteration of water flow patterns at locations and changes in adjacent land use can change the functions and values of wetland areas.

In addition to facility construction, the laying of pipelines associated with these facilities can have an impact on wetlands.

1.5.4 Land Use

Part of the siting for a refinery or terminal should consider the existing land use and compatibility with local and regional land use plans.

1.5.5 Water Pollution Control

The siting and design guidelines for water pollution control are as follows:

- *Siting*
  The most important aspect of water pollution control in the siting of a refinery is the effect of the wastewater effluent on the receiving water. Several factors which should be assessed in the siting investigation are heat load, total dissolved solids, heavy metal concentrations, and the effects of organics in the effluent.
- *Design*
  The design of a water pollution control depends on the degree of cleanup required to permit discharge of the wastewater to either a body of water or public wastewater treatment plant, and the characteristics of the refinery. The following design practices are directed primarily toward segregation of process and non-process wastewater, and the recycling and reuse of raw and treated wastewater:
  a) Refinery wastewater should be segregated and treated based on oil content and potential for reuse. Four common divisions are oil-free wastewater, oily cooling water, process water, and sanity wastewater.
  b) Raw and treated wastewater streams should be recycled to reduce the effluent volume and thereby the make-up water required. Specific practices include the use of catalytic cracker accumulator wastewater rich in H_2S (sour water) for make-up to crude desalters after stripping;
  c) Tank farm, process, and product-handling areas should be sloped and graded toward sumps or sewers to permit quick removal and collection of spills.
  d) Check valves and storage tanks should be installed at the ends of pipelines specifically for spill prevention and control.
  e) Seals should be installed on normally closed valves.
  f) Cathodic protection systems should be installed on underground pipelines and tanks or a continuous coating applied around the pipeline to prevent direct contact between the pipe and the soil.
  g) Where feasible, all pipelines should be located above ground to facilitate inspection and identification of leaks.
  h) Concrete ditches leading to either a chemical waste system or a wastewater system should be installed under pipelines.

1.6 Sources of Effluent in the Petrochemical Industry

1.6.1 Water Pollution

In chemical plants, the volume water formed by chemical reaction is generally less than the volume of water evaporated into atmosphere, so the amount of water discharged tends to be less than the water intake. However, most of the intake water is discharged.

In addition, rain water is fouled while flowing through contaminated areas of a plant and is discharged as part of the wastewater.

1.6.2 Cooling Water

Most industrial water is used as cooling water, (for example, for naphtha thermal cracking in making ethylene and ethylene dichloride), for thermal cracking in the manufacture of vinyl chloride, for removal of reaction heat in polymerization and oxidation, and for cooling fractionator condensers. Cooling water is not fouled since an indirect cooling method is generally adopted. However, there are instances of liquid leaking from the tubes of a cooler due to corrosion attack, resulting in contamination of cooling water.

1.6.3 Washing Water and Process Water

Considering the properties of fouled water, washing water is identical to process water, so the former is frequently called "process water." Water is used in washing because it dissolves various substances. For example, carbon dioxide, hydrogen sulfide, hydrochloric acid, etc. in gas are dissolved in dilute alkali water.

The amounts of washing water and process water used in petrochemical plants are small compared with those of cooling water. This wastewater contains a considerable amount of organic substances and dissolved oils, but the COD and BOD values are insufficient to indicate the amounts of organic substance contained in the wastewater from petrochemical processes.

The organic matter in wastewater from petrochemical plants should be indicated using TOC (total organic carbon) and TOD (total oxygen demand) but the TOC and TOD indications themselves are not always considered useful criteria for the detection of toxic substances in wastewater or for the selection of wastewater treating methods. As organic compounds discharged from petrochemical processes have a variety of chemical properties depending on the processes, it is necessary to pursue the emission sources. Table 1.17 shows different types of pollution in plant operations.

1.6.4 Typical Pollutants in the Petrochemical Industry

Aqueous effluents originating from the petrochemical industry are essentially characterized by the presence of the following substances:

organic substances that are not biodegradable, or only slightly so
nitrogen compounds
heavy metals.

Table 1.17 *Types of water pollution.*

Type of pollution	Plant operation	Examples of pollution
Water pollution (wastewater, waste liquid)	Cooling water	Direct cooling or quenching of decomposed gas: wastewater contains tar dust, hydrogen sulfate, and cyanide
		Breakage of indirect cooler tubes: contamination of cooling water due to liquid inside the tubes
		Steam ejector: steam condensate from ejector contains volatile hydrocarbon
	Boiler feed water	Steam ejector: steam condensate from ejector contains volatile hydrocarbon
	Washing water	Water containing hydrogen sulfate, hydrochloric acid etc. is discharged from the washing of gas
		Water containing hydrochloric acid, etc. is discharged from the washing of liquid
		Dust is contained in discharged water from the dust collector
	Process water Feed water (chemical reaction, electrolysis)	Solvent for suspension and emulsion polymerization contains catalysts, emulsifier, plastic monomer, etc.
		Steam condensate from steam stripping: dissolves hydrocarbons
		Steam condensate originating from dilution steam for naphtha thermal cracking: contains carbon, phenol, and light oil
	Leakage (loss)	Leakage from pump and agitator shafts, valve stems, and flanges, and due to operational error

1.6.5 Petrochemical Waste Treatment

Petrochemicals have been defined as bulk chemicals derived principally from natural gas, petroleum, or both. A careful check should be made of processes proposed or used for the manufacture of petrochemicals to decrease the possibility of water-soluble organics entering water supplies. The following methods should be considered:

- recycling and reuse of waste streams
- quenching with oil or chemicals other than water that do not produce waterborne wastes
- use of alternative processes that do not produce waterborne wastes
- use of air coolers or of cooling towers in place of once-through cooling water
- elimination of waste products in the manufacturing operation before they become associated with waste streams
- processing of waste streams to reduce the amount of chemicals in wastewater leaving the plant.

The extensive use of automated controls, alarms, and checks by operators to prevent loss of chemicals is also important. It is essential that adequate facilities be installed to prevent uncontrolled release of chemicals and wastes to sewers or receiving water. A very effective means of quality control is the use of large lagoons capable of holding several days' production of wastewater. This allows the water to be checked before being released to receiving water.

1.6.6 Fertilizer

The liquid effluents arising from a fertilizer factory originate from a variety of sources and may be summarized as follows:

a) Ammonia-bearing waste from ammonia plants.
b) Ammonia and urea waste from urea manufacturing plants.
c) Ammonium salts such as ammonium nitrate, ammonium sulfate, and ammonium phosphate.
d) Phosphates and fluoride waste from phosphate and super phosphate plants.
e) Acidic spillages from sulfuric acid, nitric acid, and phosphoric acid plants.
f) Spent solutions from the regeneration of ion-exchange units:-acid from cation exchange units and alkali from regeneration of anion exchange units.
g) Phosphate, chromate, copper sulfate, and zinc wastes from cooling tower blowdown.
h) Salts of metals such as iron, copper, manganese, molybdenum, and cobalt.
i) Sludge discharged from clarifiers and backwash water from sand filters.
j) Carbon slurry from partial oxidation units.
k) Scrubber wastes from gas purification processes containing contaminants such as:
   - mono and diethanol amines (MEA and DEA)
   - arsenic, as As_2O_3
   - potassium carbonate
   - caustic soda.

The effluents from fertilizer manufacturing are generated from a wide range of unit operations, and considerable variation between wastewater from different factories may be noted. The age, state of repair, operational management, and degree of sophistication of each manufacturing unit will play an important role in determining the degree of in-plant materials loss, and the important factors leading to excessive losses (and subsequent pollution) may be summarized as follows:

- outdated basic manufacturing plant with low efficiency and poor process control
- improper maintenance and repair, with particular emphasis on servicing of control equipment
- variations in feedstock and difficulties in adjusting process plant to cope with these variations effectively
- lack of consideration for pollution abatement and the prevention of materials loss at the original plant design stage.

Overall water requirement for fertilizer manufacturing plants may be high due to process cooling requirements. The total volume of effluent discharged is dependent to a considerable extent on the degree of in-plant recirculation, and in the case of total recycle the raw water is used primarily for make-up purposes.

Plants designed on a once-through cooling system generally give rise to high volumes of effluent, from 1000 m^3/h to volumes in excess of 10 000 m^3/h, consisting primarily of cooling water discharge.

1.6.6.1 Nitrogenous Fertilizers

A complex nitrogenous fertilizer plant based on the production of ammonium nitrate and urea products may give rise to pollutants such as ammonium nitrate, nitric acid, ammonia, urea, sulfuric acid, caustic soda, chromate, oil, grease, and boiler feed additives, contained within the overall effluent stream. The individual effluents from ammonia and urea plants can be categorized as follows:

a) Ammonia plants
  - HCN stripper outlet
  - Catalyst reduction process
  - Shift process condensate.

b) Urea plants
  - Concentrate liquor
  - Cooling water blowdown
  - Additional pollutant discharges may arise from oily water and sanitary sewage effluents.

1.6.6.2 Phosphate Fertilizers

Some examples of the sources of liquid effluents from phosphatic fertilizer manufacture are as follows:
Plant 1: Raw water intake
Effluent sources:

- Superphosphate plant
- Sulfuric acid plant
- Water treatment plant
- Cooling tower
- Other sources

Plant 2: Raw water intake – Sea water (once-through cooling)
Effluent sources:

Ammonia plant
Phosphoric acid plant
Sulfuric acid plant
Utilities plant
Cooling water make-up
Boiler blowdown and washings from ion
Exchange units and floor washing

1.6.6.3 Compound Nitrogen/Phosphorus/Potassium Fertilizers

A major component of nitrogen/phosphorus/potassium (NPK) effluent is the direct loss of fertilizer compounds from granulation units. Examples of the effluents from compound

fertilizer manufacture are as follows:
Plant 1: Raw water intake
Effluent sources:

- Ammonia plant
- Urea plant
- Phosphoric acid and NPK plants
- Water treatment plant
- Cooling tower
- Boiler plant

Plant 2: Raw water intake
Effluent sources:

- Ammonia plant
- Urea plant
- Phosphoric acid and NPK plants
- Sulfuric and nitric acid plants
- Water treatment and steam generation plant
- Methanol plant

1.7 Effect of Pollution

Wastes may be subcategorized into major and minor elements, but it should be noted that in specific instances particular minor waste components may exercise significant polluting effects.

1.7.1 Major Pollutants

General water pollution effects from fertilizer manufacturing wastes are dependent primarily on the elements nitrogen and phosphorus, in their varying chemical forms.

1.7.1.1 Nitrogen: Ammoniacal Nitrogen and Urea

These two compounds are grouped together since urea may be hydrolyzed to ammoniacal nitrogen. The pollution problems which may be attributable to ammoniacal nitrogen include toxicity, oxygen demand, and eutrophication. Ammonia can be toxic to fish and other aquatic life forms at relatively low concentrations, and urea itself may be toxic to some aquatic life.

Ammoniacal nitrogen and urea may both be oxidized biologically. As such, their presence must be considered a potential oxygen demand in a receiving water. In addition, ammoniacal nitrogen may act in its role as a fertilizer in an aquatic environment, leading to excess growth of algae and aquatic macrophytes, and contributing toward accelerated eutrophication.

The presence of high ammonial levels may also cause problems if the receiving water is used for water supply purposes due to chemical interference with chlorination (i.e. formation of chloramine intermediates) and resultant increase in chlorine demand.

1.7.1.2 Nitrate

The water pollution problems resulting from high nitrate levels may be categorized into eutrophication and public health effects. High levels of nitrate can give rise to increased eutrophication, leading to the promotion of growth of algae and macrophytes, adversely affecting water quality and amenity value. Health hazards related to nitrate in water used for supply purposes are considered to be infant methaemoglobinaemia and carcinogenic potential.

1.7.1.3 Phosphate

The presence of significant levels of phosphate has important effects on eutrophication. In terms of inorganic nutrient enrichment of receiving water, phosphate may in many instances be more important than nitrogenous compounds due to the fact that some forms of aquatic plant life may fix atmospheric nitrogen, so removing the absolute requirement for soluble forms of nitrogen to promote growth.

Under these circumstances, phosphate becomes the growth-limiting agent, and programs to control eutrophication have generally sought to reduce available phosphate limits to prevent excessive algal and macrophyte growth, with subsequent increase in nutrient retention.

1.7.1.4 Minor Constituents

In addition to pollution arising from the discharge of nitrogenous or phosphatic elements in liquid waste streams, pollution can be caused by a number of secondary waste components. The most important of these are:

- oil and grease
- hexavalent chromium
- arsenic
- fluoride.

In specific instances, one or more of these individual pollutants may give rise to detrimental effects in a receiving water, due primarily to toxicity, or cause inhibition of nitrification. In addition, oil and grease may adversely affect the oxygen transfer characteristics of a watercourse.

1.8 Olefin Plants

- *Liquid effluents*
  The main liquid effluent streams of olefin plants are oily drains, flare system pump-out, caustic oxidation effluent, dilution steam generator blow down, and fouled condensate.
- *Oily drains*
  The major oily drain sources are water draw-offs from vessels and hydro blast decoking wastewater. Hydro blast wastewater produced during cleaning of coke-fouled equipment

contains entrained coke fines which are screened before discharge to the oily wastewater treatment system.

- *Flare system effluent*
  A flare system is required for safe disposal of hydrocarbons which may be released at pressure during mal-operation and emergency conditions. The hot flare knockout drum is primarily provided in order to receive liquids from the flare seal drum, excess fuel gas, hot relief, and hot blow down.
- *Spent caustic neutralization*
  The cracked gas from the cracking furnaces is scrubbed in a caustic wash tower to remove any remaining gas, including carbon dioxide, hydrogen sulfate, and mercaptans, prior to further processing in the plant cold section. The spent caustic is purged from the wash tower and is laden with sulfidic constituents plus VOCs such as condensed oils and benzene. The spent caustic scrubbing liquor is commonly the most problematic waste stream generated by an olefin plant. This is due primarily to the sulfate concentrations, which can range as high as 6% (expressed as NaHS), depending on the cracking furnace feed stock and wash tower operation. The most effective means for on-side treatment of spent caustic is wet air oxidation, which can achieve the oxidation of reactive sulfate to soluble thiosulfate, sulfate and sulfate.
- *Fouled condensate*
  Suspect condensate consists of all condensate streams from heat exchangers where hydrocarbon side pressure is more than the heating steam. A leakage in one of these heat exchangers will result in hydrocarbon contamination of the condensate. Normally, the condensate flow to the surge tank is zero. The possible constituents in suspect condensate are propane, propylene, butane, butadiene, and pentane, with their concentrations related to the maximum solubility.
- *Dilution steam generator blow down*
  The main sources of wastewater in an olefin plant are:
  - process water below down during normal and upset operating conditions
  - process water from the quench tower
  - surface runoff from possibly contaminated or non- contaminated areas.

  The wastewater components are variable depending on the respective sources, but the major components are oil, phenols, H_2S, and hydrocarbons.

1.8.1 Polymeric Plants

- Poly ethylene plant (HDPE/LLDPE/LDPE)
  - Process wastewater
    The process wastewater discharged from the bottom of the dryer scrubber entrained polymer fines typically has following characteristics:
    temperature < 50 °C
    BOD5 < 100 ppm
    COD < 200 ppm
    Suspended solids 100 ppm max.
  - Rain water and floor-washing water
    Rain water and floor-washing water should be collected and treated separately according to their origin.

  - Polymerization area
    The ceiling of the polymerization area may be polluted with polymer powder and oil that can be sometimes spilled from pumps, compressors, and other mechanical equipment.

    Rain water and washing water falling on paved areas may carry away powder and oil, and therefore should be gathered to the basins separately, where the entrained material is retained.
  - Extrusion building area
    The floors of the extrusion buildings may be occasionally polluted by polymer/scrapes and lubricating oils.
- Polypropylene plant
  Process wastewater effluent
  The sources of continues process wastewater effluent are dryer scrubbers and palletizing sections. The wastewater contaminated by trace polymer fines leaves the bottom of the dryer scrubber. It typically has the following characteristics:
  pH 6–8
  temperature 40–60 °C
  contaminant polymer powder.
  The wastewater from the palletizing section combined oil and trace suspended solid. It typically has the following characteristics:
  pH 7–8
  suspended solids 25 ppm
  oil content 1 ppm max.
  COD 5–10 ppm
  temperature 50–80 °C.

1.8.2 Polyvinyl Chloride Plants

Polyvinyl chloride (PVC) is formed by polymerization. During the chemical process of polymerization a lot of heat is generated. To remove the heat two emulsion and suspension PVC processes have been established. The wastewater effluent coming out of an emulsion PVC plant is similar to that from a suspension PVC plant.

The sources of the wastewater effluent are the polymerization reactor additive coating, the vacuum station, and the recovered vinyl chloride monomer. The wastewater streams coming out of these sources are collected in the wastewater settling basin, which has two compartments. The wastewater contaminated with wet PVC and vinyl chloride monomer (VCM) components typically has the characteristics reported in Table 1.18.

Table 1.18 *Wastewater contaminated with wet PVC and VCM characteristics.*

Temperature	40–70 °C
pH	6–7
COD	150–250 ppm wt
BOD5	75–150 ppm wt
Wet PVC	15–20 mg per kg water
VCM	0.5–1 mg per kg water

PVC, poly vinyl chloride; VCM, vinyl chloride monomer.

1.8.3 Aromatic Plants

The effluent in aromatic plants mainly comes from naphtha hydro-treating and catalyst regeneration units under normal operating conditions.

- Naphtha hydro-treating units
  The main effluent is sour water coming from the reactor effluent separator drum.
  Depending on the quality of the naphtha feed, the sour water will contain hydrocarbons, H_2S, and NH_3.
  The typical characteristics of sour water are:
  temperature 45 °C
  HC 100 ppm wt
  H_2S 50 ppm wt
  NH_3 20 ppm wt.

  In this case, the water collected and treated in the batch stage by direct oxidization with hydrogen peroxide in the sour water treatment unit.
- **Catalyst regeneration unit**
  The catalyst regeneration unit, which is part of aromizing section, continuously regenerates deactivated catalyst from the aromizing unit and introduces it to the aromizing reactor.

  The major effluent streams consist of water from the washing drum, liquid from the oxy-chlorination drum, and liquid from the dryer package.

a) *Water from the washing drum*
   The major constituents of water from the washing drum are carbon dioxide dissolved in water with traces of carbonate sodium, hydroxide sodium, chloride sodium, and oxy-chloride sodium.
b) *Liquid from the oxy-chlorination effluent drum*
   The liquid effluent from the oxy-chlorination drum consists of some sodium salts. The specified composition of the liquid includes sodium combinations such sodium hydroxide, sodium carbonate, sodium oxy-chloride, and sodium chloride, which are neutralized with hydrochloric acid.

1.9 Environmental Protection for Industrial Waste

All industrial complexes which produce waste in higher quantity above the standards should have waste treatment facilities before final release of the wastewater to the environment. The dilution of treated wastewater to the standard level is not permitted. A monitoring system in final stage of treatment should be used. Tables 1.19–1.21 illustrate typical standards for municipal waste, effluent permissible concentrations, and characteristics of potable water.

1.9.1 Important Factors in Process Selection

The most important factors that must be considered in evaluating and selecting unit operations and processes are the following:

a) *Process applicability*
   The applicability of a process should be evaluated on the basis of past experience, published data, and data from full-scale plants and pilot plant studies. If new or unusual conditions are encountered, pilot plant studies are essential.

Table 1.19 *Typical maximum effluent standard for municipal waste (daily average).*

Effluent characteristic	Unit	Maximum concentration	Note
BOD5	mg/l	30	BOD5 should not increase to more than 50 mg/l
COD	mg/l	60	COD should not increase to more than 120 mg/l
Cl	mg/l	1	
Chloroform	MPN	100/100 ml	
Color	Color unit	16	
Detergents	mg/l	1.5	Equivalent to ABS
Dissolved oxygen	mg/l	2	
F	mg/l	2.5	
Ammonia (as N)	mg/l	2.5	
Nitrite (as N)	mg/l	50	
Nitrate (as N)	mg/l	10	
Oil and grease	mg/l	10	
pH	—	6.5–8.5	
Phosphate	mg/l	1	
Settleable solid	mg/l	0.1	
Suspended solid	mg/l	40	Should not increase to more than 60 mg/l
Sulfate	mg/l	400	Should not increase the sulfate content of supply water more than 10%
Sulfite	mg/l	1	
Turbidity	NTU	50	

BOD5, biological oxygen demand; COD, chemical oxygen demand; MPN, ABS; NTU, nephelometric turbidity unit; JYU.

b) *Applicable flow range and flow variation*

The process should be matched to the expected range of flow rates, for example stabilization ponds are not suitable for extremely large flow rates. Most unit operations and processes have to be designed to operate over a wide range of flow rates. Most processes work best at a relatively constant flow rate. If the flow rate variation is too great, flow equalization is necessary. Table 1.22 identifies critical design and sizing factors for secondary treatment plant facilities and describes potential performance impacts of flow rate and constituent mass loading variations. Design provisions for flow rate variations, in addition to flow equalization, may include flow splitting and unit process bypassing under certain peak flow rate conditions. Minimum treatment requirements, if permitted by regulatory authorities, may include primary treatment and disinfection of the entire flow and secondary treatment of a portion of the flow. The advantages of a unit process flow-splitting and bypassing strategy are that:

- the biomass the secondary treatment process can be preserved during peak storm conditions and not lost due to washout

Table 1.20 *A typical effluent: permissible concentrations.*

Contaminants	Discharge to surface runoff (mg/l)	Discharge to groundwater (mg/l)	Irrigation and agriculture usage (mg/l)
Al	5	5	5
Ba	2	1	1
Be	0.1	1	0.1
B	2	1	1
Cd	1	0.01	0.01
Ca	75	—	—
Cr^{6+}	1	1	1
Cr^{3+}	1	1	1
Co	1	1	0.05
Cu	1	1	0.2
Fe	3	0.5	5
Li	2.5	2.5	2.5
Mg	100	100	100
Mn	1	0.5	0.2
Hg	0	0	0
Mo	0.01	0.01	0.01
Ni	1	0.2	0.2
Pb	1	1	1
Se	1	0.01	0.02
Ag	1	0.05	0.01
Zn	2	2	2
Sn	2	2	—
V	0.1	0.1	0.1
AS	0.1	0.1	0.1
Cl^{-1}	Amount of chloride in industrial effluents should not exceed 250 mg/l (ppm) for fresh water	Amount of chloride in industrial effluents should not exceed 250 mg/l (ppm) for fresh water	Amount of chloride in industrial effluents should not exceed 250 mg/l (ppm) for fresh water
F	2.5	2	2
P	1	1	—
CN	0.2	0.02	0.02
C_5H_5OH	1	0	1
CH_2O	1	1	1
NH_4^+	2.5	0.5	—
NO_2^-	50	10	—
NO_3^-	50	1	—
SO_4^{2-}	300	300	500
SO_3^{2-}	1	1	1
TSS	30	30	100
SS	0	0	0

(*Continued*)

Table 1.20 (continued)

Contaminants	Discharge to surface runoff (mg/l)	Discharge to groundwater (mg/l)	Irrigation and agriculture usage (mg/l)
TDS	Total dissolved solids in industrial effluents should not increase the amount of these materials more than 10% in the underground water/river and any other sources up to a distance of 200 m in which effluent dumped	Total dissolved solids in industrial effluents should not increase the amount of these materials more than 10% in the underground water/river and any other sources up to a distance of 200 m in which effluent dumped	Total dissolved solids in industrial effluents should not increase the amount of these materials more than 10% in the underground water/river and any other sources up to a distance of 200 m in which effluent dumped
Oil and grease	10	10	10
BOD	20	20	100
COD	50	50	200
DO	>2	>2	>2
ABS (detergent)	1.5	0.5	0.5
Turbidity	50	50	50
Color	Color of source water should not exceed more than 16 standard units due to industrial effluent, dumped	75 units of color	75 units of color
Temperature	Temperature of industrial effluent should not change the temperature of source water more than ±3 °C up to a distance of 200 m	—	Temperature of industrial effluent should not change the temperature of source water more than ±3 °C up to a distance of 200 m
pH	6.5–8.5	5–9	5–9
Radio actives	0	0	0
Digestible coliform	400/100 ml	400/100 ml	400/100 ml
MPN	1000/100 ml	1000/100 ml	1000/100 ml

TSS, SS, TDS, total dissolved solids; BOD, biological oxygen demand; COD, chemical oxygen demand; DO, ABS, MPN

- the quality of the treatment plant effluent can be restored shortly after the storm event
- the entire treatment facilities need not be oversized to handle unusual events.

A disadvantage of flow-splitting and bypassing is that the effluent quality may violate the discharge permit for short periods of time. any treatment sequence designed for flow-splitting and unit bypassing should be investigated in advance to ensure it meets environmental regulation requirements.

Table 1.21 *Typical physical characteristics of potable water.*

Characteristic	Desired threshold limit value	Maximum value
Color	5 units	5 units
Odor	2	3
Turbidity	5	25
pH	7–8.5	6.5–9.2

Chemical characteristic of potable water mg/l

Characteristic	Desired threshold limit value	Maximum value
As	0	0.05
Cd	0	0.01
Cn	0	0.05
Pb	0	0.1
Hg	0	0.001
Se	0	0.01
Cr	0	0.05
Ba	0	1
Ag	0	0.05
B	0	1
Hardness	150	500
Ca	75	200
Mg	50	150
Mn	0.05	05
Fe	0.3	1
Zn	5	15
Cr	0.5	1.5
SO_4	200	400
Cl	200	600
N	0.002	0.05
Detergent	0.1	0.2
P	0.1	0.2
Total dissolved solids	500	1500

c) *Influent wastewater characteristics*
The characteristics of the influent wastewater affect the types of processes to be used (e.g. chemical or biological) and the requirements for their proper operation.

d) *Inhibiting and unaffected constituents*
The following should be identified:
- the constituents which are present
- the constituents which may be inhibitory to the treatment processes
- the constituents which are not affected during treatment.

e) *Climatic constraints*
Temperature affects the rate of reaction of most chemical and biological processes. Temperature also affects the physical operation of the facilities. Warm temperatures may accelerate odor generation and also limit atmospheric dispersion.

Table 1.22 *Effect of flowrates and constituent mass loadings on the selection and sizing of secondary treatment plant facilities.*

Unit operation or process	Critical design factor(s)	Sizing criteria	Effects of design criteria on plant performance
Wastewater pumping and piping	Maximum hour flow rate	Flow rate	Wet well may flood, collection system may surcharge, or treatment units may overflow if peak rate is exceeded
Screening	Maximum hour flow rate	Flow rate	Head losses through bar rack and screens increase at high flow rates
	Minimum hour flow rate	Channel approach Velocity	Solids may deposit in approach channel at low flow rates
Grit removal	Maximum hour flow rate	Overflow rate	At high flow rates, grit removal efficiency decreases in flow-through type grit chambers causing grit problems in other processes
Primary sedimentation	Maximum hour flow rate	Overflow rate	Solids removal efficiency decreases at high overflow rates; increases loading on secondary treatment system
	Minimum hour flow rate	Detention time	At low flow rates, long detention times may cause the wastewater to be septic
Activated sludge	Maximum hour flow rate	Hydraulic residence time	Solids washout at high flow rates; may need effluent recycle at low flow rates
	Maximum daily organic load	Food/ microorganism ratio	High oxygen demand may exceed aeration capacity and cause poor treatment performance
Tickling filters	Maximum hour flow rate	Hydraulic loading	Solids washout at high flow rates may cause loss of process efficiency
	Minimum hour flow rate	Hydraulic and organic loading	Increased recycle at low flow rates may be required to sustain process
	Maximum daily organic load	Mass loading/media Volume	Inadequate oxygen during peak load may result in loss of process efficiency and cause odors
Secondary sedimentation	Maximum hour flow rate	Overflow rate or detention time	Reduced solids removal efficiency at high overflow rates or short detention times
	Minimum hour flow rate	Detention time	Possible rising sludge at long detention time
	Maximum daily organic load	Solids loading rate	Solids loading to sedimentation tanks may be limiting
Chlorine contact tank	Maximum hour flow rate	Detention time	Reduced bacteria kill at reduced detention time

f) *Reaction kinetics and reactor selection*
Reactor sizing should be based on the governing reaction kinetics. Data for kinetic expressions usually are derived from experience, published literature, and the results of pilot plant studies.

g) *Performance*
Performance is usually in terms of effluent quality, which must be consistent with the effluent discharge requirements.

h) *Treatment residuals*
The types and amounts of solid, liquid, and gaseous residuals produced should be known or estimated.

i) *Sludge processing*
Any constraints that would make sludge processing and disposal infeasible or expensive should be identified. The extent of recycle loads from sludge processing which affects the liquid unit operations or processes should also be clarified.

j) *Environmental constraints and regulations*
Environmental factors, such as prevailing winds, wind direction, and proximity to residential areas, may restrict or affect the use of certain processes, especially where odors may be produced. Noise and traffic may affect selection of a plant site. Receiving water may have special limitations, requiring the removal of specific constituents. The characteristics of treated water imposed by the final destination and/or environmental regulations will dictate special unit operations and processes for treatment of wastewater.

k) *Chemical requirements*
The resources and amounts must be committed for a long period of time for successful operation of the unit operation or process to be clarified. The effects of the addition of chemicals on the characteristics of the treatment residuals and the cost of treatment should also be determined.

l) *Energy requirements*
The energy requirements, as well as the probable future energy cost, must be known if cost-effective treatment systems are to be designed.

m) *Operating and maintenance requirements*
Special operating or maintenance requirements needed along with the necessary spare parts and their availability and cost should be determined.

n) *Reliability*
The long-term reliability of the unit operation or process under consideration must be determined. Is the operation or process easily disrupted? Can it stand periodic shock loadings? If so, how do such occurrences affect the quality of the effluent? Because of the variations in effluent quality performance, a treatment plant should be designed to produce an average effluent concentration below the permit requirements.

o) *Compatibility*
The unit operation or process should be used successfully with existing facilities. Plant expansion should be accomplished easily.

p) *Land availability*
Sufficient space should be allocated to accommodate either the facilities currently under consideration or possible future expansion.

q) *Equipment availability*
Most of the equipment used in wastewater treatment is custom manufactured, except for items such as small pumps, motors, and valves. Some items of equipment may require special manufacturing techniques or are proprietary and only available from limited sources. The equipment components that make-up the process or system should therefore be considered carefully to determine their potential effects on the design, construction, operation, and maintenance of the facilities.

r) *Personnel requirements*
The selection of a treatment process should consider not only the amount of operating and maintenance personnel needed but also the skills required. The extent and complexity of the control systems and the staffing levels required must be evaluated carefully.

1.10 Chemical Oxygen Demand in Wastewater Systems

This section first discusses the background of the COD method, then the method used to calculate the theoretical oxygen demand. COD is the equivalent amount of oxygen consumed under specified conditions in the chemical oxidation of the organic and oxidizable inorganic matter contained in wastewater, corrected for the influence of chlorides. In American practice, unless otherwise specified, the chemical oxidizing agent is hot acid dichromate.

Micro-organisms in natural water bodies consume oxygen when degrading organic matter to biomass. BOD is a parameter which describes the oxygen consumption when microorganisms "eat" organic mass. The more organic load enters the water body, the more oxygen the micro-organisms will use for conversion. Large amounts of pollutants may cause oxygen loss in a water body and lead to harmful effects in nature so it is useful to know the oxygen consumption of wastewater before discharge.

BOD requires days to get results and COD is used because it is a lot faster. So-called standard methods for COD determination are open and closed reflux systems, where a strong oxidant is added to the water solution and boiled in open or closed reflux for a few hours, then the amount of oxidant used is measured by titration methods. COD determination with standard methods takes usually a few hours but colorimetric determination of COD requires less than an hour. COD measures the organic content of a solution.

Due to its rapidity, COD is used to measure the total amount of pollutants in water media. It is often used in water and wastewater quality determination.

The difference between COD the BOD is that in COD, the amount of oxidant used for oxidation of organic components is measured, but BOD expresses the oxygen consumed by micro-organisms when the sample is kept for 5 days at 20 °C. The dissolved oxygen is measured at the beginning and end of the test, and the oxygen consumption is the difference between amount of dissolved oxygen at the beginning and end of the test. There is a correlation factor between BOD and COD so when COD is known, the biochemical oxygen consumption in nature can be determined.

1.10.1 Determination of COD

Usually a strong oxidant, like potassium dichromate, is used in this measurement. The standard method for determination of COD is titration with open or closed reflux, where the sample is heated either in a closed or an open vessel in the laboratory. The sample is boiled for 2 hours in the presence of the oxidant.

The amount of dichromate consumed can be determined when the difference in oxidant concentration at the beginning and end of the process is determined. Potassium dichromate is considered to be the best oxidant because it has a strong oxidizing capability, it is applicable to many kinds of organic and inorganic matter, and it is easy to manipulate.

Oxidation of inorganic components interferes with COD determination since they also consume dichromate. In the oxidation process, the dichromate ion (Cr^{6+}) is oxidized to chromate (Cr^{3+}).

Baker et al. (1999) declared that the COD for chemicals in group one and group two well-correlated data group, equals the theoretical oxygen demand (ThOD).

For chemicals in groups three and four (potentially well-correlated data) COD can be estimated from the ThOD. No correlation for chemicals presented in groups five and six could be determined.

1.10.2 Calculation of Theoretical Oxygen Demand

The ThOD can be obtained for different chemicals from different studies. Because ThOD is not usually determined for all the chemicals found in the wastewater, it can be determined for every chemical using the method of Baker et al. (1999).

According to Baker et al. (1999) the amount of oxygen consumed by a single component *i* can be determined using Eqs. (1.1) and (1.2). Letters *n, m, k, j, i, h,* and *e* can be determined with Eq. (1.1). According to Baker et al. (1999) Eq. (1.1) assumes that all compounds are oxidized completely to end products. The letters inform how many molecules there are of element *i* in component *i*.

$$\begin{aligned} &C_nH_mO_eX_kN_jS_iP_h + bO_2 \rightarrow nCO_2 \\ &+ \left(\frac{m-k-3j-2i-3h}{2}\right) H_2O + kH_x + jNH_3 + iH_2SO_4 + hH_3PO_4 \end{aligned} \tag{1.1}$$

$$b = n + \frac{m-k-3j-2i-3h}{4} - \frac{e}{2} + 2i + 2h \tag{1.2}$$

To determine the $ThOD_i$, the oxygen demand for 1 g of component *i* has to be determined. Oxygen demand for 1 g of component *i* is represented by $ThOD_{O,\,i}$ and determined using Eq. (1.3), where b_i is the amount of oxygen consumed in moles per one mole component *i*, M_i is the molar mass of a single component *i*, M_{O2} is the molar mass of an oxygen molecule and ci is the concentration of component “i” in water.

$$ThOD_{O,i} = b_i \frac{M_{O2}}{M_i} \tag{1.3}$$

$$ThOD_i = ThOD_{o,i} \times c_i \tag{1.4}$$

$$\sum ThOD = \sum_i^n ThOD_i = \sum_i^n (ThOD_{o,i} \times c_i) \tag{1.5}$$

Table 1.23 shows the calculated oxygen demand per 1 mole of component *i*, the molar mass, and ThOD demand for various components.

Table 1.23 *Oxygen demand per one mole component* i*, molar mass, and theoretical oxygen demand.*

Component	Composition	Oxygen demand per one mole component, *i* b	Molecular weight Mi (g/mol)	Theoretical oxygen demand ThODi (gO_2/gi)
Methanol	CH_4O	1.5	32.03	1.5
Phenol	C_6H_6O	7	94.1	2.38
Acetone	C_3H_6O	4	58.07	2.2
2-Aminoethanol	C_2H_7NO	2.5	61.08	1.31
Benzene	C_6H_6	7.5	78.11	3.07
Cumene	C_9H_{12}	12	120.2	3.19
Propanol	C_3H_8O	5	44.1	3.63
Toluene	C_7H_8	9	92.14	3.12
Total nitrogen	NH_3	0	17.03	0
Xylene	C_8H_{10}	10.5	106.17	3.16

For example, the chemical formula of phenol is C_6H_6O. If the concentration of phenol is 360 mg/l in a wastewater sample, the ThOD determination is as follows.

According to Eq. (1.1): $n=6$, $m=6$, $e=1$, $k=0$, $j=0$, $i=0$, $h=0$. When n, m, k, j, i, h, and e are put into Eq. (1.2), the amount of oxygen molecules needed to oxidize phenol into end products can be determined:

$$b_{C_6H_6} = 6 + \frac{6-0-3-2-3}{4} - \frac{1}{2} + 2 + 2 = 7\ \text{mol}\ O_2/(\text{mol}\ C_6H_6)$$

$$ThOD_{O,i} = 7\frac{\text{mol}\ O_2}{\text{mol}\ C_6H_6}\left(\frac{31.98}{94.1\frac{g_{C_6H_6}}{\text{mol}_{C_6H_6}}}\right) = 2.38\frac{g\ O_2}{g\ C_6H_6}$$

The total ThOD is determined by summing the individual ThOD values:

$$ThOD_{C_6H_6} = ThOD_{o,C_6H_6} \times C_{C_6H_6} = 2.38\frac{\text{mg}\ O_2}{\text{mg}\ C_6H_6} \times 360\frac{\text{mg}\ C_6H_6}{\text{liter}\ H_2O} = 856.8\frac{\text{mg}\ O_2}{\text{liter}\ H_2O}$$