

ExxonMobil DESIGN PRACTICES	WATER POLLUTION CONTROL GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	Section XIX-A	Page 1 of 35
		December, 2002	

Changes shown by ↓

CONTENTS

Section	Page
SCOPE / BACKGROUND	3
REFERENCES	4
DEFINITIONS	4
CONTAMINANT/POLLUTANT	4
CONCENTRATION AND MASS UNITS	4
OIL AND GREASE	4
OXYGEN DEMAND	5
BIOX	6
DISSOLVED OXYGEN (DO)	6
PH	6
"TOXIC" COMPOUNDS/TOXICITY	6
NUTRIENTS	7
NITRIFICATION/DENITRIFICATION	7
OVERALL WASTEWATER SOURCE MANAGEMENT AND TREATMENT SELECTION.....	7
OVERALL WASTEWATER SOURCE MANAGEMENT	7
WATER REUSE	7
WATER CHEMISTRY	8
SEWER	8
DECISION TREES FOR TREATMENT UNIT SELECTION	9
TYPICAL EFFLUENT QUALITY CRITERIA	9
OIL AND PH	9
GENERAL POLLUTANT INDICATORS	10
OTHER TYPICAL PETROLEUM/PETROCHEMICAL CONTAMINANTS	10
EXAMPLES OF TOXIC COMPOUNDS	10
TREATMENT UNITS	10
TYPICAL REFINERY/PETROCHEMICAL WASTEWATER TREATING FLOW PLAN	10
HOW TO ESTIMATE WASTEWATER FLOW AND QUALITY WITHOUT DATA	11
TYPICAL REMOVAL EFFICIENCIES FOR SELECTED WASTEWATER TREATING UNITS.....	11
EQUALIZATION/PH CONTROL (FLOW AND CONTAMINANT LOAD).....	11
PRIMARY OIL AND SUSPENDED SOLIDS REMOVAL (<i>PRIMARY TREATMENT</i>).....	12
API SEPARATOR.....	12
PLATE INTERCEPTOR/SEPARATORS	12
SKIM PONDS	12
ENHANCEMENTS/FUTURE TECHNOLOGY	12
SECONDARY OIL AND SUSPENDED SOLIDS REMOVAL (<i>ADVANCED PRIMARY TREATMENT</i>)..	13
INDUCED AIR/GAS/STATIC FLOTATION (IAF/IGF/ISF).....	13
DISSOLVED AIR FLOTATION (DAF)	13
MEDIA FILTRATION	13
CHEMICAL FLOCCULATION	13



Documents

Document Sharing Hub

Section	Page	<i>WATER POLLUTION CONTROL</i> GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	ExxonMobil DESIGN PRACTICES
XIX-A	2 of 35		
December, 2002			

ENHANCEMENTS/FUTURE TECHNOLOGY	14
OXYGEN DEMAND/DISSOLVED ORGANICS REDUCTION (<i>SECONDARY TREATMENT</i>).....	14
biological treatment	14
non-biological treatment	16
enhancements/future technology	17
NUTRIENTS/AMMONIA REMOVAL/NITRIFICATION	17
SUSPENDED SOLIDS REDUCTION (<i>TSS</i>).....	18
Media Filtration	18
Gravity Settling	18
Enhancements / Future Technology.....	18
TOXICITY REDUCTION (<i>ACUTE AND CHRONIC</i>)	18
Enhanced Biological Treatment.....	18
Activated Carbon	19
Enhancements / Future Technology.....	19
DISSOLVED SOLIDS/METALS REDUCTION	19
Chemical Precipitation and Flocculation	19
Biological Removal	19
Ion Exchange.....	20
Activated Carbon	20
Membranes.....	20
Evaporation	20
WASTEWATER SLUDGE HANDLING (<i>VOLUME REDUCTION</i>).....	20
Sludge Thickening	20
Dewatering Equipment	21
REFERENCES.....	22
TABLES	
Table 1 Typical Removal Efficiencies for Selected Wastewater Treating Units	26
FIGURES	
Figure 1 Wastewater Treatment Assessment Decision Tree	28
Figure 2 Free Oil Removal Decision Tree	29
Figure 3 Oxygen Demand/Dissolved Organic Reduction Decision Tree	30
Figure 4 Suspended Solids Removal Decision Tree	31
Figure 5 Wastewater Effluent Toxicity Reduction Decision Tree.....	32
Figure 6 Wastewater Sludge Management Volume Reduction Decision Tree.....	33
Figure 7 Typical Wastewater Treatment Flow Plan.....	34

Revision Memo

- 12/02** General technical/editorial update to the entire practice. Significant changes include the following:
1. More complete coverage of equalization, diversion tankage and stormwater management.
 2. More coverage of heavy metals removal technology
 3. Corrected COD/TOD to TOC ratios

 DESIGN PRACTICES	WATER POLLUTION CONTROL GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	Section XIX-A	Page 3 of 35
		December, 2002	

SCOPE/BACKGROUND

This introduction to wastewater treatment processes and water pollution control systems provides background information on how to select the appropriate treatment technology to solve specific and general contaminant removal requirements. Details can be found in other Design Practice sub-sections that follow this introduction, EMRE reports, and technical/professional society, vendor and other, third party literature sources.

Wastewaters from the petroleum/petrochemical industry are a special category that does not conform to "sanitary" or sewage treatment practice. Many designs and selection criteria are not published in the literature; they reside with industry experts and specialty equipment vendors. Selecting specific equipment that is cost effective is also frequently complicated by government guidelines and regulations on effluent quality requirements, which can vary greatly around the world. It is very important to fully understand the effluent quality requirements, including analytical methods used for contaminant analyses, to identify the preferred wastewater treatment technology and equipment for a particular location.

Petrochemical plant wastewater treatment can be more involved than refinery treatment because of the wider variety of chemicals and processes used. Extra caution should be used in applying rules-of-thumb and specific selection criteria for treatment of specific chemical plant wastewaters.

The contaminated water or wastewater sources that require treatment facilities can vary depending upon government requirements on effluent quality or on specific definitions/designations for these streams. For example, stormwater sources from clean areas of the plant may still require monitoring and permitting in some locations, even though they do not contact petroleum or petrochemical process streams in the plant. Sometimes cooling tower blowdown streams, stormwater, contaminated groundwater, desalination plant blowdown waters and specialty streams such as spent caustics are restricted in the locations where they can be commingled with other wastewaters and subsequently treated. Hence, the person selecting the treatment system should check government guidelines/requirements and seek information on standard industry practice in the area they are located, since these requirements can limit treatment system flexibility, wastewater source segregation, reuse opportunities, even though they are logical from technical or cost standpoints. In some cases, the impacts of these restrictions are large and the person selecting the treatment system should go back to the governmental authorities to seek clarification or adjustment to the restrictions based on positive technical or environmental impact assessments.

This section of the Design Practices deals primarily with "end-of-pipe" wastewater treatment process selection. The removal of high concentrations of contaminants coming directly from process areas may be covered as part of the specific plant process. For example, highly contaminated wastewater streams with sulfides and ammonia, called "sour waters" are typically treated at the process block in a sour water stripper. Design information on these units can be found in the [Design Practice XIX-A10](#). Oil/water knockout or three phase disengaging drums, unit separators, desalters, wet gas scrubbers, caustic regeneration/minimization processes and similar equipment are usually specified for the particular process or operation. A **rough rule-of-thumb** is if the concentration of the contaminant of concern is less than 0.1 weight percent (1,000 weight parts-per-million, ppm or mg/L), it is covered in the following Design Practice sections on "end-of-pipe" treatment technology. Oil is an exception to this rule-of-thumb. The rule-of-thumb is just a guideline and should not be used as a fixed number. For example, certain organic contaminants whose concentration is about 0.2 weight percent have been successfully removed by "end-of-pipe" treatment. Water or wastewater streams with much higher concentrations are generally handled at the process where they are generated.

This section and the following ones do not directly deal with "water" treatment; the treatment of raw water sources for use in plant utilities for boilers, cooling, etc. Refer to the Offsite Design Practice sections for raw water treatment (Offsites DP Section no. [XXVI](#) and [XXVII](#)). Water reuse, potential to replace raw water to plant utilities is, however, covered in this section.

The design of water pollution control systems or wastewater treatment facilities should be viewed as any other process technology in that proper design data are needed to meet requirements in cost effective ways. Frequently, a particular location will need to embark on a sampling and laboratory analysis program to define contaminant concentrations in the wastewaters as well as flow studies to define efficient facilities, pollution prevention options, wastewater reuse opportunities and to minimize the cost of facility upgrades. The collection and analysis of these data into contaminant material balances must be thoroughly planned, similar to designing other facilities in the plant process block. In some instances when biological treatment is employed or needs to be upgraded, these data collection efforts can become quite extensive, particularly when the end-of-pipe treatment facilities must meet stringent government effluent discharge standards.

Subsection entitled, "Enhancements/Future Technology" is included in the treatment unit section of this Design Practice to reflect vendor or other technology that may be encountered by the reader. In some cases, Exxon Mobil or industry groups are evaluating the applicability of these technologies for use, and some of the technology is developed far enough to be considered as an alternative to conventional technology. However, more scrutiny is needed in evaluating this evolving technology versus conventional treatment units. In other cases, the information is provided to let the reader know developments are occurring in these areas, and future updates to this Design Practice will provide guidelines on their applicability to Exxon Mobil facilities.

Section	Page	<i>WATER POLLUTION CONTROL</i> GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	 DESIGN PRACTICES
XIX-A	4 of 35		
December, 2002			

REFERENCES

Due to the length of this section, the references have been placed at the end of this Design Practice. The references have also been grouped to match the major sections of this Design Practice, so information on specific topics can be located easily.

DEFINITIONS

CONTAMINANT/POLLUTANT

Distinctions are sometimes made between these terms; The United States Environmental Protection Agency (EPA) definitions given below illustrate how regulatory agencies view the terms:

Contaminant - The U.S. EPA definition: "Any physical, chemical, biological, or radiological substance or matter that has an adverse effect on air, water, or soil."

A more realistic definition is any substance, not naturally occurring, that has the potential to adversely affect the use of the receiving water body.

Pollutant - The U.S. EPA definition: "Any element, substance, compound, or mixture, including disease causing agents, which after release into the environment and upon exposure, ingestion, inhalation, or assimilation into any organism, either directly from the environment or indirectly by ingesting through food chains, will or may reasonably be anticipated to cause death, disease, behavioral abnormalities, cancer, genetic mutation, physiological malfunctions, or physical deformation in such organism or their offspring."

A more realistic definition is any substance added to a water body that has an adverse impact on human health or the environment.

CONCENTRATION AND MASS UNITS

- ▶ Wastewater contaminant concentrations can generally be expressed in the physical unit of milligrams per liter (mg/L), weight parts-per-million (wppm or simply ppm), or weight percent. Concentrations expressed as micrograms per liter (µg/L) and parts-per-billion (ppb) are also commonly used. When contaminant concentrations in wastewater are expressed as parts-per-million or billion, the concentration is on a weight basis and is sometimes abbreviated as wppm or wppb. For most calculations, units of mg/L and ppm and µg/L and ppb can be interchanged since the specific gravity of the wastewater is very nearly equal to that of water. For example, contaminant concentrations in salt water systems or special waste stream like spent caustic should strictly be expressed as mg/L since the specific gravity of salt water and spent caustic is greater than 1.0.
- ▶ Effluent limits can be measured and reported on a concentration or mass basis. Mass units are generally expressed as pounds or kilograms of contaminant per unit time (lbs/day or kg/day). When a facility has mass limits on their effluent, the facility has greater flexibility to meet the limits than those with concentration limits, since the effluent flow rate can many times be adjusted to meet the daily mass limits.

OIL AND GREASE

Oil and grease is a key indicator test for effluent compliance in the petroleum industry and is reported in units of ppm or mg/L. It measures the total of dissolved and suspended "oil" fractions extracted from a wastewater sample by an organic solvent, typically n-Hexane (freon is no longer used) or other similar solvents. Caution should be used in interpreting the results of this test since it can measure naturally occurring organic compounds, which may give artificially high readings in the oil test.¹

Suspended Oil - Suspended or "free" oil is the amount of total oil and grease that can be removed by filtration, and a portion of which can be removed by physical separation, such as an API Separator or Dissolved Air Flotation (DAF) unit.

Dissolved Oil - Dissolved or soluble oil is the portion of total oil and grease that is not removed by filtration. Dissolved oil can be removed by treatment processes such as biological treatment, chemical oxidation, or activated carbon adsorption.

- ▶ The analytical procedure for distinguishing suspended oil from dissolved oil is a glass fiber filter, which has the nominal rejection rate of 1 micron size particle. Hence, in practice, dissolved oil is considered to be those hydrocarbons or organic compounds that are truly soluble in the wastewater stream, plus those finely dispersed oil droplets that are not filtered, and are less than 1 micron. Similarly, suspended oil in wastewater samples can be considered to be those compounds or hydrocarbons measured in the test, whose oil droplet size particles are greater than 1 micron.

Solids

- ▶ **Total Solids (TS)** - Total solids is the term applied to the residue after evaporation of a sample and its subsequent drying in an incubator or oven at 217 to 221°F (103 to 105°C). Total solids includes total suspended solids and total dissolved solids (organic and inorganic) and is reported in units of ppm or mg/L.¹
- ▶ **Total Suspended Solids (TSS)** - Total suspended solids consists of the amount of suspended matter removed by a glass fiber filter (nominally > 1µm particle size) when a wastewater sample is dried at 217°F (103°C) and is reported in units of ppm or mg/L.

 DESIGN PRACTICES	WATER POLLUTION CONTROL GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	Section	Page
		XIX-A	5 of 35
		December, 2002	

mg/L. Inorganic particles such as clay or grit as well as organic particles (biological solids including algae, most bacteria and other wastewater microorganisms) contribute to a waste streams suspended solids concentration.¹

Total Dissolved Solids (TDS) - Total Dissolved Solids is a measure of all dissolved material in a solution, including inorganic salts (e.g., NaCl, MgCl₂, etc.) that typically make up the bulk of the TDS measured in the standard lab test. TDS is used to determine the salt levels of wastewater. Measurement for TDS consists of passing a sample through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to a constant weight at 356°F (180°C). The material remaining on the filter paper is the total dissolved solids and is reported in units of ppm or mg/L. Conductivity can be used for a quick substitute measurement for TDS (reported in units of micromhos or microsiemens). As a rule-of-thumb, for wastewater streams at pH 7, the TDS of that stream in ppm (mg/L) can be approximated by multiplying the conductivity in units of micromhos or microsiemens by 0.7.

Mixed Liquor Suspended Solids (MLSS) - Mixed liquor suspended solids is the concentration of total suspended solids in the aerated section of a biological treatment unit or lagoon. If Powdered Activated Carbon (PAC) is used, it will be included in

MLSS and MLVSS measurements, unless special test methods are employed to estimate the amount of PAC, and allow a distinction between PAC and microbial mass. MLSS is normally expressed in units of ppm or mg/L.

✦ **Mixed Liquor Volatile Suspended Solids (MLVSS)** - Mixed liquor volatile suspended solids is the portion of the MLSS which volatilizes at 1022°F (550°C). Biological solids (microorganisms) are the main contributor to MLVSS. MLVSS can be used to roughly measure the amount of biomass in lagoon or in biological treatment system, but should not be used to measure the activity of the biomass nor the ability to remove contaminants. MLVSS is normally expressed in units of ppm or mg/L.

OXYGEN DEMAND

Oxygen demand is a key process parameter in a biological treatment system. It usually refers to oxidation of organic matter in the biological system. Other contaminants such as sulfides and ammonia also contribute to the oxygen demand. Therefore, the oxygen demand parameter should be used for monitoring purposes. For an estimate of total oxygen demand calculation,

✦ use the stoichiometric guidelines below by adding the following individual oxygen demands, depending upon which ones are present:

<u>For every ppm (mg/l) of:</u>	<u>Required O₂ demand</u>
TOC	3.4 ppm (mg/l)
NH ₄ -N (for biological nitrifying systems)	4.6 ppm (mg/l)
H ₂ S	1.9 ppm (mg/l)

Biochemical Oxygen Demand (BOD) - Biochemical Oxygen Demand is a general measure of organic material in wastewater samples that can be biologically degraded. It is the quantity of oxygen consumed during the biological decomposition (oxidation) of material in water. Certain inorganic compounds that exert an immediate oxygen demand (e.g., sulfite) will be detected in the BOD test. The lab test must be run carefully and repeatedly to obtain an accurate measurement. BOD is usually measured over a specific time period; a five-day period is commonly used, with the result expressed as BOD₅. If the biological decomposition is allowed to proceed to completion, the quantity of oxygen consumed is termed the ultimate BOD, often designated BOD_{ult} and is normally measured over 20 days. In this case, some nitrogen compounds can be oxidized, a process called nitrification. BOD₅ is normally expressed as ppm or mg/L and can roughly be estimated at 0.6-0.7 of BOD_{ult} or COD.¹

✦ **Chemical Oxygen Demand (COD)** - Chemical Oxygen Demand (COD) is a measure of the amount of organic or reduced inorganic compounds in a sample that can be oxidized by a strong oxidizer, usually potassium dichromate and sometimes potassium permanganate. The COD test does not oxidize ammonia. COD of a wastewater is generally greater than the BOD since the wastewater may contain material that cannot be biologically degraded. The COD test is simpler and faster than the BOD test. Caution must be used when analyzing the COD in brackish or high salt (chloride) wastewater streams (Chloride concentrations over 2,000 mg/l or sodium chloride concentrations of 3,300 mg/l) since the chlorides will interfere with the test results. For reference, sea water has about 33,000 mg/l of salt, mostly sodium chloride, with chloride content of 18,000-20,000 mg/l. COD is expressed as ppm or mg/L.¹

✦ **Theoretical Oxygen Demand (ThOD)** - The Theoretical Oxygen Demand of a wastewater is the oxygen required to oxidize stoichiometrically all organics or reduced inorganic compounds to CO₂, SO₄, NO₃, etc. end-products. For most organics, with the exception of some aromatics, the ThOD is equal to COD and TOD. ThOD is normally expressed as ppm or mg/L.

Total Organic Carbon (TOC) - Total Organic Carbon is used to measure the quantity of organically bound carbon in a sample. A special analytical instrument breaks down the organic molecules into their carbon equivalent before measuring the amount of carbon present in the sample. TOC is commonly used as a replacement for BOD since the test for TOC is significantly faster than the 5-day test for BOD, and the BOD test can sometimes give variable results. TOC is normally expressed as ppm or mg/L.¹

Section	Page	WATER POLLUTION CONTROL GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	ExxonMobil DESIGN PRACTICES
XIX-A	6 of 35		
December, 2002			

Total Oxygen Demand (TOD) - The total oxygen demand test measures the amount of oxygen required to oxidize all oxidizable substances in a sample, including the biodegradable organic matter. It is measured using a special analytical instrument. TOD is normally expressed as ppm or mg/L.

BIOX

- Abbreviation for **B**iological **O**Xidation and commonly used to describe the activated sludge type biological treatment system but can be used in reference to other biological oxidation processes used to treat wastewater.

DISSOLVED OXYGEN (DO)

Dissolved oxygen level, measured in ppm or mg/L, is an important monitoring parameter for biological systems and receiving water bodies. It indicates whether a biological treatment unit can sustain a healthy microbial population or whether the receiving water body can sustain microbial, aquatic fish, or plant life. A minimum DO value for healthy biological treatment systems is between 1 and 2 ppm (mg/L). The maximum concentration in water under normal conditions (saturation concentration) is between 8 and 10 ppm (mg/L).¹

pH

pH is a measurement of the acidic or basic character of a solution at a given temperature. It is defined as the negative logarithm (to the base 10) of the hydrogen ion concentration ($-\log[H^+]$). Pure water is slightly ionized with a pH of 7, and at equilibrium the ion product, K_w , is $[H^+][OH^-] = 1.01 \times 10^{-14}$ at 25°C. Generally, quality of receiving bodies of water need pH ranges between 6.5 to 8.5 for healthy aquatic life. Wastewaters outside the 5.5 to 9.5 pH range (before being commingled in the mixing zone of the wastewater effluent and the receiving water body) can potentially cause harm to the receiving water

- aquatic life or biological treatment microorganisms.¹

"TOXIC" COMPOUNDS/TOXICITY

Toxic compounds are those specific chemicals that have been shown to cause death or adverse effects to organisms at certain concentrations. "Toxic," "Hazardous," "Dangerous," "Carcinogenic," "Mutagenic," and several other terms are used to describe chemical effects in water systems. However, this is a complicated area since many "toxic" compounds can be essential nutrients to human and aquatic life at low concentration, such as ammonia, cobalt, zinc, and copper.

Wastewater effluent "toxicity" refers to laboratory tests that are made on the effluent where aquatic organisms, like fish or shrimp, are exposed to different percentages of the effluent for a certain period of time. These tests are frequently referred to as biomonitoring or bioassays, and the test procedures differ for determining acute versus chronic toxicity. For acute toxicity, the test results are commonly expressed as LC50 or lethal concentration at which 50 percent of the organisms are expected to die in a set period of time. Typically, the LC50 is based on either a 24, 48, or 96-hour test period. For chronic toxicity, the test results are expressed as a no-observed-effect concentration (NOEC) and is the effluent concentration where there is no significant difference between the test organisms and the control organisms. Survival, growth, and reproduction of the test organisms is compared to the control organisms for the chronic toxicity test. Typically, the duration of chronic toxicity test is 7

- days. The procedures and interpretation of these aquatic test methods can be quite complex. In situations where there is any doubt about the test methods, the lab performing the tests, the interpretation of results, or a biomonitoring test is included into an effluent permit for the first time, EMBSI (ExxonMobil Biomedical Sciences, Inc, Clinton, NJ) personnel should be consulted.

HEAVY METALS

Recent regulatory trends include effluent quality standards for heavy metals that are more stringent and prescriptive than in the past. In general, biologically treated petroleum wastewaters do not contain significant concentrations of heavy metals. There are some metals in crude oils, raw water sources, trace constituents in industrial inorganic chemicals such as caustic or lime and some that come from corrosion products of the materials of construction in refineries and petrochemical plants. In some locations, specialized treatment may be needed at the end of the wastewater treatment system to remove these metals to regulatory driven effluent concentration or mass limits. Metals such as selenium, mercury, arsenic, vanadium and zinc are typical ones found in trace amounts in refinery wastewaters. Before end- of -pipe treatment facilities are considered, a sampling and lab analysis program should be undertaken to identify the sources, to see if they can be reduced or substituted, to avoid the cost of end -of -pipe facilities. Typical sources and treatment technology for heavy metals are provided below:

	WATER POLLUTION CONTROL GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	Section	Page
		XIX-A	7 of 35
		December, 2002	

Metal	Sources	Treatment Technology Options
Arsenic	Desalter brine, tank water draws	Co-precipitation (Al and Fe salts)
Copper	Utility blowdowns, corrosion, tank draws	Co-precipitation
Mercury	Desalter brines, sour waters	Activated carbon, ion exchange
Nickel	Desalter brines, sour waters, corrosion, utility bd, tank draws	Co-precipitation
Selenium	Desalter brine, sour waters, tank draws, raw water	Co-precipitation
Zinc	Utility bd, tank draws, raw water, lube processing areas	Co-precipitation

NUTRIENTS

Nutrients are chemical elements such as nitrogen, potassium, phosphorous, sulfur, cobalt, zinc, and copper, which are essential for plant or animal growth and effective biological treatment. As a rule-of-thumb, a ratio of BOD₅, nitrogen, and phosphorus (BOD₅:N:P) = (100:5:1) is needed for effective biological activity in wastewater treatment systems. Typically 0.05 to 5 ppm of micronutrient metals are needed for healthy biotreatment (Fe, Cu, Mn, An, Mo, Co, Se) for petroleum and petrochemical wastewaters feed to a bio system. Other metals are required higher concentrations, tens to hundreds of ppm (Ca, Mg, K, Na). In most instances, all of these metals are in the mixtures of wastewaters treated at a refinery. If some locations need to add them, they need to be done so as to avoid exceeding any mass or concentration limits in the effluent discharge permit or license.

NITRIFICATION/DENITRIFICATION

Nitrification is a biological process where ammonia is converted/oxidized to nitrate (NO₃⁻). The process involves one microorganism species converting ammonia to nitrite (NO₂⁻) and then a different microorganism species converting the nitrite to nitrate. This term should not be confused with "denitrification," which refers to the biological process of converting nitrites/nitrates to nitrogen gas (N₂).^{40 46}

OVERALL WASTEWATER SOURCE MANAGEMENT AND TREATMENT SELECTION

OVERALL WASTEWATER SOURCE MANAGEMENT

As part of an overall water/wastewater management strategy, several issues must be considered, including wastewater reuse opportunities, government restrictions on types of wastewaters allowed to go to sewers, safety, "pollution prevention" goals, and stormwater management. Normally, a comprehensive review of wastewater sources, including flow and source assessment and lab analysis, is needed to define a cost effective overall water management strategy. A considerable effort should be planned and made in this area before facilities are designed. Considerable savings can be realized in facilities if a complete water management material balance and strategy are prepared.

Stormwater handling can be an important factor, especially when considering new treatment facilities. Treatment facilities are sized on removal performance and flow rate. Frequently, the equalization or diversion of stormwater can have a large impact in reducing the size of these facilities.⁵⁻¹⁷

WATER REUSE

Water reuse can result in a significant reduction in the volume and cost of water (raw and discharged wastewater) used/generated at a refinery or chemical plant. The three major types of reuse are: reduction, recycle within the unit, and reuse (direct or cascade reuse, segregation and reuse, and treatment and reuse).

Reduction of the amount of water used in a process generally results in an increase in the contaminant level and the temperature of the effluent wastewater. If this is acceptable from a process, safety, and materials standpoint, it can be used to lower raw water usage. A typical large reduction in raw water usage is obtained by increasing the cooling tower cycles.

Recycle refers to when wastewater is reused in the process from which it originated. Examples of this are return of sample coolers to the cooling tower or a pumparound on a water scrubber tower. A purge stream off of the recycle loop is needed to control the level of contaminants. Other measures, such as heat removal, chemical treatment, or contaminant removal may also be required.

Reuse refers to when wastewater is reused by routing or cascading it from one unit to another. For example, stripped sour water (SSW) may be reused in the desalter to reduce raw water makeup and contaminant concentration, such as pH.



Section	Page	<i>WATER POLLUTION CONTROL</i> GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	 DESIGN PRACTICES
XIX-A	8 of 35		
December, 2002			

originating in the SSW. The advantage of reuse over recycle is that contaminant buildup is less likely. Each process has minimum water quality requirements. If the quality of the wastewater from a process meets the minimum water quality requirements of another process, it can be reused directly. If not, segregation of certain wastewaters from a combined stream or treatment of the wastewater before reuse may be necessary.

Guidelines for developing a water reuse program can be found in [Design Practice XIX-B, Water Reuse](#). The section also gives examples of reuse by process unit along with critical parameters for each case.

WATER CHEMISTRY

Understanding the water chemistry is an integral part of wastewater management. The ionic and molecular (both organic and inorganic) species in the water and their interaction affect water usage and wastewater treatment. For example:

- Dissolved solids may precipitate out as a scale if the water temperature or pH is changed or if the water is concentrated by recycle or evaporation. Scale reduces heat transfer efficiency in exchangers.
- pH or chlorides level in the water affect the corrosivity of the water.
- High pH may cause or increase emulsification resulting in poor oil/ water separation.
- Organics in water, if combined with nitrogen at the right conditions, will result in biological growth and potentially biological fouling.
- Ammonia and hydrogen sulfides in water may need to be stripped before reuse or treatment. If not, they can evolve when the pH is changed.
- A narrow pH band (7 to 8.5) is required to obtain healthy biomass in biological treatment system.

SEWER

Generally, there are two major types of sewer systems: combined and segregated sewer systems. The segregated sewer system can be divided as follows:

- **Industrial/Process Sewers or Oily Water Sewers** which collect process wastewater and hydrocarbon contaminated wastewater including rainwater or firewater runoff from areas normally subject to hydrocarbon/oil contamination and condensate/blowdown with hydrocarbon/oil or chemical contaminants.
- **Chemical Sewers** which collect acid, caustic, or other chemical wastewaters which require neutralization or treatment prior to discharge to industrial sewers.
- **Storm Water Sewers or Clean Water Sewers** which collect rainwater runoff, firewater, and condensate/blowdown that is not normally subject to hydrocarbon/oil, or toxic chemical contamination.

The **Combined Sewer Systems** are those systems which combine two or more types of sewers as defined above. The combined sewer system is the most common sewer type in ExxonMobil. However, new projects, government regulations, and costs of end-of -pipe treatment are making many locations to go to more segregated systems.

There are advantages and disadvantages of segregating stormwaters. In almost all cases, it is cost effective to divert clean stormwater (those stormwaters that do not contact process areas or other contaminated locations) to a separate ditch or sewer system. In some locations, this water is collected in an impoundment basin and used as a fire water supply. Studies have shown that excessive stormwater mixed with contaminated process waters results in excessive sludge generation in the wastewater treatment equipment and solubilizing of hydrocarbons that would otherwise stay in the oil phase. However, there are special cases where segregating stormwater can be costly and can increase the concentration of contaminants to the wastewater treatment equipment, resulting in the potential for exceeding permit limits for individual contaminants or toxicity tests. Hence, several factors need to be considered in integrating stormwater handling in the overall wastewater management plan.

Stormwater that is from contaminated areas within the plant can also be managed properly to reduce downstream impact on treatment facilities by using the first flush principle. The diversion of the dirty, first 30 to 60 minute flush of stormwater to a diversion tank, if allowed by regulatory authorities, for eventual work off into the treatment system can be an effective strategy. The water after the first 30 to 60 minutes can be clean and diverted to clean stormwater conveyances or impoundment basins for eventual discharge.

Sewers can be constructed underground or aboveground. The aboveground sewer has the advantages of easier maintenance and detection for leaks or infrastructure damage. However, it needs to be pressurized. Economical and operating factors for segregated/combined and aboveground/underground sewer system should be considered when building a new sewer system.

Segregated Sewer System - As mentioned above, it is frequently cost effective to segregate "clean" from "dirty" wastewaters in separate sewer systems. Segregated sewer systems are also frequently needed when hazardous or volatile contaminants are present in high concentration.

 DESIGN PRACTICES	WATER POLLUTION CONTROL GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	Section XIX-A	Page 9 of 35
		December, 2002	

DECISION TREES FOR TREATMENT UNIT SELECTION

This section consists of decision trees that will give general guidance to select wastewater treatment technology for different types of contaminant removal. The decision trees are presented in [Figures 1](#) through [6](#) and are listed below. For those situations that do not fit into the general decision trees, contact ER&E environmental specialists for assistance.

- Wastewater Treatment Assessment ([Figure 1](#))
- Free Oil Removal ([Figure 2](#))
- Oxygen Demand/Dissolved Organics Reduction ([Figure 3](#))
- Suspended Solids Removal ([Figure 4](#))
- Wastewater Effluent Toxicity Reduction ([Figure 5](#))
- Wastewater Sludge Management Volume Reduction ([Figure 6](#))

TYPICAL EFFLUENT QUALITY CRITERIA

Government regulations and guidelines on the quality of wastewaters discharged from industrial facilities can vary greatly depending upon the location in the world. In some cases, town/cities or regions impose restrictions in addition to states and centralized country requirements. A key factor affecting the water quality criteria imposed on the treated wastewater effluents is receiving water use and location. Much tighter restrictions are placed on facilities that discharge into fresh water bodies that have downstream drinking water or other recreational uses involving the public or important aquatic plant and animal life. Less stringent requirements are sometimes placed on effluents that go into government owned treatment works prior to discharge into the aquatic environment.

- ▶ Effluent quality limits are generally placed on the the effluent wastewater without dilution, but mixing zones allow the effluent concentrations of most contaminants to be higher than that needed in the receiving water body to protect aquatic resources. Near the discharge point, a mixing zone exists where constituent concentrations are between the effluent and fully mixed values. The characteristics of the mixing zone are important because they can reduce the effect of toxic chemicals by speeding their dilution. The mixing zone is not significant for dissolved oxygen analyses because BOD exertion is slow compared to the travel time within the mixing zone. The mixing zone size will vary depending on the mode of discharge e.g., pipe, multiport diffusers, etc. Because the mixing zone factor may be significant, i.e., up to a dilution factor of 40, it is important to include its effect when determining the effluent quality and when negotiating with the authorities for the site specific regulations on the wastewater effluent discharge quality.

The general requirements for industrial plant facilities are a definition of effluent contaminant parameters in terms of concentrations (weight parts-per-million, ppm (mg/L), or mass limits (lbs or kg per day) or both. Quality requirements for industrial wastewater effluents have changed significantly over the past decade. Past regulations have focused on conventional contaminants or indicators of pollution such as oil and grease, biochemical oxygen demand, pH, temperature and suspended solids. In some locations, regulatory authorities are continuing to reduce the allowable concentrations and mass limits of these conventional indicators of pollution. In other areas, the emphasis now is on the control of "toxic" or "hazardous" compounds. Specific effluent concentration and/or quantity limits are being imposed on industrial facilities for compounds

- ▶ such as phenolics, benzene, cyanide, ammonia, hydrogen sulfide and heavy metals. In some locations, regulatory agencies are placing limits on nitrogen or phosphorus discharges which can potentially cause uncontrolled vegetative growth in receiving bodies of water (called eutrophication), reducing the receiving water available oxygen. Some environmental agencies are focusing on environmental compliance or enforcement of existing limits, which means more frequent monitoring and reporting. The capability of new analytical methods to measure very low concentrations is creating the need for increased emphasis on reducing specific "toxic" constituents, such as mercury. However, artificially low limits should be challenged if they do not have a clear adverse environmental impact, rather than just their capability to be measured at low concentrations. In locations that require maximum water reuse, concerns should be focused on avoiding excessive concentration of the contaminants that need to be treated prior to discharge. Also, new projects in petroleum facilities and chemical plants are changing the types and quantities of compounds entering the wastewater system. Some of these compounds may require monitoring and reporting to government authorities. Other emerging issues that can potentially impact effluent limits are more sophisticated biomonitoring methods, outfall sediment quality, mixing zone modeling, and watershed overall quality.¹⁸⁻²³

OIL AND pH

Petroleum and petrochemical facilities almost always have "oil" (oil and grease) and pH limits. A key limitation is that this oil will not cause a visible sheen on the surface of the receiving body of water. Quantitative limits generally range from 5 to 50 ppm in the effluent for land-based facilities. Because acid and base materials are used, pH limits are generally applied and are commonly between 6 and 9 for operating temperature between 50 and 100°F (10 and 38°C). Exceptions are made for particular

Section	Page	<i>WATER POLLUTION CONTROL</i> GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	 DESIGN PRACTICES
XIX-A	10 of 35		
December, 2002			

locations such as stormwater which may have a lower pH due to localized affects of acid rain, outside of the control of the facility.

GENERAL POLLUTANT INDICATORS

A listing of general pollutant indicators that frequently are required by regulatory agencies of most industrial facilities are given below. This listing is provided to guide the reader in developing sampling and analytical requirements for treatment facilities.

- Temperature
- Dissolved Oxygen
- Oxygen Demand (BOD, COD, TOC)
- Odor
- Suspended Solids
- Total Dissolved Solids
- Toxicity or Bioassays

OTHER TYPICAL PETROLEUM/PETROCHEMICAL CONTAMINANTS

Frequently, government regulations require sampling and analysis of plant wastewater effluents for known compounds present in petroleum/petrochemical wastewaters, listed below.

- Phenol/Phenolics
- Hydrogen Sulfide (Sulfides)
- Ammonia (and other nitrogen compounds in effluents)
- Selected Heavy Metals (e.g., Lead, Mercury)

EXAMPLES OF TOXIC COMPOUNDS

"Toxic," "Hazardous," "Priority," "Black Listed," "Dangerous" and several other terms have been used to describe organic compounds and heavy metals that governments are particularly interested in regulating because of their human or aquatic toxicity impacts. Some governments have not required measuring these, since the treatment systems in certain locations are known to remove these compounds, so measuring some of the general indicator compounds like BOD is sufficient to monitor the "toxic" compounds as well. In other locations, government agencies have required sampling and measuring these compounds (such as benzene or lead) to ensure that the specific compounds are low enough in the effluent. Hence, there are no clear cut guidelines on these compounds because of the location specific impacts that must be considered as well as mixing zone influence of the particular water body. For example, the concentration in the effluent can be much higher than that allowed in the water body, since the effluent will mix with the water body near its outfall. Check with local regulations on these compounds as well as the general and other typical compounds listed above.

TREATMENT UNITS

TYPICAL REFINERY/PETROCHEMICAL WASTEWATER TREATING FLOW PLAN

A flow plan illustrating a typical wastewater treatment system is presented in [Figure 7](#). The purpose of this figure is to provide a general idea of how the treatment units fit together, for what purposes, and where the various waste streams enter and leave the treatment system. The flow plan also illustrates that there are several alternative technologies that can be selected to remove the targeted compound(s). Selection of the treatment units and layout of the wastewater treatment plant will depend primarily upon the type of processes in the refinery/chemical plant and the effluent criteria (concentrations or tests) required by the government. An important element of preparing a figure like [Figure 7](#) is collecting sufficient flow and contaminant data from all the major wastewater sources and preparing material balances, with some statistical analysis of the data.

OIL REMOVAL/SEPARATION AT SOURCES- No/Low Oil to Sewer and More Equalization Tankage

Several locations have implemented a program of reducing major oil sources to the sewer and wastewater treatment systems. The result has been reducing oil losses, gaining value for the recovered oil, improving wastewater treatment, reducing treatment chemical costs and dramatically reducing waste disposal volumes. Guidelines are available on the Wastewater and Waste BestNet to assist in planning for an effective program.

 DESIGN PRACTICES	WATER POLLUTION CONTROL GUIDELINES FOR SELECTING WASTEWATER TREATMENT SYSTEMS PROPRIETARY INFORMATION - For Authorized Company Use Only	Section	Page
		XIX-A	11 of 35
		December, 2002	

In recent years, refineries have been processing heavier and sour crudes. These crudes have caused increased separation problems at the desalter and other downstream equipment such as API separators and flotation units. The result has been more oil going into the biox systems, during upset or stormwater conditions, causing foam and poor settling biomass in the clarifier. Some locations have put dedicated tankage to improve oil water separation for the desalter washwater, and at the WWT system to protect the downstream biological systems, and to recover more oil. Even in cases where the desalter is the latest technology, including bielectrics, AGAR type oil water interface detectors, new generation demulsifiers are used, and EMRE designed mudwash systems, some sort of settling tankage or further oil/water separation may be needed, when the type of oil does not separate well or binds with mud to form stable emulsions. This trend will likely continue in the future.

HOW TO ESTIMATE WASTEWATER FLOW AND QUALITY WITHOUT DATA

In most cases, a focused and well-planned wastewater flow and quality study should be conducted at the plant site. This includes sampling and laboratory analysis of key wastewater streams to provide a basis for a cost effective treatment strategy. In situations where new petroleum or petrochemical process units are added to an existing plant, or where rough, early screening estimates are needed for a plant that does not exist, prior data from ExxonMobil studies can be used for estimating purposes. Information sources given in the selected references refer to refinery process units only.²⁴⁻²⁶

TYPICAL REMOVAL EFFICIENCIES FOR SELECTED WASTEWATER TREATING UNITS

Contaminants can be removed from wastewater using many different types of treating units. Selection of the proper treatment unit will depend upon the contaminant that must be removed and the effluent limit for that contaminant. [Table 1](#) provides typical removal efficiencies for the more common wastewater treating units. The information contained on this table should be used as a guideline only since actual removal rates vary with the influent wastewater quality and several other factors that must be considered prior to equipment design and specification.

TREATMENT UNITS (Cont)

EQUALIZATION/pH CONTROL (FLOW AND CONTAMINANT LOAD)

Equalization facilities are provided to equalize flow and contaminant loads to downstream treatment units. For flow, the equalization facility will dampen out normal and peak flow variations that come from the process blocks or during rain events. Equalization provides a nearly constant flowrate to downstream treatment units, thus reducing the impact of flowrate on process control and improving treatment unit reliability. Downstream treatment unit size and cost can be minimized since the units can be designed based on the equalized flowrate and not on peak flow. Equalization also dampens out variations in contaminant concentrations, which occur in daily operations and during upsets. This provides a more uniform feed concentration to downstream treatment units which in turn ensures a more consistent performance from each downstream unit and a consistent overall effluent quality.

♦ Ideally, a wastewater treatment plant should have three different equalization facilities; one for the diversion and management of process rainwater, one for high contamination off-spec wastewaters, and one to equalize the wastewater contaminant concentration and flowrate upstream of the advanced primary treatment units such as flotation units and biological treatment units. If equalization and diversion tankage are sized adequately, then the three types of equalization can be combined into two tanks, one for stormwater management and the other for equalization of contaminants and flow. Equalization is especially important for biological treatment systems. Diversion of rainwater generally takes place either upstream of the oil/water separation facilities or is incorporated into the operation of the oil/water separation facilities. For example, the forebay of an API separator can be designed to divert the incoming rainwater, based on flowrate, water level, or time, to a sump for pumping to a diversion tank or basin. Once the rain event is over, the contents of the diversion tank or basin can then be bled back to the treatment plant at a controlled rate.

♦ Under normal dry weather flow conditions, wastewater passing through the oil/water separation facilities will typically flow into an equalization tank before going to the biological treatment unit. The equalization tank is generally located downstream of the oil/water separation facilities to minimize the amount of oil and solids that enter the tank. However, as mentioned previously, the processing of sour and heavy crudes that cause oil/water separation problems, particularly at the desalter, may require separate tankage and oil removal. Equalization upstream of a biological unit is necessary to minimize the variability in the contaminant loading that can upset the performance of a biological unit and other treatment units.

Care must be taken when selecting the type of equalization facilities. Some locations may be allowed to use an open basin whereas others may be required to use closed tanks or covered basins. In the U.S., consideration must be given to the volatile organic content, particularly benzene, of the streams entering sewers, impoundments, and other facilities to determine if special equipment features are needed to minimize vapor emissions.

It is essential to have a pH control system upstream or integrated with biological treatment units. A biological treatment unit operates within a narrow pH range (approximately 7 to 8.5), and performance is very sensitive to wide swings in pH. Additional pH adjustment facilities may also be necessary to ensure the plant effluent falls within the regulated pH range.

