

Waste Management
in the Chemical and Petroleum Industries

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Contents

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Dedicated to the loving memory of my Parents,
grandparents, and to all
who contributed so much to my work over the years.

Preface

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

Wastewater quality and the quantity produced determine the means of disposal and the costs of disposal. Suspended solids, total dissolved solids, and oxygen demand of produced waters have the most impact on wastewater treatment.

Wastewater is a complex mixture of organic and inorganic compounds and the largest byproduct by volume generated during chemical processing and both conventional and unconventional oil and gas recovery operations. The potential of oilfield-produced water to be a source of freshwater for water-stressed oil-producing countries and increasing environmental concerns, in addition to stringent legislations on produced water discharge into the environment, have made produced water management a significant part of the oil and gas business.

In marginally economic coal bed projects, the water disposal costs and attendant environmental accounting are critical factors in the investment decision; water disposal costs can economically make or break a marginal project.

Before investing in a coal bed methane (CBM) process, multiple questions need to be answered concerning the water to be produced – questions concerning quantity, flow-rates, chemical content, disposal means, monitoring, and environmental regulations. Perhaps no other factor affects the economics and feasibility of CBM projects as much as water removal and disposal.

In heavy oil production, between 2 to 4.5 volume units of water are used to produce each volume unit of synthetic crude oil in an ex situ mining operation. Despite recycling, almost all of it ends up in tailings ponds. However, in Steam Assisted Gravity Drainage (SAGD) operations, 90–95% of the water is recycled and about 0.2 volume units of water is used per volume unit of bitumen produced.

A major hindrance to the monitoring of oil sands-produced waters has been the lack of identification of individual compounds present. By better understanding the nature of the highly complex mixture of compounds, including naphthenic acids, it may be possible to monitor rivers for leachate and also to remove toxic components. Such identification of individual acids has for many years proved impossible, but a recent breakthrough in analysis has begun to reveal what is in the oil sands-produced waters.

The extraction and use of shale gas can affect the environment through the leaking of extraction chemicals and waste into water supplies, the leaking of greenhouse gasses during extraction, and the pollution caused by the improper processing of natural gas.

A challenge to preventing pollution is that shale gas extractions vary widely in this regard, even between different wells in the same project; the processes that reduce pollution sufficiently in one extraction may not be enough in another.

Chemicals are added to the water to facilitate the underground fracturing process that releases natural gas. Fracturing fluid is primarily water and approximately 0.5% chemical additives (friction reducer, agents countering rust, agents to kill microorganisms). Since (depending on the size of the area) millions of liters of water are used, this means that hundreds of thousands of liters of chemicals are often injected into the soil.

Only about 50 to 70% of the resulting volume of contaminated water is recovered and stored in above-ground ponds to await removal by tanker. The remaining “produced water” is left in the earth where it can lead to contamination of groundwater aquifers, though the industry deems this “highly unlikely.” However, the wastewater from such operations often leads to foul-smelling odors and heavy metals contaminating the local water supply above-ground.

This book unravels the essential requirements for the process design and engineering of the equipment and facilities pertaining to the wastewater treatment units, solid waste disposal, and wastewater sewer systems of oil and gas refineries, chemical plants, oil terminals, petrochemical plants, unconventional oil and gas industries (coal seam gas or coal bed methane, shale gas and oil sands production), and other facilities as required. Included within the scope are:

- Liquid and solid disposal systems.
- Primary oil/solids removal facilities.
- Further oil and suspended solids removal (secondary oil/solids removal), such as dissolved air flotation units.
- Granular media filters and chemical flocculation units.
- Chemical addition systems.
- Biological treatments.
- Filtration and/or other final polishing.
- Sewage systems handling domestic and medical sanitary appliances of buildings.
- Drainage systems carrying surface and rainwater.
- Wastewater gathering systems.
- Clean water drainage, e.g., from buildings and paved areas.

- Evaporation ponds and disposal by natural percolation into the subsoil in permeable ground.
- Sanitary sewage treatment.
- Sludge handling and treatment.

It is obvious that the aim of any drainage/effluent disposal system should be to segregate uncontaminated water from contaminated water or effluents and to segregate different types of effluents in order to reduce the size, complexity, and costs of any treatment units that may be required for handling the contaminated water and effluents before they are discharged from a unit.

All wastewater effluents from industry that are discharged to public and/or natural water sources or directed for recycling purposes inside the industry, and that may contain a wide variety of matters in solution or suspension, should be controlled according to the requirements imposed by the final destination. However, in any case, elimination of the waste or the hazard potential of the waste should be the ultimate goal in the management.

Under no circumstances should effluent water cause oil traces on the surface or embankments of the receiving water, or affect the natural self-purification capacity of the receiving water to such an extent that it would cause hindrance to other users.

Under no conditions should polluted streams be combined with unpolluted streams if the resultant stream will then require purification. In general, the main sewer systems in the industry will be segregated according to the following categories:

- Stormwater sewer systems.
- Oily water sewer systems.
- Non-oily water sewer systems.
- Chemical sewer systems.
- Sanitary sewer systems.
- Special sewer systems.

In all areas, including process, offsite, and utility units, provisions should be made to anticipate any of the above mentioned sewer systems as required.

The treatment of wastewaters involves a sequence of treatment steps. Each wastewater treatment process involves the separation of solids from water in at least some part of the operation and the removal of biochemical oxygen demand (BOD) to some extent.

The end of pipe treatment sequence can be divided into the following elements: primary or pre-treatment, intermediate treatment, secondary treatment and tertiary treatment plus ancillary, sludge dewatering, and disposal operations.

The key to optimizing the treatment sequence for provision of maximum water treatment at minimum cost is to identify the rule of each unit operation and optimize that operation. Optimizing the performance of specific unit operations, such as API separators, dissolved air flotation, biological treatment, etc., can best be achieved if:

1. The properties of influent streams are considered.

2. The chemical principles that are used in solids pre-treatment are understood.

3. The variety of chemicals available for solids treatment is recognized.

4. The properties of effluent water are established based on the local environmental regulations and final disposal.

5. The protocols for quantifying results are identified.

In general, most industries require water for processing or other purposes; much of this water after use is discharged either to public and/or natural water sources or directed for recycling purposes inside the industry.

Such discharge, which may contain a wide variety of matter in solution or suspension, should be controlled according to the requirements imposed by the final destination and/or environmental regulations.

Moreover, according to the type of plant and the method of plant operation, the sources of solids in a wastewater treatment plant can be uncovered. Solids may also be formed by interaction of waste streams in the sewer.

Wastewaters contain metal ions, such as iron, aluminium, copper, magnesium, and so on, from corrosion of the process equipment, chemicals used in treating cooling water, salts in the water intake, and chemicals used in processing.

Insoluble metal hydroxide floc may be formed when alkaline wastes are discharged and raise the pH of wastewater above neutral. The wastes, containing considerable concentrations of phenols, sulfides, emulsifying agents, and alkalines, should be segregated. In general, discharging any material to the oily sewer system or other drainage system should be investigated in line with the final waste treatment and disposal targets.

In view of the above, this book will unravel the fundamental engineering for waste recovery, treatment, and disposal systems in the petroleum, chemical, and unconventional oil and gas processing industries. These new fundamental discoveries will enable the development of practical solutions to these pressing environmental issues.

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Biography

Alireza Bahadori, PhD is a research staff member in the School of Environment, Science & Engineering at Southern Cross University, Lismore, NSW, Australia. He received his PhD from Curtin University, Western Australia. For the better part of 20 years, Dr Bahadori had held various process engineering positions and involved in many large-scale projects at NIOC, Petroleum Development Oman (PDO), and Clough AMEC PTY LTD.

He is the author of over 200 articles and 6 books. His books have been accepted/published by prestigious publishers such as John Wiley & Sons, Springer, Taylor & Francis and Elsevier. Dr Bahadori is the recipient of highly competitive and prestigious Australian Government's Endeavour International Postgraduate Research award as part of his research in oil and gas area. He also received top-up award from State Government of Western Australia through Western Australia Energy research Alliance (WA:ERA) in 2009. Dr Bahadori Serves as a member of editorial board for a number of journals such as *Journal of Sustainable Energy Engineering* which is published by Wiley-Scrivener.

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Wastewater Treatment

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 waters, and pose risks to animals and wildlife.

1.1 Characteristics of Wastewaters

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

- Biochemical Oxygen Demand (BOD). This 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.
- Total Nitrogen (TN) and Total Phosphorus (TP). These are the sum of all forms of nitrogen and phosphorus in the water, respectively.
- Fecal microbes (which include viruses, bacteria, and protozoans). These are found in wastewater and may cause disease.
- Suspended solids, biodegradable organics, nutrients, refractory organics, heavy metals, dissolved inorganic solids, and pathogens are important contaminants that may be found in the oil, gas, and chemical processing

industry’s wastewaters. Table 1.1 presents a list of important wastewater contaminants and reasons for their importance.

Table 1.1 *Contaminant importance in wastewater treatment.*

Contaminants	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 (Biochemical Oxygen Demand) and COD (Chemical Oxygen Demand). If discharged untreated to the environment, the biological stabilization of these materials can lead to the depletion of natural oxygen resources and to 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.

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

Table 1.2 shows typical waste compounds classified as priority pollutants. The more stringent rules deal with the removal of nutrients and priority pollutants. When wastewater is to be reused, rules normally include requirements for the removal of refractory organics, heavy metals, and in some case dissolved inorganic solids.

Table 1.2 *Typical waste compounds classified as priority pollutants*.

Name (Formula)	Concern
	Non-metals
Arsenic (As)	Carcinogen and mutagen. Long term: sometimes cause 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 fume. A 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. A carcinogen.
Dichloromethane (CH_2Cl_2)	Toxic. A carcinogen, narcotic.

Name (Formula)	Concern
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 material.
Toxaphene ($C_{10}H_{10}Cl_8$)	Toxic by ingestion, inhalation, skin absorption.
Silvex [$Cl_3C_6H_2OCH(CH_3)COOH$]	Toxic material; use has been restricted.

1.1.1 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. A widely-accepted means of testing a wastewater for suspended solids is to filter the wastewater through a 0.45 μm porosity filter. Anything left on the filter after drying at about 103 °C is considered a portion of the suspended solids. Table 1.3 provides another classification system for the solids found in wastewater.

Table 1.3 *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}

1.1.2 Heavy Metals

Any cation having an atomic mass (weight) greater than 23 (atomic mass of sodium) is considered a heavy metal. Motivations for controlling heavy metal concentrations in gas streams are diverse. Some of them are dangerous to health or to the environment (e.g., mercury, cadmium, lead, chromium), some can cause corrosion (e.g., zinc, lead), 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 that exhibit hyper accumulation can be used to remove 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.

1.1.3 Dissolved Inorganic Solids

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

The following procedure can be used to determine the inorganic dissolved solids in wastewaters. A sample of wastewater is filtered through a 0.45 μm filter, filtrate is collected, the water is vaporized first (at 103 °C) and then the organic fraction (at 550 °C) 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.

1.1.4 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:

1. Selecting a wastewater system with a low content of regulated contaminants that respects the local legislation for land application.

2. Application of a decontamination process to remove toxic metals.

3. The necessary step of sterilization for monocultures 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 the environment. The presence of these toxic organic compounds can add constraints to the ultimate disposal of these sludges and/or reduce the possibilities for their beneficial use.

Tables 1.4 and 1.5 provide some organic compounds that are considered toxic and/or carcinogenic.

Table 1.4 *Toxic organic compounds; occupational exposure to carcinogenic substances.*

Compound	Site	Comment
Organic substances for which there is wide agreement on carcinogenicity		
4-Aminodiphenyl	Bladder	A contaminant in diphenylamine
Benzidine	Bladder	Ingredient of aniline dyes, plastics, and rubber
Beta-naphthylamine (2-NA)	Bladder	Dye and pesticide ingredient; synonym, 2-naphthylamine exposed workers have 30 to 60 times more cases of bladder cancer
Bis (chloromethyl) ether	Lung	Used in making exchange resins; exposed workers have 7 times more cases of lung cancer; synonym, BCME
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; an antioxidant
Ethyleneamine	Unknown	Carcinogenic in animals; used in paper and textile processing and manufacture of herbicides, resins, rocket and jet fuels

Compound	Site	Comment
3, 3-Dichlorobenzidine	Unknown	Carcinogenic in animal species; exposure accompanies benzidine and betanaphthylamine
Methyl chloromethyl methyl ether	Unknown	Carcinogenic in animals; synonym, CMME; BCME contaminants CMME; used in resin-making, textile, and drug production.
4, 4-Methylene bis (2-chloroaniline)	Unknown	Synonym MOCA. Tumorigenic in rats and mice. Skin absorption may be the hazard. Curing agent for iso-cyanate polymers.

Table 1.5 *Industrial substances suspected of carcinogenic potential for humans.*

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

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

1.1.6 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 of the organic priority pollutants are also classified as volatile organic compounds (VOCs).

Representative examples of the priority pollutants are shown in Table 1.2. 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: (1) volatilization (also gas stripping); (2) degradation; (3) adsorption to particles and sludge; (4) transport through the entire system; (5) generation as a result of chlorination or as byproducts of the degradation of precursor compounds.

1.1.7 Volatile Organic Compounds

Wastewaters are collected and treated in a variety of ways, some of which result in the emission of volatile organic compounds (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 vapour 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 byproduct 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.

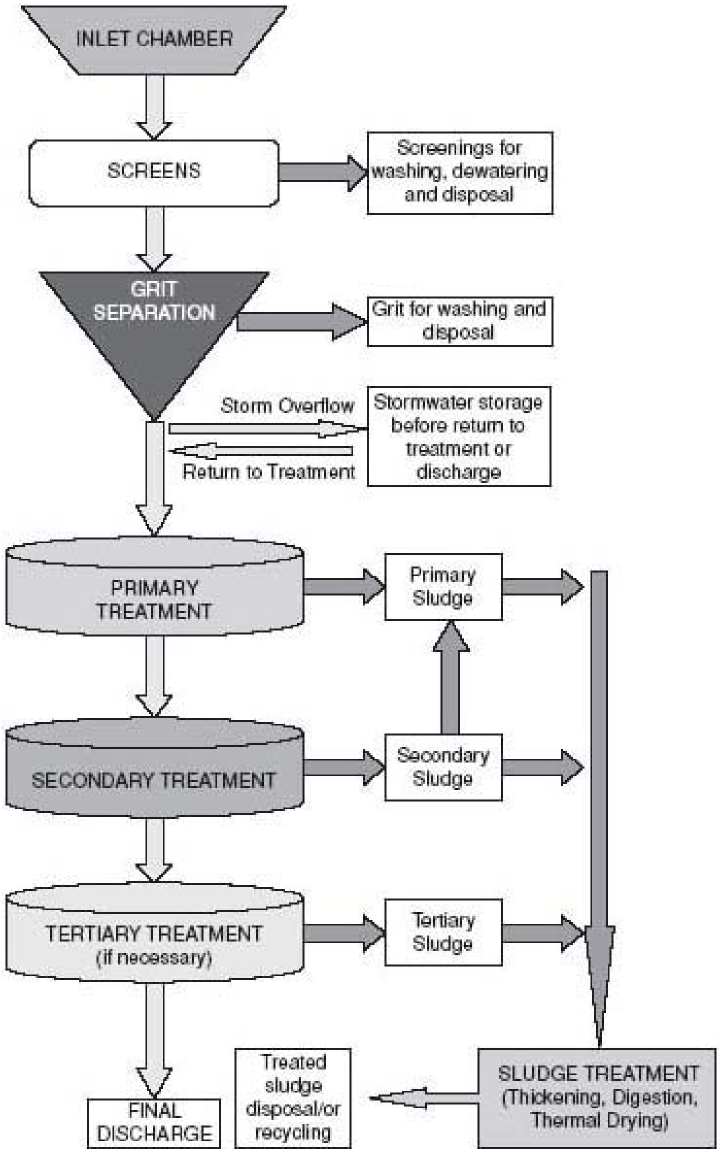
Organic compounds that have a boiling point ≤ 100 °C and/or a vapor pressure > 1 mm Hg (or 133.3 Pa) at 25 °C are generally considered to be volatile organic compounds (VOCs), e.g., vinyl chloride. The release of these compounds in sewers and treatment plants, especially at the head works, is of particular concern with respect to the health of collection system and treatment plant workers.

1.2 Treatment Stages

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

The 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 wastewater treatment stages.

[Figure 1.1](#) A simplified schematic of wastewater treatment stages.



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 blow-down streams (cooling tower, boiler, and gasifier) and so on. Each of these sources produces wastewater with slightly different characteristics and treatment requirements.

Table 1.6 provides typical wastewater qualities for some of the wastewater streams in the oil, gas, and chemical processing industries.

Table 1.6 *Typical wastewater qualities.*

Parameter	Unit	Oily Wastewater	Stripped Sour Water	Combined High TDS Waters (Ion Exchange Waste, Boiler Blowdown, RO Reject)	Cooling Tower Blow-down
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
Cl2 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	–	–

1.2.2 Discharge Options and Quality Requirements

Produced water in the 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 four discharge alternatives listed below are all technically feasible. Selection of the preferred alternative is a function of the selected process, recycling opportunities,