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Affected Publication: **API Publication Number 4602, Minimization, Handling, Treatment and Disposal of Petroleum Products Terminal Wastewaters, August 1994**

On page 1-1, paragraph 1, line 5, the word "to" has been omitted.

The text should read:

"Although wastewater generation at terminals is relatively minor, increasingly strict regulation of wastewater from even minor sources is making it more critical **to** understand and optimize..."

On page 4-16, Table 4-2, the word "napthenes" should be replaced by "naphthenes."

On page B-17, Figure B-8, the carbon drums are 165 lbs in size, not 500 lbs.

Pages 9-60, 9-62, 9-64, B-11, B-12 and B-13:

The calculations of activated carbon capacity based on pilot and full-scale testing were based on an erroneous value for the weight of carbon in two of the four studies. The erroneous values were based on 500 lb carbon drums. The corrected pages, based on 165 lb carbon drums, are attached. Please paste them into your document.

HEALTH AND
ENVIRONMENTAL
SCIENCES
AND
MANUFACTURING,
DISTRIBUTION AND
MARKETING
DEPARTMENTS

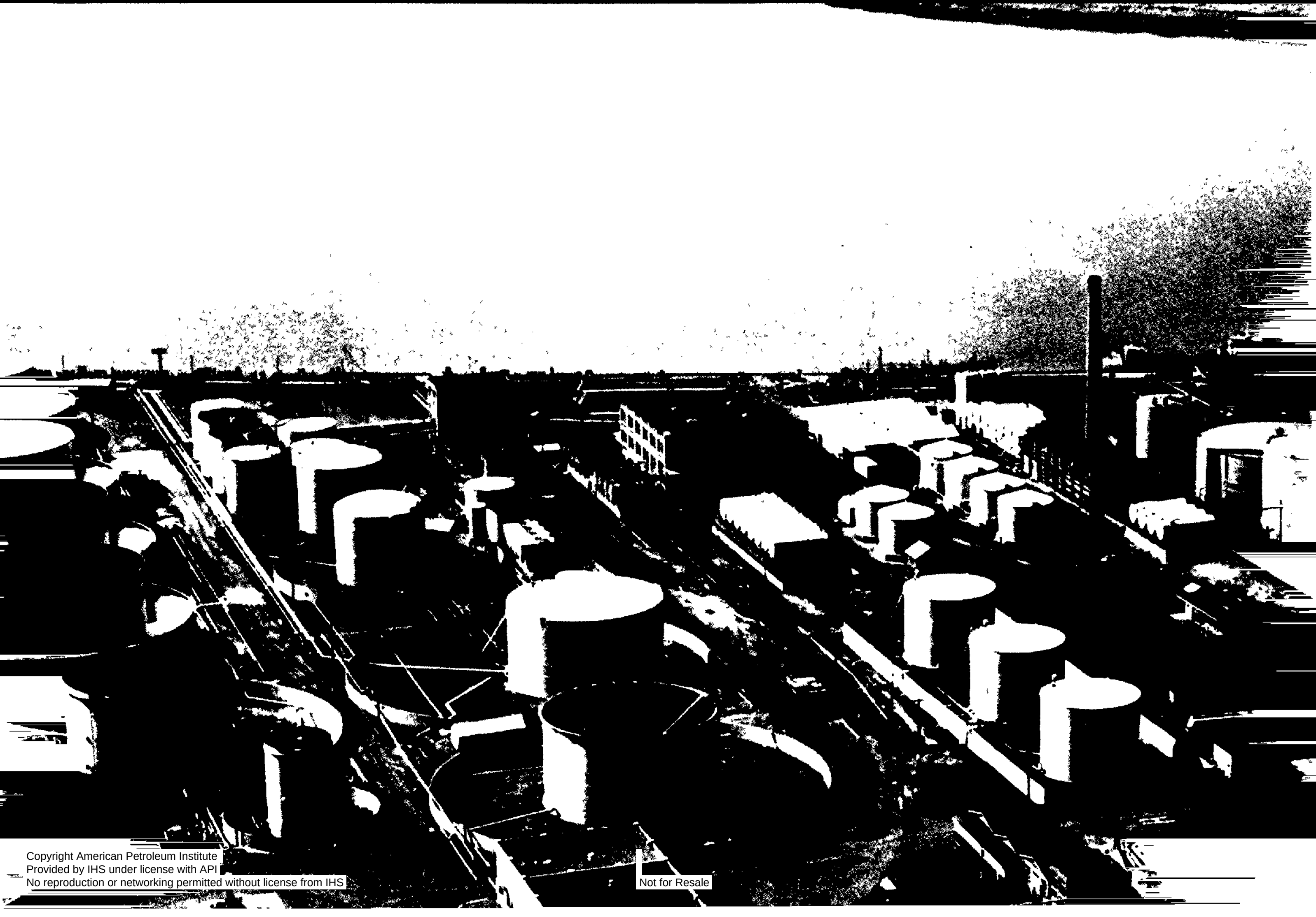
STEP
Strategies for Today's
Environmental Partnership

American Petroleum Institute
1220 L Street, Northwest
Washington, D.C. 20005

API PUBLICATION
NUMBER 4602

AUGUST 1994

Minimization, Handling, Treatment, and Disposal of Petroleum Products Terminal Wastewaters



STEP

Strategies for Today's
Environmental Partnership

One of the most significant long-term trends affecting the future vitality of the petroleum industry is the public's concerns about the environment. Recognizing this trend, API member companies have developed a positive, forward looking strategy called STEP: Strategies for Today's Environmental Partnership. This program aims to address public concerns by improving our industry's environmental, health and safety performance; documenting performance improvements; and communicating them to the public. The foundation of STEP is the API Environmental Mission and Guiding Environmental Principles.

API ENVIRONMENTAL MISSION AND GUIDING ENVIRONMENTAL PRINCIPLES

The members of the American Petroleum Institute are dedicated to continuous efforts to improve the compatibility of our operations with the environment while economically developing energy resources and supplying high quality products and services to consumers. The members recognize the importance of efficiently meeting society's needs and our responsibility to work with the public, the government, and others to develop and to use natural resources in an environmentally sound manner while protecting the health and safety of our employees and the public. To meet these responsibilities, API members pledge to manage our businesses according to these principles:

- To recognize and to respond to community concerns about our raw materials, products and operations.
- To operate our plants and facilities, and to handle our raw materials and products in a manner that protects the environment, and the safety and health of our employees and the public.
- To make safety, health and environmental considerations a priority in our planning, and our development of new products and processes.
- To advise promptly, appropriate officials, employees, customers and the public of information on significant industry-related safety, health and environmental hazards, and to recommend protective measures.
- To counsel customers, transporters and others in the safe use, transportation and disposal of our raw materials, products and waste materials.
- To economically develop and produce natural resources and to conserve those resources by using energy efficiently.
- To extend knowledge by conducting or supporting research on the safety, health and environmental effects of our raw materials, products, processes and waste materials.
- To commit to reduce overall emission and waste generation.
- To work with others to resolve problems created by handling and disposal of hazardous substances from our operations.
- To participate with government and others in creating responsible laws, regulations and standards to safeguard the community, workplace and environment.
- To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.

Minimization, Handling, Treatment, and Disposal of Petroleum Products Terminal Wastewaters

Health and Environmental Sciences Department
and
Manufacturing, Distribution, and Marketing Department

API PUBLICATION NUMBER 4602

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PORT ARTHUR, TEXAS

AUGUST 1994

American Petroleum Institute

FOREWORD

ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

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The author wishes to express his appreciation to his colleagues within Texaco's Marketing, Pipeline, and Research Departments and to members of the API Marketing Terminal Effluent Task Force, who provided much valuable input on operations and procedures in petroleum products terminals. Special thanks for their guidance and assistance are owed to Mr. Dave Pierce, to task force chairman Mr. Robert Goodrich, and to API's Ms. Priscilla Young.

ABSTRACT

This report is intended to be a basic guide and information resource for all wastewater operations at petroleum products terminals. It includes the regulatory framework for wastewater issues, a detailed description of the sources of terminal wastewater and associated contaminants, guidance on means for analyzing the wastewater situation at a terminal, on means for minimizing wastewater flow and contamination, on means for handling and disposing of wastewater, and on available methods for treating wastewater with various types of contaminants. The regulatory discussion focuses on the effects of wastewater and hazardous waste regulations on wastewater handling and treatment. This is followed by a description of petroleum products terminals operations and associated wastewater generation and typical contaminants. The remainder of the report covers methods for investigating and designing wastewater operations at terminals. First is an overview of wastewater handling, treatment, and disposal options. Means for characterization and minimization of terminal wastewater flow and contamination are covered. Last is an overview of wastewater treatment options for terminal wastewater. The types of treatment appropriate for removing various types of contaminants are listed, along with opportunities for source reduction of these contaminants. General factors for wastewater treatment are outlined and wastewater treatment methods applicable to the types of contaminants expected in petroleum products terminal wastewater are reviewed.

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PREFACE

The American Petroleum Institute (API), through its Marketing Terminal Effluent Task Force is conducting a multi-year program to evaluate and identify practical and environmentally sound technology options for handling and treating waters generated at petroleum product distribution terminals. The results of this program are intended to provide industry and regulatory agencies with sound technical information to make informed decisions on appropriate alternatives for individual terminal facilities.

This document provides comprehensive information to allow terminal engineers or operations staff to identify technology options for minimizing, handling, treating and disposing of water and wastewaters. The report covers typical terminal operations, an overview of regulatory requirements, wastewater source identification and reduction, onsite and offsite disposal options, wastewater treatment technologies and design. The information is a culmination of prior studies done by the API, as well as industry-supplied data and information from publicly available sources.

Prior work has shown that operations and wastewater characteristics at petroleum product distribution terminals can vary significantly, as do the regulatory requirements in different geographical jurisdictions. Hence, it is recommended that terminal operators or engineers carefully review the requirements for each facility prior to implementing control measures. This comprehensive compilation of information and treatment process options should greatly aid in these reviews.

The task force acknowledges and greatly appreciates the excellent efforts of Texaco's Port Arthur Research staff, in particular Dr. Byron Klock, for their extensive work in preparing this useful and comprehensive report. The work was a major multidisciplined effort covering many facets of terminal operations, specialized industry treatment technology and various fields of engineering, chemistry and aquatic toxicology.

R.R. Goodrich

On behalf of the Marketing and
Terminal Effluent Task Force

Chapter 1

INTRODUCTION

Petroleum products terminals are used with transportation operations to move products from their source in refineries down to the consumers. They are relatively simple facilities comprising product storage tanks, the means for connecting the tanks to transportation operations, and other supporting equipment. Although wastewater generation at terminals is relatively minor, increasingly strict regulation of wastewater from even minor sources is making it more critical understand and optimize handling, treatment and disposal of terminal wastewater to ensure that effective treatment is accomplished at reasonable cost.

This report is intended to be a basic guide and information resource for all wastewater operations at petroleum products terminals. It includes the regulatory framework for wastewater issues, a detailed description of the sources of terminal wastewater and associated contaminants, and guidance on means for analyzing the wastewater situation at a terminal, on means for minimizing wastewater flow and contamination, on means for handling and disposing of wastewater, and on available methods for treating wastewater with various types of contaminants.

Chapter 3 is an overview of the regulatory framework for petroleum products terminal wastewater issues. Although not a substitute for detailed understanding of environmental regulatory law, it provides an outline of the issues most likely to be applicable to petroleum products terminals. Most of this chapter covers wastewater permits for discharge to public waters or municipal treatment plants, and provides guidance on the issues covered by these and on permit application and negotiation procedures. Since hazardous waste disposal regulations can potentially be applied to wastewater, guidance is provided on such regulations, and on the effects of these on wastewater handling, treatment, and disposal.

Chapter 4 describes petroleum products terminals operations and associated wastewater generation. The function of terminals in the transportation network, and the various types of terminals, are outlined. Terminal operations and products are discussed, along with the wastewater sources from these. The impact of a typical terminal wastewater on the environment is described to place this in context. Finally, the nature of typical contaminants in terminal wastewaters is discussed.

The remaining chapters are devoted to methods for investigating and designing wastewater operations at terminals.

Chapter 5 provides an overview of wastewater handling, treatment, and disposal options. Since the means utilized for final disposition of the wastewater strongly affects the required upstream operations, the choices of disposal options, with their advantages and disadvantages, are discussed first. This is followed by an outline of a model system, with optimized techniques for minimizing wastewater flow and contamination, and of treating the wastewater. Finally, the general factors to be considered in selecting wastewater designs are discussed.

Chapter 6 is a guide to characterization of terminal wastewater flow and contamination. The first section covers various means for measuring continuous and sporadic flows, while the second section describes wastewater sampling in some detail, and provides an overview of analytical techniques.

Chapter 7, on source reduction, is a technical guide to means for reducing the flow and contamination in terminal wastewaters. Stormwater segregation and minimization of contamination are described first. This is followed by detailed techniques on minimizing oil contamination of terminal wastewater, and minimizing flow of the principal contaminated water source, tank bottoms water. Finally, means for minimizing flow or contamination from other likely terminal wastewater sources are covered.

Chapter 8 provides information on various aspects of terminal wastewater handling design. The topics include routing and storage of various types of stormwater, contaminant load equalization, particularly for sporadic tank bottoms draws, and design of tank bottoms collection systems.

Chapter 9 is an overview of wastewater treatment options for terminal wastewater. It opens with a discussion of the effects of the means chosen for wastewater disposal on the likely needs for treatment, ranging from essentially no treatment to possibly very thorough treatment. Next, the types of treatment appropriate for removing various types of contaminants are listed, along with opportunities for source reduction of these contaminants. General factors for wastewater treatment are outlined, including the modes of treatment (continuous vs. periodic treatment, permanent vs. mobile installation). Finally, wastewater treatment methods applicable to the types of contaminants expected in petroleum products terminal wastewater are reviewed. This discussion is meant to provide an overview of available treatment methods, but not design guidelines, which must be obtained from more specialized and detailed sources.

Appendix A is a set of blank forms on terminal wastewater, to be used as a tool in developing information on the wastewater situation at a given terminal.

Appendix B provides summaries of treatment results from use of pilot or full-scale treatment in actual installations to serve as a guide to the effectiveness and practicality of various types of treatment.

Chapter 2

DEFINITIONS

The following terms are used throughout the report, and may not be familiar to those persons who do not normally deal with petroleum products terminals or wastewater. In addition to the following, definitions of specialized terms are given throughout the report at the point where they are used.

Ballast Water	Water placed in empty ships and barges to stabilize their motion while under way.
Barrel	In the petroleum industry, a unit of volumetric measure equal to 42 gallons. Abbreviated *bbl.*
Bioassay	A test of water quality which directly measures the degree of adverse effects on living aquatic organisms.
BTEX	Benzene, Toluene, Ethylbenzene, Xylenes, simple aromatic compounds comprising benzene, methyl benzene (toluene), ethylbenzene, and three dimethyl benzenes (xylenes), commonly found as high-octane components of gasoline.
CFR	Code of Federal Regulations, the US federal law code. Environmental regulations are contained in section 40 CFR.
CWA	Clean Water Act, the Federal law designed to protect the quality of public waters.
DIPE	Di Iso Propyl Ether, a high-octane petrochemical used as a gasoline supplement to enhance octane and reduce vehicle emissions. Formula: $(CH_3)_2HC\text{-}O\text{-}CH(CH_3)_2$
Downstream	That portion of the petroleum industry involving crude oil refining, products distribution, and products marketing.
EPA	Environmental Protection Agency, the Federal agency which administers Federal environmental laws by developing and enforcing environmental regulations.
Hazardous Waste	A term defined in RCRA to mean solid waste which either fails tests for hazardousness (*characteristic* hazardous waste) or is defined by its method of generation as being hazardous (*listed* hazardous waste).

LEL & UEL	Lower Explosive Limit & Upper Explosive Limit, measures (as percent of fuel vapor) of the ability of a fuel-air mixture to explode when exposed to an ignition source. At fuel percentages below the LEL, the mixture is too *lean* to explode (not enough fuel to sustain combustion). At fuel percentages above the UEL, the mixture is too *rich* to explode (not enough oxygen to sustain combustion). The atmosphere in most petroleum products storage vessels is above the UEL.
Midstream	That portion of the petroleum industry involving crude oil transport from producing operations to refining operations.
M	In the petroleum industry, a numerical prefix meaning a thousand (equivalent to the metric system prefix *kilo*).
MM	In the petroleum industry, a numerical prefix meaning a million.
MTBE	Methyl Tertiary Butyl Ether, a high-octane petrochemical used as a gasoline supplement to enhance octane and reduce vehicle emissions. Formula: $CH_3\text{-}O\text{-}C(CH_3)_3$
NPDES	National Pollutant Discharge Elimination System, the Federal regulations controlling the treatment and disposal of wastewaters discharged to public waters.
Oil	In wastewater terminology, used to mean oil & grease or TPH.
Oil & Grease	A water quality test which measures the amount of material extractable into a solvent (usually Freon) by weighing the residue left by evaporating the solvent. Sometimes abbreviated O&G.
pH	A measure of the acid - base balance in water, with pH 1 being extremely acidic, pH 7 being neutral, and pH 14 being extremely alkaline. By definition, the negative base ten logarithm of the activity (approximately equal to the gram-molar concentration) of hydrogen ions.
POTW	Publicly Owned Treatment Works, municipal wastewater treatment plants which normally treat domestic sewage along with some commercial and industrial wastewater. Most POTWs employ settling and biological wastewater treatment.
RCRA	Resources Conservation and Recovery Act, the Federal law which regulates the generation, handling, treatment, and disposal of solid and hazardous wastes.

SDWA	Safe Drinking Water Act, the Federal law controlling activities which affect the quality of drinking water sources.
Sludge	Generally, solid or semi-solid material which separates by settling from wastewater.
Solid Waste	A term defined in RCRA to mean discarded material other than air emissions and wastewater discharges.
TAME	Tertiary Amyl Methyl Ether, a high-octane petrochemical used as a gasoline supplement to enhance octane and reduce vehicle emissions. Formula: $CH_3\text{-}O\text{-}C(CH_3)_2CH_2CH_3$
Tank	Most commonly, a vertical cylindrical vessel used for storing petroleum products, with bottom and sides made from steel plates, and usually with a fixed or floating metal roof. Storage capacities range from 500 to 300,000 barrels.
Tank Bottoms	The material, usually a mixture of water and solids, which collects at the bottom of petroleum product storage tanks. Sometimes used to mean tank bottoms water.
Tank Bottoms Water	Water which collects at the bottom of petroleum product storage tanks and is periodically removed.
Terminal	A facility used to store petroleum products along the distribution chain from the petroleum refinery to the final consumer.
Toxicity	Adverse effects (lethality, growth suppression, reduced fecundity) on aquatic organisms.
TPH	Total Petroleum Hydrocarbons, a water quality test similar to oil & grease, but limited to petroleum-derived hydrocarbons by excluding other extractable materials such as sulfur and polar organic compounds.
Truck Wash Water	Water, usually containing detergent, soil particles, and some oil, produced by the washing of petroleum product tanker trucks. Similar in nature to car wash water.
Upstream	That portion of the petroleum industry involving exploration for and production of crude oil.

Chapter 3

OVERVIEW OF REGULATORY REQUIREMENTS

3.1 Overview

This section contains a general description of environmental legislation and resulting regulations that relate to effluent (wastewater) discharges from petroleum products terminals. The writeup is arranged by areas, with each area defined by the primary federal legislation for that area.

This discussion is not intended to address all regulatory requirements related to petroleum product terminals, but to provide pertinent information on some of the most important issues related to wastewater treatment plants and effluent discharges. Due to the complexity of the regulations, petroleum product terminals should obtain guidance from environmental regulatory specialists when dealing with specific permitting or compliance issues.

3.2 Wastewater Discharges: Federal Water Pollution Control Act of 1972 and Amendments and Safe Drinking Water Act of 1974

The Federal Water Pollution Control Act of 1972, also known as the Clean Water Act (CWA), provides the EPA with the authority to regulate the direct or indirect discharge of wastewater to waters of the United States. Indirect discharges are those which reach the receiving waters after treatment in a municipal sanitary sewage treatment plant, called a "publicly owned treatment works", or POTW, in the regulations. Direct discharges are those which are sent directly from the commercial or industrial facility to the receiving water without further treatment. Direct wastewater discharges are regulated under the National Pollutant Discharge Elimination System (NPDES) in accordance with Section 402 of the CWA. Indirect wastewater discharges are regulated in accordance with Section 307(b) of the CWA.

3.2.1 NPDES PERMITS

In general, any direct discharge of pollutants to waters of the United States from a point source requires an NPDES permit. "Waters of the United States" is interpreted very broadly to mean virtually any surface waters not solely on private property; even dry stream beds or drainage ditches are included. However, groundwater is *not* included, so if the water is sent to a well, or into a french drain, percolation pond, evaporation pond, or infiltration gallery, then an NPDES permit is probably not needed. A number of court cases have addressed the question of whether discharges to groundwater with a close connection to surface water may require an NPDES permit. The prevailing view appears to be that a permit is not needed, but the issue has not been completely resolved nationally. Also, for discharges to ground, another type of wastewater permit may be required by the Safe Drinking Water Act or local regulations. Also, note that an NPDES permit allows water which would otherwise be classified as hazardous waste to be exempted (see below).

3.2.1.1 Point Source

A "point source" is any discharge to public waters resulting from collection and conveyance of wastewater, by means including pipes, sewers, ditches, channels, and so forth. A nonpoint source is water which leaves the property by running off the land (e.g., down a hillside) in sheet flow, i.e., not collected or channeled. In general, if the water is collected before discharge, the discharge becomes a point source. As noted, any point source discharge containing pollutants as defined in the CWA (except stormwaters, in some cases) sent directly to public waters must have an NPDES permit. If the facility has more than one point source, each source must be permitted (although all the sources at a facility are usually covered by a single NPDES permit). Point sources are referred to as *Outfalls* and are assigned unique numbers. Each outfall may have different parameters to be monitored and controlled, and different levels of control.

3.2.1.2 Permit Application

An NPDES permit is an official document which specifies the legal conditions for discharging wastewater. It is obtained by filing a permit application with the proper authority (see below), using special forms. The usual application contains a facility description, the volumes and characteristics of all point source wastewaters, and the type of treatment being applied (or planned to be applied) to the wastewater. An application must be filed at least 180 days before the first discharge occurs, or 180 days before the expiration of an existing permit. It is essential to make the application as complete and accurate as possible. The wastewater flow and contaminant levels need to be accurately described, since these are often used as the basis for the permit limits.

3.2.1.3 Legal Status of Permits

Obtaining a permit usually requires knowledge of correct procedures as applied to each location (many states and municipalities have requirements which differ considerably from federal requirements); obtaining expert help, either within the company or from outside consultants, is recommended. Severe civil and criminal penalties can be assessed for violating the Clean Water Act, even if the violation was not intentional. If the proposed permit contains provisions which cannot be met by the facility (for instance, if effluent standards are stricter than can be achieved by the facility treatment system), then the permit should not be accepted; once the permit *is* accepted, all violations become subject to the penalties noted.

3.2.1.4 Permitting Authority

The authority to issue NPDES permits is ultimately controlled by the EPA. However, the EPA can, and has in most cases, given this permitting authority to the individual states. In states not so authorized, both EPA and state discharge permits may be required. States can also delegate permit writing for federal or state permits to local agencies. At each level (state and local) downwards, *more stringent* limits can be applied; on the other hand, more lenient low-level standards do *not* override stricter upper level standards.

3.2.1.5 EPA Guidelines

EPA has established detailed national permitting guidelines for various industrial categories such as petroleum refineries and chemical plants. At this time, no such national guidelines are available for petroleum products terminals, probably because of the relatively small impact such facilities have on the environment. Because of this lack of national guidelines, NPDES permit limits for terminals are set by EPA regional offices, or by states, localities, or other local agencies. This leads to considerable variety in the types and stringency of permits issued across the country. Another source of variation is the change of permit requirements with time: older permits are usually less complex and less stringent. The following provides a general indication of the types of permit requirements which can be expected.

3.2.1.6 Effluent Contaminant Parameters

Effluent limitations (concentrations, mass emissions, and other) imposed under NPDES permit programs can include, but are not limited to, any of the following parameters (see 4.11.3 for a more complete discussion of the parameters):

Conventional parameters are those contaminants which are typically found in sewage or stormwater runoff. These parameters have an adverse effect on the receiving water, but also are indicators of the quality of wastewater treatment which produced the effluent. EPA defines the list of conventional parameters, which currently includes BOD_5, oil & grease, TSS, and pH.

Priority pollutants are those identified by EPA as being worthy of special attention due to a combination of their toxicity and their likelihood of being found in industrial and municipal effluents. Most priority pollutants would not be expected to be found in petroleum products terminal wastewater. Some which are found include benzene, toluene, ethylbenzene, and some of the heavy metals such as copper and zinc.

Nonconventional parameters are regulated parameters commonly found in some commercial or industrial discharges, but not included in the conventional or priority pollutant categories. Nonconventional parameters include COD, ammonia, and phenolic compounds, and several other parameters.

Toxicity limits are based on bioassay tests on the effluent, rather than chemical analyses. In a bioassay, living aquatic organisms of various types are exposed to the effluent at various dilutions for set time periods, and the responses such as lethality (death), growth (weight increase), and reproduction (number of descendants) are measured. Generally, the limits for acute toxicity (typically measuring short-term lethal effects) are expressed in terms of the concentration or dilution of the effluent (in terms of percent) which is lethal to half of the test organisms. This is called the median lethal concentration (LC_{50}). Chronic toxicity (typically measuring longer term lethal or sublethal effects such as growth) is typically expressed as the maximum effluent concentration which is seen to have no effect on the organisms, the no observed effect concentration (NOEC). Toxicity limits are becoming favored by regulatory authorities since they provide a broad-based indication of the adverse effects, or lack thereof, of the effluent on the receiving water.

3.2.2 BASES FOR PERMITS

There are a variety of bases which Federal, state, and local agencies use to set permit limits, or to establish the guidelines which are used to set permit limits. These include technology bases, receiving water quality bases, and bases other than these.

3.2.2.1 Technology Basis for Permits

The technology basis provides limits which are supposed to reflect the capabilities of treatment technologies. Examples include the oil and grease levels to be expected from oil/water separators, suspended solids levels to be expected from clarifiers, and BOD levels to be expected from biological treatment systems. Clearly, such limits must make assumptions as to the quality of the water fed to the treatment: the oil separability, the solids settleability, and the biodegradability of the biofeed water components. Permittees are not required to use the technologies assumed in the development of standards, so long as the technology used provides equally good treatment.

Technology-based limits must consider the cost and economic achievability of the treatment. The degree to which the permit writer must consider the costs varies according to the contaminant and the situation (e.g., whether the facility is existing or new), and is beyond the scope of this document. However, under current laws, cost *must* be considered to some degree. Often, EPA considers the cost on the basis of the dollars per pound of contaminant removed, and relates this cost to costs of existing treatment already being practiced within the same or other industries. Appropriate cost levels for some petroleum product terminal wastewater treatments have not yet been established; hence, the reasonableness of costs for such treatments may be subject to negotiation.

3.2.2.2 Receiving Water Quality Basis for Permits

The supposed overall goal of wastewater regulations is the restoration of the receiving water to certain quality standards. One such standard is "fishable", meaning that aquatic life of various types is protected; another standard is "swimmable", meaning that human health will not be endangered by exposure to the water. The problem faced by regulators is setting effluent quality standards for all dischargers to a receiving water which will enable the receiving water to meet its quality standards. A general approach is the setting of allocations for various parameters to each discharger, such that when each discharger meets its allocation, the total contaminant load on the receiving water will, when the receiving water flow and assimilative capacity (ability to remove contaminants by natural processes in the water) are taken into account, result in the water meeting the standards. Clearly, except for small streams with few dischargers, this can be a complex task. In order to simplify the task, many regulatory bodies will establish general effluent standards which, when met, will approximately result in the desired receiving water quality. In many areas, receiving waters (streams, rivers, lakes, estuaries, bays) are assigned to various classes, with each class having its own set of quality standards.

In setting standards based on receiving water quality, regulators do not consider the cost of the treatments required to achieve the standards (unlike the technology-based limits discussed above). This fact leads to the possibility of standards being set which cannot be economically met by dischargers, and makes it critical that the standards be set on the basis of sound scientific principles.

A special type of receiving water quality standards are toxicity standards. These standards are generally divided into *acute* and *chronic* toxicity standards. Acute standards are short-term (generally 48 or 96 hours) lethality standards, typically expressed as LC_{50}. The function of these standards is avoidance of adverse effects in the immediate vicinity of the effluent discharge. To determine the allowed dilution for the effluent standard, the concentration of the effluent in the mixing zone is calculated based on the effluent flow, the stream flow, the size of the mixing zone, and the degree of mixing. In some cases, there is no mixing zone, if, for example, the effluent discharge is the sole source of water in the stream. Chronic standards are long-term standards, intended to provide full protection to aquatic life after the effluent is completely mixed with the receiving water. The effects can thus be calculated by dividing the effluent flow by the receiving water flow, and comparing this with the bioassay dilution which shows no adverse effects of the effluent.

One type of biological standard which is being considered is the bioconcentration standard, which is based on the fact that certain materials accumulate in living organisms over the life of the organism, and also are passed up the food chain as the organisms are eaten by other organisms. These standards are generally stricter than the normal bioassay standards, since levels of contaminants which do not show any effects in a bioassay test can result in significant accumulation for relatively long-lived organisms, and can, via the food chain, affect organisms not used in the bioassay tests (an example is pesticides which accumulate in fish bodies, and affect the birds which eat the fish). It should be noted that not all contaminants are subject to bioconcentration, since this requires that (1) the contaminant be ingested by the organism, (2) the contaminant must be stored, and accumulate, in the organism's tissues, (3) the stored contaminant must not be significantly metabolized, and (4) the organism must be eaten by another organism which itself will store and not metabolize the contaminant.

Yet another type of biological standard receiving regulatory attention is bioassays of *sediment*, which refers to material from an effluent which is deposited on the receiving water bottom as insoluble particles. Clearly, such materials must be either insoluble in the effluent, or precipitated from the effluent in the receiving water. The reason such materials are separately regulated from water-soluble toxins is that high levels can build up on the receiving water bottom over time, and potentially result in adverse effects on the organisms (*benthic* organisms) which live in the sediment, and on aquatic animals which feed on these. Contaminated sediments regulation presents complex issues, such as the likelihood of material depositing from the effluent (which is affected strongly by the receiving water velocity and turbulence), the possibility of a given sediment being contaminated because of upstream dischargers, and the long-term nature (sediments accumulate over decades) of the problem.

3.2.2.3 Bases for Permits Other Than Receiving Water Quality or Technology

Although EPA can generally trace its effluent standards back to statutory requirements that they be based on treatment technology or protection of receiving water, other regulatory bodies may not be required to meet such requirements. In many cases, as a result, standards appear to be issued arbitrarily, with no sound basis. Some limits, for example, are set equivalent to the analytical limit of detection for the contaminant; besides being without scientific foundation, these are usually moving targets, since analytical techniques are being constantly improved. In other cases, limits are set equal to drinking water quality, even though the water in question (e.g., brackish or saline water) may never be used for drinking water. Sometimes, limits are set which ignore the assimilative capacity of the receiving water. Ammonia, for example, is toxic to fish at elevated concentrations, but is also readily removed from water by being taken up as a nutrient by algae and other aquatic plants. Likewise, almost all organic materials are subject, however slowly, to biodegradation by the multitude of bacteria and other micro-organisms which are found in the natural environment (the only surviving ancient organic materials are those which come from environments which are too anaerobic [e.g., coal and oil] or too dry to sustain biological activity). A related issue is *bioavailability*, meaning the extent to which the contaminant is able to exert adverse effects. Heavy metals are quite toxic *as the free ions*; but in fact, most aquatic heavy metals are in a chemical form (precipitated or chelated) which renders them much less harmful to aquatic life. In fairness to the regulatory community, it should be pointed out that determination of the effects of effluents is a highly complex issue, and requires a great deal of scientific information which is not currently available. Under these circumstances, development of discharge standards will necessarily involve some degree of arbitrariness. It is not improper, however, to examine proposed permit limits for their bases and to discuss these with regulatory personnel.

3.2.2.4 Mass Emission Limits vs. Concentration Limits

Outside of the mixing zone (water volume in which effluent mixes with receiving water), the only emission standards which make sense for protecting the environment are mass emission limits (e.g., pounds/day), since it is the quantity of a contaminant, not its emitted concentration, which exerts effects on the downstream receiving water. Despite this, many non-EPA limits are concentration limits, not mass emission limits. One reason for this is simplicity, since it is easy to set single concentration limits for all dischargers, but more difficult to determine the proper mass limits, which depend on the size of the facility, and the flow and assimilative capacity of the specific receiving water. In addition, it is easier to determine compliance with concentration limits by collecting a sample and analyzing it. To determine compliance with mass emission limits, the effluent flow must also be taken into account.

The greatest disadvantage of concentration limits is that they strongly inhibit flow reduction as an ingredient of pollution prevention. As discussed below (5.4.4), flow reduction is generally to be encouraged as a means for achieving more cost-effective treatment (since equipment is smaller) and achieving more thorough treatment (since it is generally easier to remove concentrated contaminants than dilute contaminants). However, when flow is reduced, concentrations generally increase (although not necessarily proportionally), and thus flow reduction jeopardizes compliance with concentration limits. If a facility is considering flow reduction, and has concentration limits in its permit, it should carefully consider the effects of the flow reduction on permit compliance.

3.2.3 PERMIT APPLICATION AND NEGOTIATION PROCEDURES

Obtaining an NPDES permit is a multi-step process, initiated by the original application, followed by issuance by the regulatory authority of a draft permit, then by negotiation of the permit provisions, and finally by acceptance of the revised permit by the discharger and the regulatory authority. The process is generally quite lengthy, and more than a year can be required for obtaining the final permit.

Factors to consider in making the permit application include:

- Current operations should be accurately described. It is particularly important to accurately characterize the facility wastewater with regard to concentrations and mass emissions of those contaminants listed on the application form, even though this may be difficult for a terminal with infrequent discharges of diverse wastes (see 8.3). *The temptation to report lower than realistic levels of contaminants should be resisted, since these reported levels are often used as one basis for setting standards* ("if you can do that well now, you can do that well forever").

- In general, the permitting process is so onerous and time-consuming that it is very desirable to minimize the chances that the permit will have to be renegotiated before it expires. For this reason, anticipated changes in facility operations over the duration of the permit should be described, and the impact of these changes on wastewater quality should be estimated as accurately as possible. As an example, the facility may be planning to begin handling oxygenated fuel components, which would be expected to increase the amount of soluble organic matter in the wastewater, and which may justify obtaining higher limits for such material. In general, any change such as the above or an expansion which will lead to increased emissions is better covered in the original permitting than in renegotiation.

- Most permit applications require specification of the treatment technology. To avoid being locked in to what may turn out to be inappropriate treatment, it may be desirable to specify a range of possible treatments, and to state that the type and degree of treatment needed to meet the final permit requirements will be utilized. As described at length in latter sections of this report, the type of water handling and treatment which is appropriate for each facility varies widely from terminal to terminal, and is best determined by careful examination of the situation at each facility, not by regulatory fiat. *Unless required by statute, imposition of the type of water handling and treatment in the permit should be strongly resisted. Allowing such specification may result in inadequate treatment, in treatment which is not cost-effective, and in a water handling and treatment system which cannot be adjusted to meet changing conditions.*

As noted above, expert assistance, including experienced environmental legal assistance, should be obtained in the permit negotiation process from technology and regulatory specialists in that area. Some factors and procedures to consider in the negotiation process include:

- If not stated in the draft permit, the statutory basis for all permit conditions should be requested, and the statutes and regulations should be examined for agreement with the permit conditions. Most draft permits, including those which limit toxic parameters, are required by law (see 40 CFR §124.8 and §124.56) to include a fact sheet which explains the basis for each limit. Specific justification on the fact sheet for each permit condition should be requested if it is not already present.

- Any specialized terms in the permit should be defined; if they are not, definition should be requested. Any limitations based on chemical or biological analysis should have the exact method of analysis specified by reference.

- Sampling and reporting requirements should be examined for agreement with terminal operations. For a facility which discharges its wastewater sporadically, frequent sampling will not be meaningful or cost-effective. Reporting schedules need to allow sufficient time for results to be obtained from (frequently overloaded) analytical laboratories.

- Although not a sure method, it may help to provide technical evidence on the unsoundness of certain proposed limitations. It is inappropriate, for example, to set permit limits which require the treated effluent to have lower levels of certain constituents than would be found by the receiving water in its natural state. Examples would include salinity or conductivity limitations on discharge to saline water, or turbidity limitations on discharges to muddy streams. (Note that this argument does *not* apply to manmade pollution, since regulators can legitimately achieve restoration of water quality by requiring discharges to be better than the receiving water).

  Likewise, permit writers should be asked to justify the environmental benefits of discharge standards, particularly those which appear to be extremely restrictive. As supporting data for this type of approach, the published toxicity and water quality criteria data for the contaminants in question should be collected and compared with the discharge standards.

- Some draft permits contain concentration regulations at the limit of detection of the specified analytical method. As those who are familiar with analyses know, it is quite common to receive false positive results (i.e., the contaminant is shown as being present when it is actually absent) at the detection limits. For this reason, limits should not be specified as being below the *quantitation limit*, which is a statistically validated value which can be accepted with confidence.

- To ensure fairness, copies of recent discharge permits from similar facilities in the region should be obtained (as public records) and examined. If it appears that there has been unequal treatment for similar circumstances, this should be protested.

- Regulatory personnel are commonly overworked (as indicated by the length of time required to obtain a permit), and permitting may thus be expedited by making their job easier. Some steps in this direction include:
  - Establish and maintain a good working relationship with the regulatory personnel handling the permit application.
  - Explain facility operations clearly, since some regulators, particularly those newly hired, are not familiar with these.

- Whenever draft permit provisions are questioned, provide as much technical information as possible to justify the change.
- Provide useful information to support any proposed changes. For example, calculate appropriate mass emissions when these are sought in place of concentration limits.
- When replying to a draft permit, supply a redlined or marked-up copy of their document instead of just a summary of proposed changes. This is easier for the permit writers to deal with.

3.2.4 DISCHARGES TO PUBLICLY OWNED TREATMENT WORKS

Publicly owned treatment works (POTWs) is the regulatory term for municipal wastewater treatment plants, used mostly for treatment of domestic sanitary wastes, but also used for treating commercial and industrial wastewaters within the territory served by the POTW. Many petroleum products terminals discharge to POTWs, whose pretreatment regulations are generally less stringent than NPDES limits for discharge to public waters since the POTW's treatment plant takes over the main function of removing contaminants from the discharger's wastewater. POTWs generally have pretreatment standards for non-domestic wastes, based on regulations imposed by EPA (see 40 CFR §403) and state standards, and on locally-developed standards. POTWs are widely divergent in the nature and degree of their limitations, but commonly found restrictions include:

- Bans on discharge of flammable material (to protect sewers and the treatment plant).

- Bans of discharge of settleable solids (to keep sewer lines open).

- Bans, or limitations, on discharge of storm water (to keep treatment works from being hydraulically overloaded).

- Bans of materials which "interfere with or pass through" the treatment works. "Interfere with" means to chemically or physically harm the treatment system, and "pass through" means to not be removed by the treatment.

- Limits on specific materials, such as BOD_5, phenols, lead, and BTEX.

In addition to restrictions on discharges, POTWs also generally impose treatment charges of various types, including the following:

- Connection charges for making sewer hookups.

- Charges based on the amount of water discharged.

- Charges on the amount or concentration of discharged contaminants of various types, including BOD, oil & grease, phenols, and others.

Also, it may be necessary to pay for installation of a sewer line from the facility to the nearest sewer main. In some cases, major dischargers are asked to partly pay for construction of a new treatment plant.

3.2.5 DISCHARGES TO GROUND: THE SAFE DRINKING WATER ACT

Under the Safe Drinking Water Act, drywells or septic systems used to place non-sanitary (non-sewage type) waste into the ground are classified as Class V wells. Individual permits are not normally needed for such wells, but inventory information must be submitted to the regulators (see 40 CFR §144.24, §144.26, and §144.25). To legally operate Class V wells, the water disposed of must not have the potential for causing groundwater beneath the well to become unfit for drinking if the groundwater is or is likely to be used for that purpose. Further details can be found in Section 2.1 of API Recommended Practice 1633, "Handling Water Discharges from Automotive Service Facilities Located at Petroleum Marketing Operations".

3.3 Hazardous Wastes: Resource Conservation and Recovery Act of 1976 and Amendments

Were it not for benzene, most wastewaters from petroleum products terminals would not be potentially classified as hazardous wastes under the Resource Conservation and Recovery Act of 1976 (commonly known as RCRA). However, in 1990, regulations were issued (40 CFR §261.24) which made any *solid waste* containing more than 0.5 mg/L extractable benzene under conditions of the Toxicity Characteristics Leaching Procedure (TCLP) a hazardous waste. Under this procedure, *water* which contains more than 0.5 mg/L dissolved benzene is potentially a hazardous waste. Typically, tank bottoms water from gasoline tanks, and from other sources in a petroleum products terminal, will contain more than 0.5 mg/L benzene, which raises RCRA TCLP issues on its handling and disposal.

In the following discussion, the generally understood implications of RCRA regulations are presented. However, RCRA is a very complex law with severe penalties, and expert regulatory and legal advice should be obtained before taking action on hazardous waste issues. Also, it is important to note that the following discussion *only* applies to the federal EPA rules on solid and hazardous wastes. Since some states and localities have their own definitions and regulations, which may be stricter or broader than the federal rules, and which apply *in addition to* the federal rules, legal advice should be sought on those regulations as well.

3.3.1 DEFINITIONS

The following discussion uses certain specialized terms, which are summarized as follows (the references should be consulted for details):

Product recovery means that the petroleum product is being separated from the water, is removed from the process as a separate stream, and is reclaimed for its original use. The recycled material is not a solid waste as long as it fits the following regulatory definitions:

> In 40CFR §261.2 (e)(1), the regulations state, "Materials are not solid wastes when they can be shown to be recycled by being: (i) Used or reused as ingredients in n industrial process to make a

> product, provided the materials are not being reclaimed; or (ii) Used or reused as effective substitutes for commercial products; or (iii) Returned to the original process from which they are generated, without first being reclaimed. The material must be returned as a substitute for raw material feedstock, and the process must use raw materials as principal feedstocks."

Wastewater treatment system tanks are stationary devices constructed primarily of non-earthen materials which are part of a system discharging to an NPDES discharge or a POTW (40 CFR §260.10). This has been interpreted by EPA to require that the tanks be designed to be water tight, and to be self-supporting without earthen support when filled to capacity.

90-day storage tanks are tanks and containers (see 40CFR §262.34) designed and operated to prevent migration of wastes out of the tank, and capable of detecting and containing any released materials (40 CFR §264.190 - §264.199). Most tanks will meet these requirements by being double-walled, by being placed in an impermeable vault, or by being surrounded by an impermeable membrane. The CFR reference should be consulted to determine other requirements for design and operation of secondary containment tanks.

RCRA Part B TSD permits are full-blown RCRA permits for treating, storing, and disposing of (TSD) hazardous wastes (40 CFR §264). TSD permits are very difficult, expensive, and time-consuming to obtain, and difficult and expensive to operate under. Almost always, obtaining TSD permits is not an attractive option for petroleum products terminals, so equipment and procedures for handling hazardous wastes must be arranged to avoid the necessity of obtaining these permits.

RCRA generator numbers are EPA-assigned identification numbers for all generators of hazardous wastes (40 CFR §262). In addition to obtaining the number, the generator is responsible for proper on-site storage of the waste, proper manifesting and transportation of the waste off-site, and proper final disposal of the waste by the recipient.

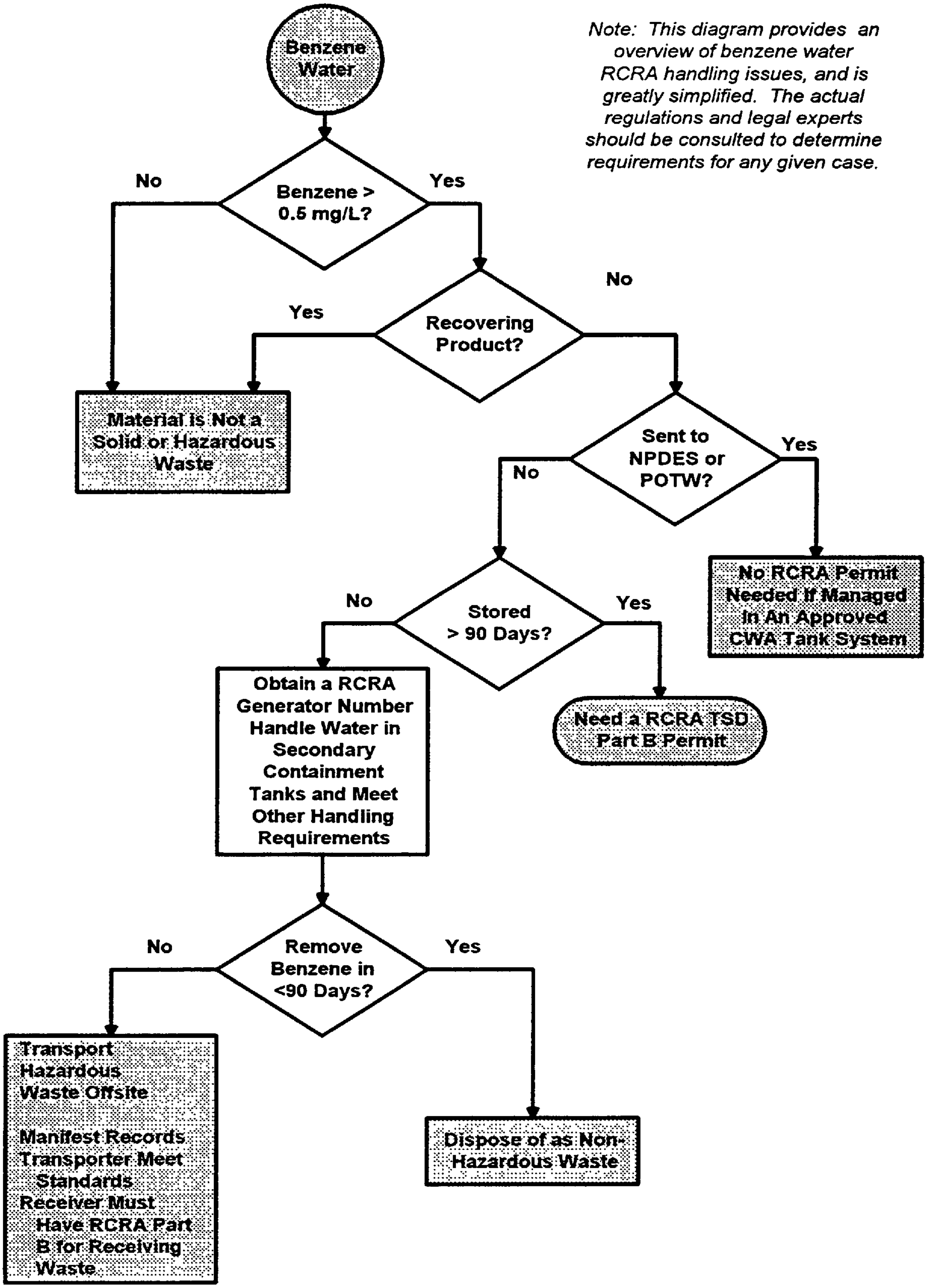
3.3.2 WASTEWATER HANDLING OPTIONS UNDER RCRA

3.3.2.1 Benzene-Contaminated Wastewater

The options for handling, treating, and disposing of benzene-contaminated water are outlined graphically in Figure 3-1. Some of the specific questions which arise in this process, and summary answers, are given below. Please note, however, that many of these determinations are case-specific. It is recommended that appropriate authorities be consulted before managing any potentially hazardous wastes.

- If the wastewater is classified as a hazardous waste, at what point in its processing is this classification applied? *Wastewater is generated as a solid, and potentially hazardous, waste only after it is discarded from a product recovery operation such as a product recovery tank or an oil/water separator. Upstream of that point (i.e., in product tankage or product recovery processing), it is not yet a regulated waste (40 CFR §261.2(e)(1)(i)-(iii)).*

FIGURE 3-1
RCRA GUIDE FOR BENZENE-CONTAINING WATER



Note: This diagram provides an overview of benzene water RCRA handling issues, and is greatly simplified. The actual regulations and legal experts should be consulted to determine requirements for any given case.

- How long can the wastewater which is potentially hazardous be stored without RCRA involvement, and what must be done if the water is stored longer than that? *Generally, once wastewater is generated, either it can be sent to a permitted NPDES discharge or POTW without a time limit on storage, or it cannot be stored or processed for more than 90 days without obtaining a RCRA TSD permit (40 CFR §262.34).*

- What types of handling and treatment allow the wastewater to be exempted from RCRA regulation? *If the wastewater is stored and handled in tanks, and sent to a permitted NPDES discharge or hard-piped to a POTW, it is not subject to RCRA regulations (40 CFR §261.4(a)(2)).*

- If the wastewater is discharged under an NPDES permit, or is sent to a POTW with an NPDES permit, are there any RCRA concerns for the internal handling of the wastewater upstream of this discharge? *Only that the water be handled in tanks and hard piped (no earthen ditches or ponds upstream of treatment) to the treatment system, outfall, or municipal sewer.*

- If the wastewater is shipped offsite as a hazardous waste, what permitting and record keeping are required for generating and transporting the material? *The facility must obtain a RCRA generator number, must keep records on the waste generation, must store the waste in tanks with secondary containment, must use an approved hazardous waste transporter, must manifest each waste shipment, and must ensure that the final destination for the waste is a RCRA TSD facility permitted to receive, store, treat, and dispose of such wastes (40 CFR 262).*

- If the water is shipped offsite as a hazardous waste, what permitting is required by the receiving facility? *The facility must have a RCRA TSD permit which specifies that wastes of the type being shipped will be received and processed (40 CFR §262.20(b)), or, less commonly, has an NPDES permit which states that RCRA hazardous wastes will be accepted.*

- If the water is shipped offsite as a hazardous waste to another company, are there any potential liabilities for the terminal (and its owner) if this disposal is done improperly? *Yes, the waste generator retains legal liability for the waste for all time. If disposal of the waste in question, or other wastes, is done improperly, then the generator could be held liable for whatever penalties are imposed on the disposal facility and its customers.*

- Under what conditions can benzene be removed from wastewater without RCRA regulation? *The need for a RCRA permit can be avoided by disposing of the treated wastewater to an NPDES discharge or to a POTW, provided any storage and treatment at the facility is done in tanks, not impoundments (40 CFR §261.4(a)(2) and 40 CFR §264.1(g)(6)). If the wastewater is transported offsite as non-*

> *hazardous waste, the hazardous constituent (benzene) can be removed without a permit so long as the storage and treatment are done within 90 days, and the material is handled in tanks with secondary containment and other technical requirements are met (40CFR §264.190 - §264.199).*

Figure 3-2 shows various wastewater handling flow schematics and their RCRA implications.

3.3.2.2 Benzene-Containing Products Mixed With Water

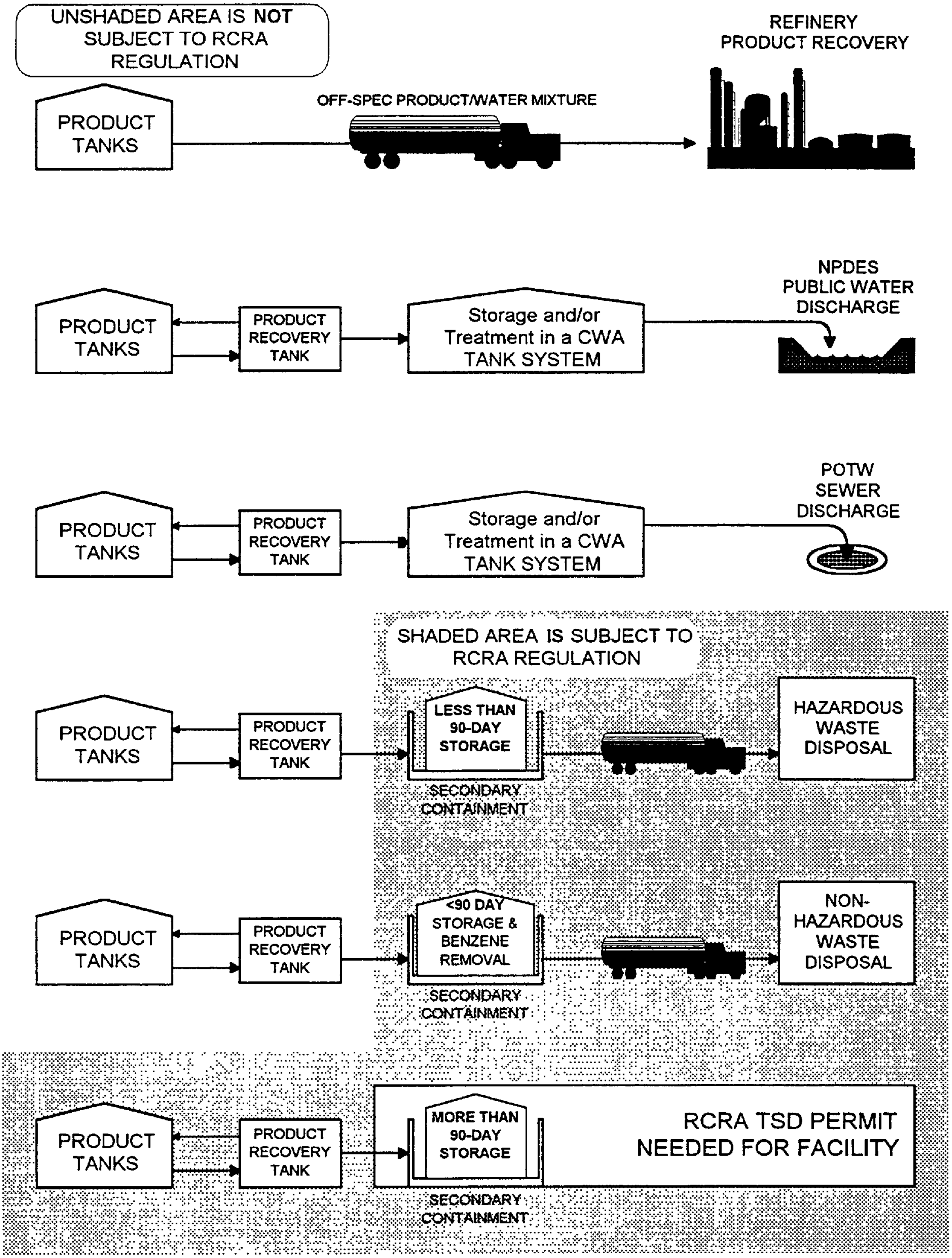
It is important to note that RCRA regulations are *environmental* regulations, and apply only to *wastes*, not to *products*. There are, clearly, a very large number of materials, manmade and natural, which would be classified as hazardous wastes if the hazardousness standards were inappropriately applied to them. RCRA, however, was designed to protect the environment from hazardous materials; materials which are not released to the environment (by disposal or discharge) are not covered. As one aspect of this, petroleum products are not subject to RCRA regulation while being manufactured, transported, or used; if disposed of or discharged (which is very rare, since all petroleum products have value), RCRA (or other environmental) regulation would apply.

The most likely point of confusion is when a mixed stream of petroleum products and water is being handled. As described in 4.9.1, water is often found in contact with petroleum products, and is transported along with them. The fact that water (an unwanted material) accompanies product does not make the mixture of the two a waste, even though the water phase will ultimately be disposed of as a waste. The RCRA regulations handle this situation by defining the point of waste generation as being *the point just beyond the step in which product is separated* (this same point is covered in 3.3.2.1, above). To re-state this point, *mixtures of product and water, even if mostly water, can be classified as product, so long as there is legitimate recycling of product from the mixture.*

In the petroleum industry, it is very common to re-process products which do not meet specifications for their use; the term for these is off-spec products. These off-spec products often contain water. Refineries commonly send mixtures of products recovered from process vessels or wastewater (slop oil) back through crude oil distillation. Pipeline terminals often take cuts of materials at the interface between different products and send it back to refineries for reprocessing. In the case of petroleum products marketing terminals, off-spec products from the service stations served by the terminal are often received back by the terminal, and mixtures of products from the terminals, sometimes mixed with water, are often sent back to a refinery for reprocessing. So long as the receiving facility (the terminal or the refinery, respectively) accepts the mixture for recovery of useful product, the mixture is not classified as a hazardous waste for purposes of generation, transportation, storage, or processing, even though benzene levels in the mixture exceed the RCRA TCLP standards.

FIGURE 3-2

TANK BOTTOMS WATER HANDLING SCENARIOS



3.3.2.3 Other Hazardous Wastewater Constituents

Although benzene is found in most petroleum products terminal wastewater since it is a normal component of gasoline, there are also other contaminants which could be present in tank bottoms water, and which would cause the water to potentially be a hazardous waste at the following concentrations:

Contaminant	Limit, mg/L	Reason for Listing
Arsenic	5.0	Found in crude oils, water-soluble
o-Cresol	200	Made in refining, water-soluble
m-Cresol	200	Made in refining, water-soluble
p-Cresol	200	Made in refining, water-soluble
Cresols	200	Made in refining, water-soluble
Lead	5.0	Used as a gasoline additive
Selenium	1.0	Found in crude oils, water-soluble

Wastewater which contains these contaminants at levels in excess of the limit will have the same hazardous waste restrictions as wastewater contaminated with benzene. However, handling may be different, in that benzene is easily removed by stripping (see 9.9), but the above contaminants cannot be so removed. The various cresols can be removed by various treatments (cresols are highly biodegradable, for instance), and lead can usually be removed by filtration, but arsenic and selenium can be quite difficult to remove (9.14).

3.3.3 NON-AQUEOUS HAZARDOUS WASTES

In addition to the issue of benzene-contaminated wastewater, there are also other hazardous wastes which might be generated in a petroleum products terminal, which will be solid wastes with the following characteristics:

- Ignitability. If the waste is ignitable (flash point less than 140 F) under the RCRA test conditions, then it will be hazardous. Some product-contaminated sludges may fall in this category.

- Reactivity. If the waste contains sufficient cyanide or sulfide to release more than the regulated amount of hydrogen cyanide or hydrogen sulfide when acidified, it will be hazardous. It is unlikely that petroleum products terminals will normally generate reactive wastes from normal operations. However, since anaerobic biological activity converts sulfate to sulfide (by sulfate-reducing bacteria), it is possible that alkaline tank bottoms water stored for long periods might accumulate enough sulfide to fail the reactivity standard.

- Corrosivity. If the pH of the waste is less than 2.0, or more than 12.5, it will be classified as corrosive. Such wastes should be rare in petroleum products terminals.

- Leachability. If more than regulated amounts of any or several chemical constituents are leached from the waste when it is subjected to specified leaching tests, it is hazardous. The regulated materials include toxic heavy metals and selected organic constituents. Possible materials which would fail this test are tank bottom sludges and wastewater treatment sludges. More than likely, these sludges will pass the test, since heavy metals are not common in petroleum products terminals, and most of the regulated organic compounds are not expected to be in terminal products or wastes. However, if wastes are derived from leaded product storage tanks, or from removal of lead-based paints (e.g., spent blasting sand), then the lead leachability test could be failed for that waste. Also, as noted above, benzene is one of the regulated materials, and may appear in solid wastes at excessive levels as well as in wastewater (the wastewater disposal exclusions do not apply to non-aqueous wastes).

Chapter 4

TERMINAL OPERATIONS

4.1 Introduction

Petroleum products terminals are collection and distribution points along the complex distribution network which connects the refineries which manufacture the products and the service stations and other destinations which serve end users. This network is shown schematically on Figure 4-1. Along this network, products are transported by various means, including pipelines, tanker ships, barges, rail cars, and tank trucks. The terminals are distinguished from other parts of the network by having tank capacity to store products, and by having equipment for connecting the tanks to the transportation system. Similar distribution networks exist for crude petroleum, and for petrochemical products; this report, however, is restricted to petroleum products distribution, and to the petroleum products portion of the (not uncommon) combined operations.

Unlike those parts of the petroleum industry further upstream such as producing and refining operations, the distribution network is characterized by *batch*, not *continuous*, transfers. Batches of products are collected from refineries, sent as discrete batches through the transportation system, and finally sold as batches to the end users. Much of the work in the distribution network is spent on accounting for the location, quantity, and quality of the product batches.

4.2 Petroleum Products Distribution Network

Although not part of this report, the other elements in the petroleum products distribution network are intimately connected to the terminal facilities, and so are described briefly below.

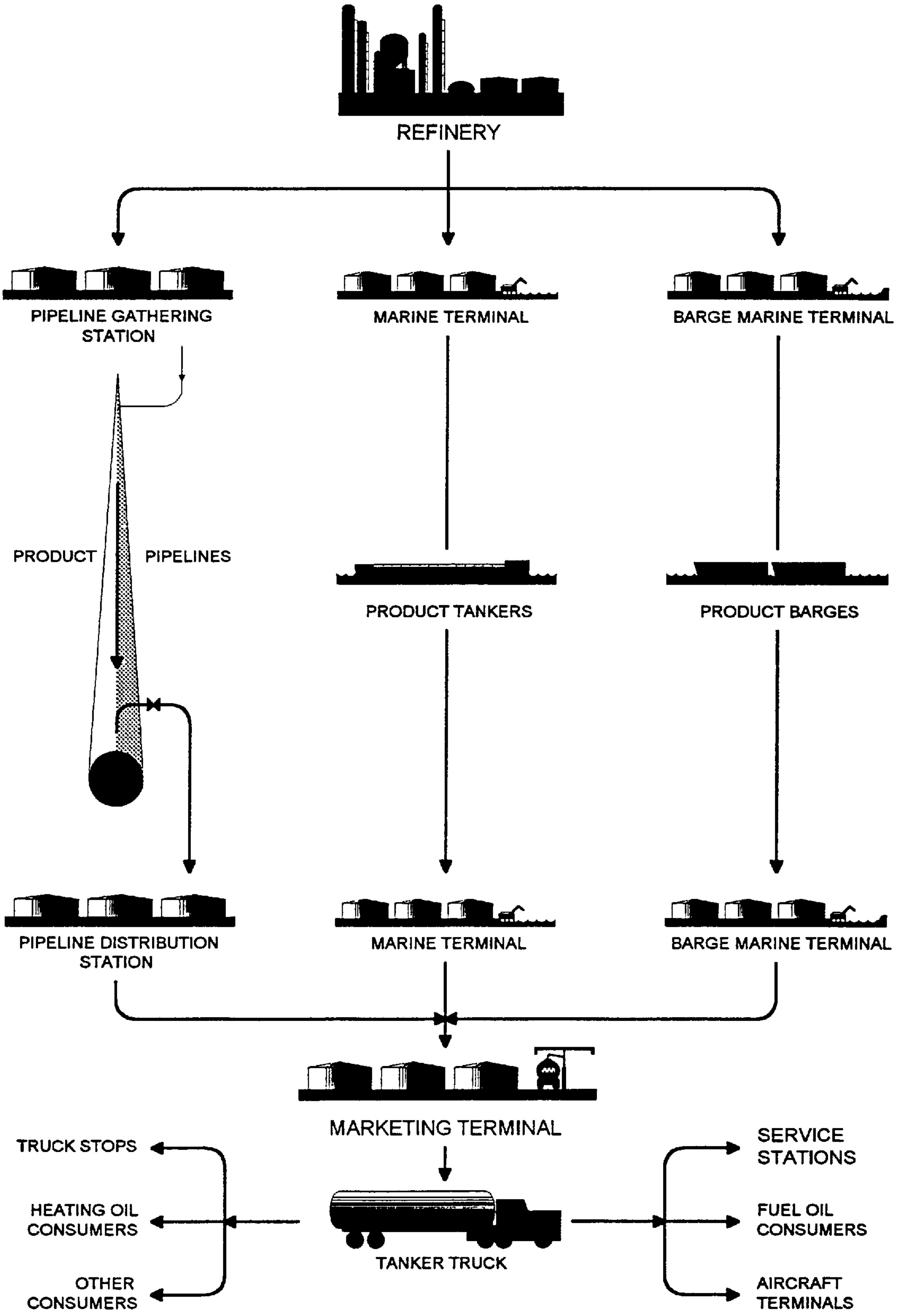
4.2.1 POINTS OF ORIGIN

All petroleum products are manufactured in petroleum refineries. Most of the refineries which supply the U.S. market are domestic, although the amount of overseas refining for U.S. markets is increasing as crude supplies shift overseas and U.S. environmental regulations on refineries become stricter. Overseas refineries deliver their products by tanker ship to marine terminals, described below. Domestic refineries connect to the transportation network in various ways. In some, direct loading of tanker ships and barges is done. In others, the products are sent into the pipeline system through originating pipeline stations, described below. Many refineries operate (or are directly linked to) a marketing terminal which serves the retail area in the vicinity of the refinery; except for small refineries, this is a minor destination for the plant's products.

FIGURE 4-1

PETROLEUM PRODUCTS DISTRIBUTION NETWORK

Distribution shown is typical. Many combinations and variations exist.



4.2.2 TRANSPORTATION

4.2.2.1 Pipelines

Pipelines of various sizes and capacities provide a great nationwide arterial system for products distribution, and handle far more volume of products than any other means of transportation. At the heart of the pipeline system are the high-volume transcontinental pipelines, which pump products over long distances at high pressure through large diameter pipes. In addition, many other smaller pipelines are used to feed into or out of the transcontinental lines, and to connect other parts of the distribution network. Pipeline operations comprise the lines themselves, pumping operations to move products into the pipeline and to boost pressure along the line, and valving systems for splitting products out of the pipeline at various points.

Products move through pipelines as discrete batches. By various means (including gauging of supply and receiving tanks, flow metering, and quality checks), the identity of the material moving through the line at a given point is precisely determined to ensure the integrity of the batch (i.e., to avoid *commingling* of the various product batches sent through the same line).

4.2.2.2 Water Transport

Tanker ships are self-powered vessels used for marine (including Great Lakes) transport to coastal locations, and to those inland river ports which serve deep-draft vessels. Barges are towed shallow-draft vessels used mostly for inland water transport on rivers, canals, and lakes. In both, the vessels are divided into sealed compartments for carrying various products. When empty, vessels ride high, and are subject to pitching and rolling; for this reason, empty vessels are commonly filled with ballast water, taken on near the point of vessel product delivery (often from the water body at the vessel location) and discharged near the point of the vessel loading (often at the facility supplying the products). Unless the vessel has dedicated compartments for ballast water, the ballasting operation may make ballast water contaminated with the products previously in the compartment.

4.2.2.3 Rail Transport

Although used extensively for relatively low-volume products such as chemicals and lubricants, rail cars are not a major part of the petroleum products distribution network. Rail transport is done in tanker cars of about 20,000 to 40,000 gallons capacity.

4.2.2.4 Tank Trucks

Tank trucks, in sizes ranging from 5000 to 12,000 gallons, though little used for long-distance transport, are essentially the only means employed for the final leg of the products journey to the retail (service station and truck stop) outlets and other final points. Bulkheads within the tank trailer enable transport of several different products together.

4.2.3 FINAL PRODUCT DESTINATIONS

The final destinations are the points at which the users of the petroleum products receive the products. Since the products are mostly used as transportation fuels, the largest-volume users are vehicles.

4.2.3.1 Service Stations and Truck Stops

Service stations supply cars and trucks with various grades of gasoline and with diesel fuel. Products are normally received by tanker truck from marketing terminals, and stored in underground or aboveground tanks which supply the fuel pumps. In some cases, off-specification products (including product/water mixtures) collect in the underground tanks, and are transported back to the marketing terminal for reprocessing. Truck stops are essentially large service stations which supply diesel fuel to commercial trucks, mostly tractor-trailers.

4.2.3.2 Other Fuel Users

Gasoline and diesel fuel are also supplied in bulk to industrial and commercial operations of various types. Railroads are supplied with diesel fuel, agricultural operations with gasoline and diesel fuel for farm machinery engines, and truck and car fleets of various types are supplied with gasoline and diesel fuel. Home heating oil trucked to homes and other facilities by local distributors. Heavy oil fuels are supplied to power plants, asphalt plants, and to ships.

4.3 Petroleum Products Terminals Functions

As noted above, there are various types of terminals along the distribution network which serve the basic functions of collecting, storing, and distributing products. These can be characterized by their functions, as described below.

4.3.1 PIPELINE ORIGINATING STATIONS

Pipeline originating stations serve as collection points for one or several refineries, or for other products suppliers. They collect products (often through gathering pipelines) over time in tanks at relatively slow rate, and send them at high rate into the main pipeline system. Batch delivery volumes are large compared to those in marketing terminals. Operations include control room coordinating of valve switching and tank transfers, field operation and inspection of equipment, maintenance of equipment, product batch accounting, and management of these functions.

4.3.2 PIPELINE DISTRIBUTION STATIONS

Pipeline distribution or breakout stations are the inverse of the originating stations: products are taken at high rate from the main pipelines into tanks, and sent out at relatively slow rates to downstream points. Operations are similar to those of originating stations.

4.3.3 MARKETING TERMINALS

Marketing terminals, which are the majority of petroleum products terminals, receive bulk transportation fuels by various means, including pipelines and water transport, and distribute them to retail outlets (service stations and truck stops) by tanker truck. In addition to tank operations, truck loading rack operations are the main functions of these terminals. Many marketing terminals coordinate retail operations for the area served by their products. Marketing terminals may also supply home heating oil (similar to diesel) by tank truck to users, either as a sole product or in conjunction with transportation fuels, and may distribute aircraft fuel to airports or airbases by tanker truck.

4.3.4 AIRPORT TERMINALS

Airport terminals are service stations for aircraft. Generally located at major airports, they provide bulk storage for aviation gasoline and jet fuel, and distribute these to the aircraft in fueler trucks or through a pipeline and hydrant system.

4.3.5 MARINE TERMINALS

Marine terminals receive products in large-volume batches from tanker ships at high rate into tankage, and send them out at lower rates to downstream points. The terminals may also supply fuels (diesel and bunker fuels) for vessels.

4.4 Products Terminal Distribution Facilities

Two of the main functions of terminals are receipt of products and delivery of products. The equipment for these two functions are similar. Products are received from and delivered to pipelines, ships, barges, rail tank cars, and tank trucks.

4.4.1 PIPELINE TRANSFERS

Terminals are generally at the end of pipelines, and so take products directly out of, and place products directly into, the pipeline via pipe networks equipped with valves and pumps. Terminals that employ spur pipelines obtain products by taking cuts out of the product batches passing by in the main trunk line.

4.4.2 SHIP AND BARGE TRANSFERS

Products are transferred into tanker ship and barge compartments with high-volume pumps and hoses, which are connected to the vessel's fill nozzles. Ships generally have their own pumps for transferring products through hoses to shore.

4.4.3 TANK TRUCK TRANSFERS

Tank truck transfers are done in systems called *racks*. Since the majority of truck transfers are those into trucks, the general term is *loading racks*. Loading racks are similar in layout to service station fuel bays, with pump islands between the truck bays, and overhead canopies for rain protection. They are equipped with filling hoses or pipes which are connected directly to the truck tank. Two methods of loading are used: top loading or bottom loading, depending on the location of the truck tank fill nozzle. Products are metered into the tanks, and vapors displaced by the products are generally taken from the tanks into vapor treatment or vapor balancing systems (see 4.9.7). Loading racks normally have concrete floors, which are sloped to drain into a spill containment system to ensure that accidental spills will not run off onto the surrounding ground.

4.4.4 RAIL TANK CAR TRANSFERS

Rail tank car transfers are somewhat similar to truck transfers. Rail cars are generally top loaded. Compared to pipeline product deliveries, rail car products generally do not contain significant amounts of entrained water.

4.5 Storage Facilities

4.5.1 VERTICAL TANKS

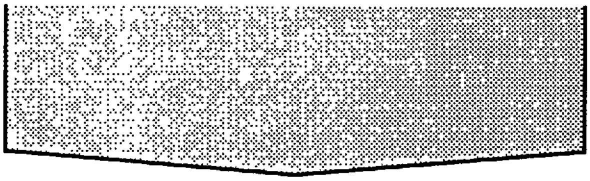
The standard storage vessel for bulk petroleum products (in volumes from 1000 to several hundred thousand barrels) in terminals is the vertical cylindrical tank. These tanks are essentially cylinders (*shells*) made of joined curved steel plates, with steel bottoms and various styles of roofs. The joints in modern tanks are welded, but older riveted tanks are still in service. The tank shells are supported on foundations, usually concrete rings, but other types of support such as piers are also used.

4.5.1.1 Tank Bottoms

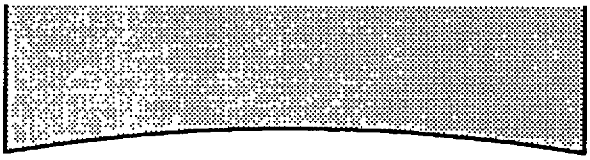
The bottoms of tanks are made of joined steel plates, and have three shapes, as shown on Figure 4-2. Cone-bottom tanks have the low point in the center, crowned tanks are high in the center, and low around the perimeter, and flat-bottom tanks have nominally straight and level bottoms.

FIGURE 4-2

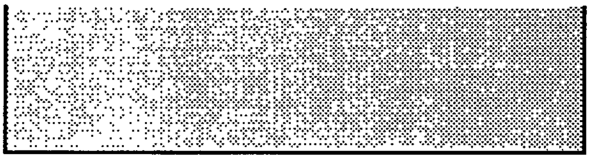
TANK BOTTOM CONSTRUCTION



CONE BOTTOM



CROWN BOTTOM



FLAT BOTTOM

4.5.1.2 Tank Roofs

All petroleum products tanks for transportation fuels in terminals have roofs, which serve to prevent product losses, preserve product purity, reduce fire hazards, and control air pollution. In addition, the roofs greatly reduce the amount of rainwater which would otherwise enter the tank, jeopardize product quality, and have to be drained as contaminated water.

4.5.1.3 Fixed Roofs

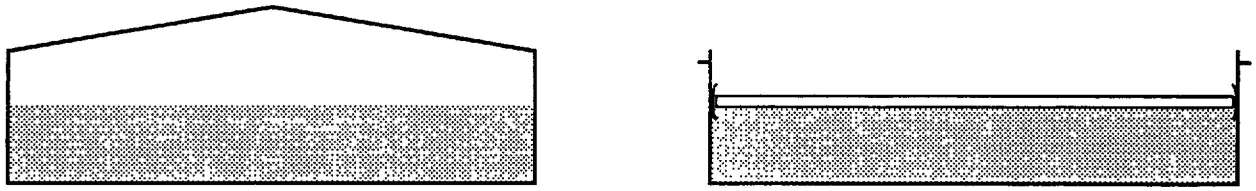
The main distinction between tank roofs is between fixed roofs (also called *cone roofs*) and floating roofs. Fixed roofs (Figure 4-3a), as the name implies, are steel covers permanently attached to the top of the tank shell. These types of roofs convert the tank into a closed vessel, with the following consequences:

- Entry of rain water will not occur except through leaks
- When product is withdrawn from the tank, air must be allowed in to prevent creating a vacuum in the vapor space, and collapsing the tank

- When product is placed in the tank, air must be released to prevent developing pressure in the tank, and rupturing it.

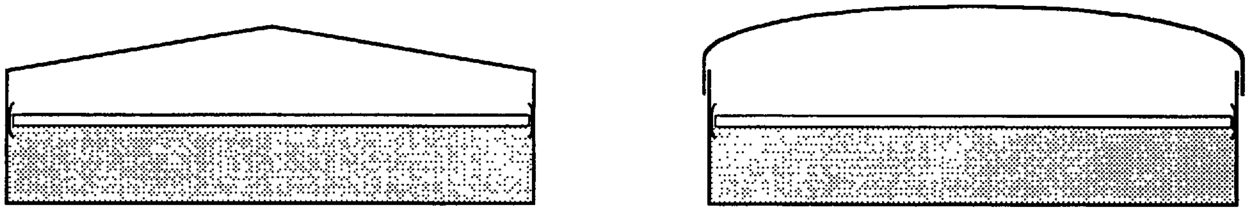
FIGURE 4-3

TANK ROOFS



(A) FIXED OR CONE ROOF

(B) OPEN-TOP FLOATING ROOF



(C) COVERED FLOATER

(D) GEODESIC DOME

4.5.1.4 Floating Roofs

Floating tank roofs (Figure 4-3b) come in several styles, but typically are disks, several inches smaller in diameter than the inner tank shell diameter, made of steel or aluminum plates. The connection between the roof and the tank shell is made with *floating roof seals*, which are described below. The flotation is accomplished in various ways, but typically is achieved with pontoons, which are closed air-filled chambers attached to the bottom of the roof, or by double-deck roofs, which are essentially hollow roofs filled with air. Tanks fitted only with floating roofs are commonly called *open-top floaters*. Floating roofs ride up and down with the product level, with the following consequences:

- Rain water can enter the tank by hitting the inner tank shell, running down to the seal, and partially penetrating the seal to enter the tank.
- Most of the rain entering the tank shell will be collected on the floating roof. This rainwater is drained through a tank drain, as described below.
- Product withdrawal and placement are accommodated by the movements of the floating roof, so there is no need for venting air in or out of the tank, and no need for treating vent air.

4.5.1.5 Dual Roofs

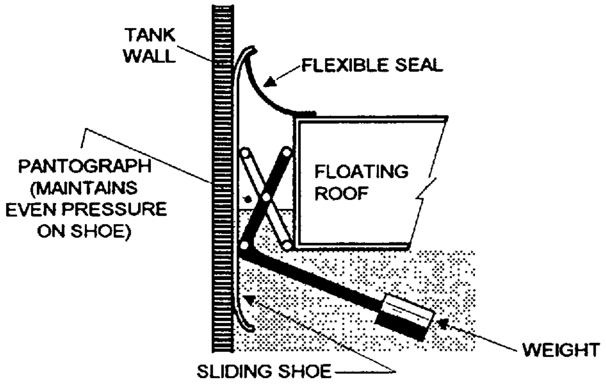
In some tanks, both types of roof are used together, as shown in Figure 4-3c. Some tanks originally fitted with floating roofs have fixed roofs added later, which are called *covered floaters*. Some tanks originally built with fixed roofs have floating roofs added later. Both these, and tanks originally built with two roofs, are called *internal floaters*. Although obviously more expensive, the dual-roof tanks have the mutual advantages of their roofs:

- Rain water is kept out of the tank.
- The need for further controlling air emissions is eliminated (the fixed roof is vented to atmosphere without controls).

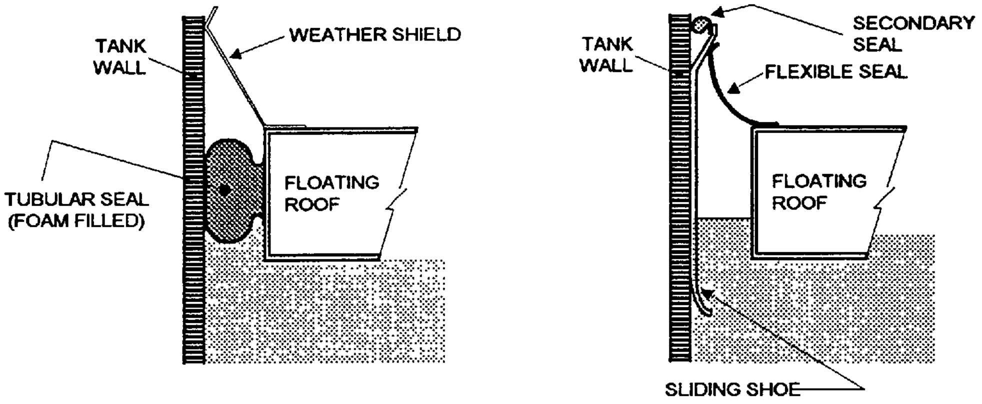
A relatively new type of tank roof is the geodesic dome (Figure 4-3d), a lightweight metal roof which is usually placed over tanks equipped with open floating roofs. In addition to their method of construction being different from cone roofs, these roofs are generally not tightly sealed to the tank shell. Advantages for such roofs are similar to those of the covered floaters.

FIGURE 4-4

FLOATING ROOF SEALS



(A) SLIDING SHOE WITH PANTOGRAPH HANGAR



(B) TUBULAR SEAL

(C) SECONDARY SEAL

4.5.1.6 Floating Roof Seals

The seals placed between the tank shell and the floating roof have a challenging job: to maintain a tight seal between the roof and shell, and still allow free vertical movement of the roof. As shown on Figure 4-4, this is accomplished with two basic approaches.

Figure 4-4a shows the conventional, or sliding shoe, type of seal. In this type, the sealing surface is a metal cylinder (the shoe) which is kept pressed against the tank shell by mechanical means (the pantographic device is shown). The gap between the shoe and the roof is sealed with a flexible vapor-tight fabric.

Figure 4-4b shows the tubular type of seal, in which a tube inflated by air, liquid, or elastomeric foam is attached to the roof, and maintains a seal with the shell by pressing against it. Tubular seals are generally equipped with sheet metal weather shields, to protect the tube and help keep rainwater out of the seal area.

Both of the above types of seals are known as *primary seals.* Mostly as an air emissions control measure, many tanks are also equipped with *secondary seals*, shown on Figure 4-4c. The secondary seal is located above the primary seal, and supplements its action. As noted above, floating roof seals help prevent rainwater entry into the tank, but cannot completely eliminate it, since a seal which is capable of moving can also allow some liquid passage. Maintaining seals in good condition, and using secondary seals, can help to reduce rainwater intrusion.

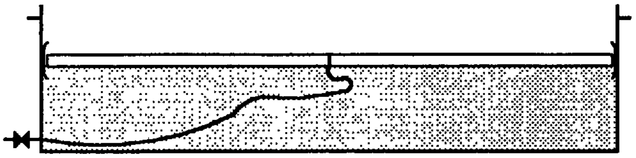
Details on floating roof seals can be found in (REA Staff), Chapter 28.

4.5.1.7 Floating Tank Roof Drains

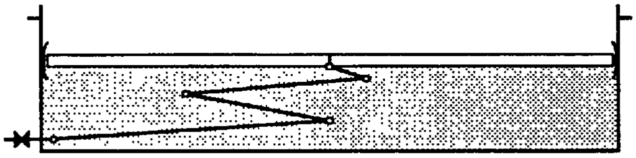
The rainwater which falls on a floating roof must be drained to prevent the roof from sinking. This can be handled by a direct drain (essentially, a hole in the roof) into the tank, but while this will not greatly harm the main functions of the roof, it will clearly eliminate the function of keeping water out of the tank. For this reason, most floating roofs are equipped with an internal drain, as shown on Figure 4-5. The internal drain is a jointed pipe, or a flexible hose, which connects the low point of the roof (usually the center) to a nozzle through the bottom of the tank. Potential problems with roof drain lines are leaks: if the top connection leaks, then water can still enter the tank; if the line itself leaks, then product could be released through the drain nozzle.

FIGURE 4-5

FLOATING ROOF DRAINS



ROOF DRAIN THROUGH HOSE



ROOF DRAIN THROUGH JOINTED PIPE

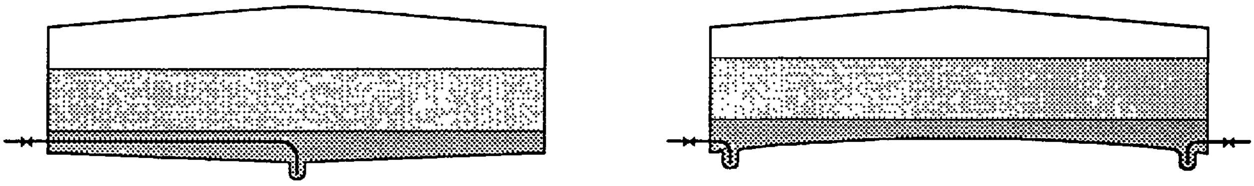
4.5.1.8 Tank Nozzles

Tank nozzles are sections of pipes welded into the side of tanks to permit delivery and withdrawal of tank materials. Product is placed into and withdrawn from the tank through the main product nozzle. Often, this nozzle is located some distance above the bottom of the tank to prevent tank bottoms water from contaminating the withdrawn product.

Water draw nozzles can be directly connected to the side of the tank, but optimum withdrawal of water can be achieved if water sumps (depressed areas in the tank bottom, shown on Figure 4-6) are used with internal turned-down water draw piping. The water draw nozzle configuration depends on the type of tank bottom employed. In cone bottom tanks, a single sump is usually placed in the center of the tank. In crowned-bottom or flat-bottom tanks, sumps are usually placed around the perimeter (typically, up to four sumps and nozzles per tank) to ensure water draw from the whole tank (tank bottoms are not perfectly level)

FIGURE 4-6

TANK WATER DRAW SUMPS

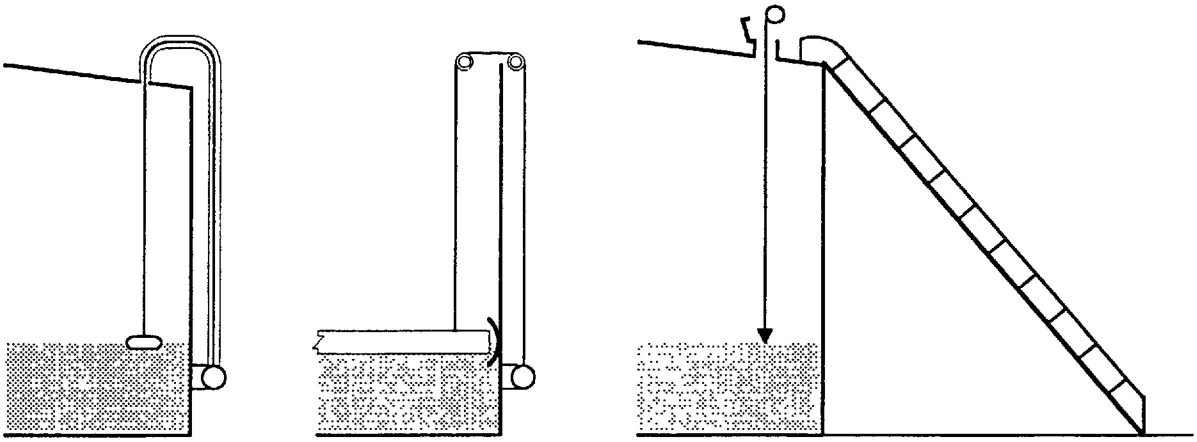


CONE BOTTOM TANK

CROWN BOTTOM TANK

FIGURE 4-7

TANK LEVEL GAUGING



AUTOMATIC

FLOATING ROOF

MANUAL TAPE GAUGE

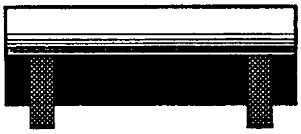
4.5.1.9 Tank Gauging

Tank gauges are devices to externally show the product elevation in the tank. Although sight gauges can be used, the normal technique (Figure 4-7) employs a cable attached to a float inside the tank (for fixed roof tanks) or to the floating roof (for tanks so equipped). The outside portion of the cable is attached to an indicator scale, or to an automatic gauge. Means for determining water levels in product tanks are described in 7.4.1.1.

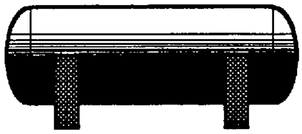
4.5.2 HORIZONTAL TANKS

Horizontal tanks, also called drums, are closed vessels: horizontal steel cylindrical shells with steel heads on the ends. As shown on Figure 4-8, the heads can be flat, elliptical, or hemispherical. In a petroleum products terminal, horizontal tanks (which cost more per unit volume than vertical tanks, and occupy more land area per unit volume) are generally used only for low-volume storage of low-throughput materials such as gasoline additives. By the nature of their use, horizontal tanks do not usually accumulate water bottoms. For those cases where water is found, a vertical section, called a *water leg*, is frequently attached to the bottom of the drum (Figure 4-8c) to facilitate water separation.

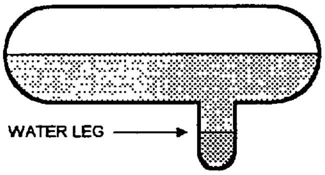
FIGURE 4-8
HORIZONTAL TANKS



(A) FLAT END



(B) ELLIPTICAL END



(C) HEMISPHERICAL END

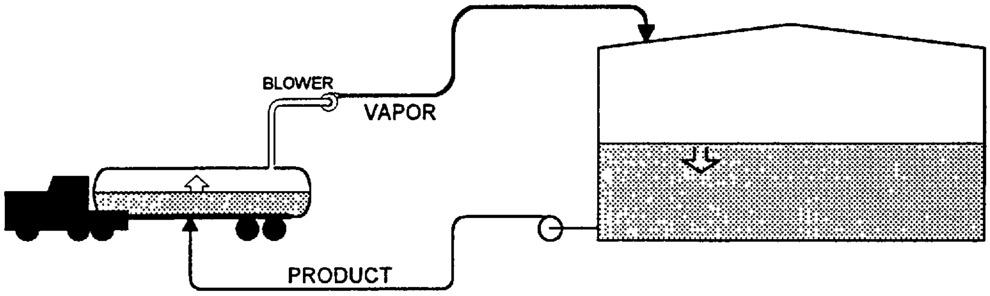
4.5.3 VAPOR CONTROL

Product storage and transfer from and to closed vessels such as ships, barges, rail tank cars, tank trucks, and fixed-roof tanks (without floating roofs) also involves air transfer to fill the void left by product removal and to allow room for product delivery. In the latter case, the displaced air is usually saturated with vapors from the product in the vessel, and so can become a source of air emissions if discharged to the atmosphere.

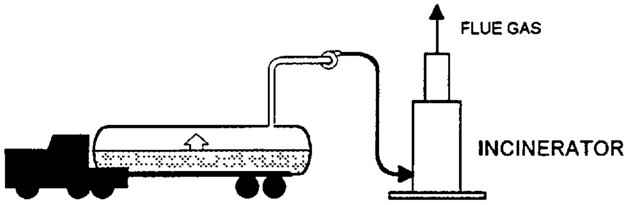
In addition, fixed-roof tanks *breathe* (move air in and out) as tank temperature changes as a result of day-to-night or weather changes: when the tank cools off, the air inside contracts, and fresh air is drawn in. When the tank warms up, the air in the tank expands, and is released as contaminated air through the tank vents or vent line.

Various means have been devised to minimize this type of emission, as described below and shown on Figure 4-9.

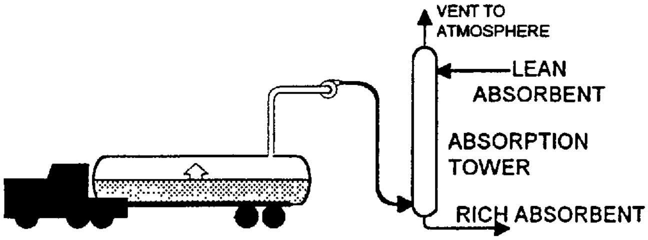
FIGURE 4-9
HYDROCARBON VAPOR CONTROL



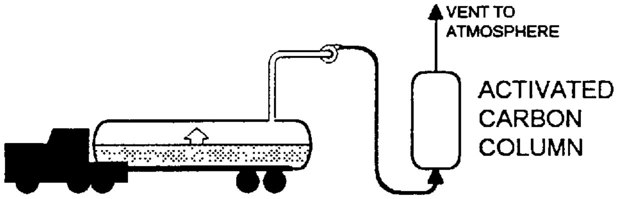
VAPOR BALANCING



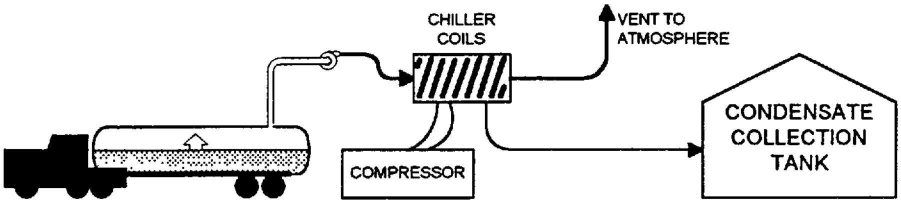
VAPOR INCINERATION



VAPOR ABSORPTION



VAPOR ADSORPTION



CRYOGENIC VAPOR RECOVERY

4.5.3.1 Vapor Balancing, Incineration, and Absorption

The following vapor emission control processes do not normally produce wastewater. Vapor balancing involves moving displaced air from the vessel being filled with product to the vessel being emptied. Vapor incineration involves routing the contaminated displaced air into a combustion device, either an ordinary burner or a catalytic combustion chamber, and burning the hydrocarbons. If the amount of hydrocarbon vapors in the contaminated air is insufficient to maintain combustion, supplemental fuel such as natural gas or propane is used. Vapor absorption is the dissolving of a vapor into a liquid stream. As a means for removing hydrocarbon vapors from contaminated air, the air can be contacted with an absorption oil which itself has a low vapor pressure (i.e., has a high boiling point) and an affinity for hydrocarbons, in a device known as a *scrubber*. The used absorption oil can be sent on to other uses (e.g., fuel), or can be regenerated, usually with heat.

4.5.3.2 Vapor Adsorption

Adsorption is the attachment of a material to the surface of a solid. In the context of hydrocarbon removal from air streams, adsorption is almost always done with activated carbon, which has a high adsorptive capacity for hydrocarbons. Once the capacity of the carbon has been used up, the carbon must be either replaced or regenerated, usually with heat. If steam is used to regenerate the carbon, and the effluent steam is condensed, then a small periodic wastewater stream contaminated with hydrocarbons will be generated.

4.5.3.3 Cryogenic Vapor Recovery

Cryogenic treatment of contaminated air involves passing the air over a chilled surface (heat exchanger) operated at a low enough temperature to condense most of the hydrocarbons. At the same time, the moisture in the air will be condensed (as in an air conditioner), and thus create a (usually) small wastewater stream contaminated with hydrocarbons.

4.6 Products Handled

4.6.1 INTRODUCTION

Although some terminals may handle products such as petrochemicals and lubricating oils, the coverage of this document is limited to petroleum products used for transportation fuels (and closely related products such as home heating oil), and those materials such as additives associated with them.

4.6.2 MANUFACTURE

Petroleum products, by definition, are materials obtained from the refining of crude oil, or petroleum. Petroleum is a very complex mixture of hydrocarbons (carbon-hydrogen compounds), which also contains sulfur compounds (such as mercaptans), nitrogen compounds (such as porphyrins), oxygen compounds (such as naphthenic acids), and organo-metallic compounds (vanadium, nickel, and iron complexes). Various refining processes are used to convert petroleum into useful products, including (but not limited to) desalting (removing entrained brine droplets), crude distillation (separation of crude oil into various boiling point fractions by distillation at atmospheric pressure and under vacuum), hydrotreating (removal of sulfur and nitrogen from compounds by catalytic treatment with hydrogen to make hydrogen sulfide and ammonia), reforming (conversion of low octane paraffins and cycloparaffins by catalytic dehydrogenation to high octane aromatics), catalytic cracking (conversion of heavy oil to lighter products with reduced sulfur and nitrogen by catalytic processing, usually with a fluidized catalyst), hydrocracking (conversion of heavy oil to lighter products with reduced sulfur and nitrogen by catalytic processing in the presence of hydrogen), alkylation (joining C_3 and C_4 paraffins and olefins to make high octane C_6-C_8 paraffins), and coking (thermal conversion of heavy oil to lighter products and petroleum coke, a solid product). All of these processes employ fractionation to separate their products according to boiling point range. Final refinery products generally are characterized by their boiling point range, as described below.

4.6.3 BASIC PETROLEUM PRODUCT CHEMISTRY

To aid in understanding the following product descriptions, the following provides an overview of basic hydrocarbon chemistry. Hydrocarbons are chains of carbon molecules of various sizes (number of carbon atoms, represented by C_X, where X is number of carbon atoms per molecule) and structures, with those carbon bonds not attached to other carbon atoms (carbon always makes four bonds in hydrocarbons) being attached to hydrogen atoms. They are divided into 4 classes: paraffins, olefins, cycloparaffins, and aromatics.

An important concept in hydrocarbon chemistry is isomers, which are compounds with the same chemical formula (same number of atoms of each element), but different structures. Figure 4-10a shows the simplest such example, normal butane and isobutane, each with the formula C_4H_{10}. Because carbon bonds to itself readily, and can be attached to various numbers of other carbons, the number of isomers for a given formula rises rapidly with the number of carbon atoms: butane has two isomers, pentane has five, and octane (a common gasoline molecule) has 18 isomers. Although the various isomers have many similar properties, they can also differ in important respects: normal octane has an octane value of -17, while iso-octane (2,2,4-trimethyl pentane) has an octane number of 100.

4.6.3.1 Paraffins

Paraffins, or alkanes, are *saturated* molecules, i.e., they contain only single carbon-carbon and carbon-hydrogen bonds. Figure 4-10b shows some paraffin structures. As shown in the examples, paraffins have various degrees of *branching* (attachment of carbon atoms to more than two other carbon atoms). Straight-chain (or *normal*) paraffins have very low octane (normal heptane has an octane number of zero), while highly branched paraffins have very high octanes.

4.6.3.2 Olefins

Olefins, or alkenes, are unsaturated molecules, i.e., they contain carbon-carbon double bonds as shown on Figure 4-10c. Although olefins can contain more than one double bond, this is usually avoided in petroleum products because such molecules have a tendency to form polymers (gums).

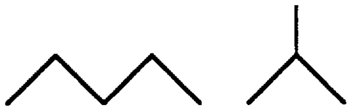
4.6.3.3 Cycloparaffins

Cycloparaffins, or naphthenes, are paraffins which contain a ring structure as shown in Figure 4-10d. Generally, only five-membered rings (cyclopentanes) and six-membered rings (cyclohexanes), with various side-chain substitution, are found in petroleum products.

FIGURE 4-10

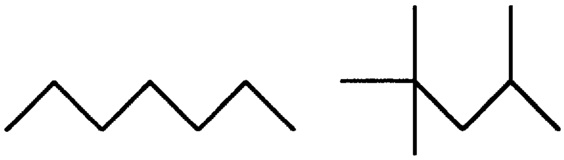
PETROLEUM PRODUCTS CHEMICALS

The formulas below use a common notational method in organic chemistry, in which each line is a carbon-carbon single bond (e.g., each line has a carbon atom at its apexes). Any of a carbon atom's four bonds not filled by bonding to other carbons is filled by single bonds to hydrogen atoms. In ethers, single bonds between carbon and oxygen are shown as a line.



n-butane isobutane

(A) BUTANE ISOMERS



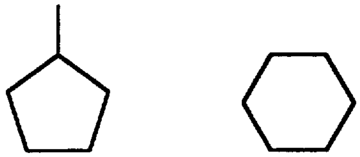
n-hexane
octane rating = 0

iso-octane
octane rating = 100

(B) PARAFFINS, WITH BRANCHING

2-butene

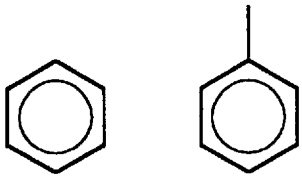
(C) OLEFINS



methyl
cyclopentane

cyclohexane

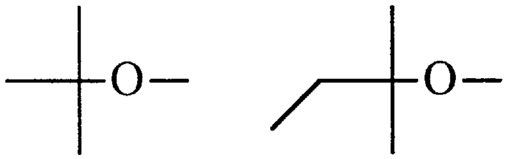
(D) CYCLOPARAFFINS



benzene

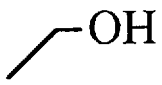
toluene
(methyl
benzene)

(E) AROMATICS



methyl *t*-butyl
ether (MTBE)

t-amyl methyl ether
(TAME)



CH_3-OH

ethanol methanol

(F) ETHERS AND ALCOHOLS
(GASOLINE OXYGENATES)

4.6.3.4 Aromatics

Aromatic hydrocarbons are six-membered ring structures with each ring carbon having 1.5 bonds to the adjacent ring carbon; the electrons in the ring bonds are delocalized (able to move freely around the ring), which gives such structures unusual chemical stability and properties. Aromatic hydrocarbons can be viewed as derivatives of benzene, the simplest aromatic compound. As shown on Figure 4-10e, common components of gasoline are benzene, toluene (methyl benzene), xylenes (dimethyl benzenes), ethylbenzene, and higher weight molecules. Aromatics have very high octane.

Table 4-1

Petroleum Products Boiling Points

	Boiling Points, F		
Product	**Initial**	**Final**	**Midpoint**
Gasoline	-40	420	212
Diesel Fuel	300	580	450
Avjet	300	550	420

4.6.4 GASOLINE AND AVGAS

Gasoline, sometimes referred to as mogas, is the transportation fuel used in most internal combustion automobile engines. It is characterized by having relatively high volatility (to enable it to evaporate in the engine cylinder) and high octane (to give it resistance to pre-combustion, or *knock*, in a high-compression engine). As shown in Table 4-1, the normal gasoline boiling point range is -40 - 420 F, with a typical mid-point boiling point of about 212 F, and a normal molecular size range of C_4-C_9, with a typical mid-point of about C_7. As shown on Table 4-2, a typical gasoline has a wide range of paraffins, olefins, cycloparaffins, and aromatics. Note that this composition is *typical*, not *average*. Gasolines vary widely in their composition, depending on the crude oil source, the refinery processing, and the season (gasolines are blended to be more

Table 4-2

Typical Gasoline Composition, Weight Percent

Number of Carbon Atoms Per Molecule	Normal Paraffins	Iso-Paraffins	Aromatics	Napthenes (Cyclo-paraffins)	Olefins	Total
C4	2.965	0.136			0.512	3.613
C5	3.436	6.676		1.397	5.780	17.289
C6	2.437	3.939	1.765	1.988	7.351	17.480
C7	1.287	5.669	6.957	1.976	2.460	18.349
C8	0.493	7.131	10.408	1.601	0.205	19.838
C9	0.175	1.876	6.336	0.509		8.896
C10	0.060	0.612	5.656	0.077		6.405
C11	0.359	3.172	2.289	0.299		6.119
C12	0.072	0.215	0.208			0.495
C13	0.294	0.107				0.401
Total	11.578	29.533	33.619	7.847	16.308	98.885

volatile in cold weather, and so contain more light molecules).

Gasolines commonly contain additives to improve engine performance and reduce fuel system corrosion; these are described below. In recent years, non-hydrocarbon blending components known as oxygenates have been added to gasoline in various blends to improve octane and reduce tailpipe emissions. These are also described below.

Avgas, or aviation gasoline, is a very high octane fuel used in aircraft piston engines. For obvious reasons, avgas has very high quality standards of cleanliness.

4.6.5 DIESEL, HEATING OIL, AND AVJET

Diesel, or diesel fuel, is used in diesel engines in automobiles, trucks, and other heavy mobile and stationary equipment. As shown in Table 4-1, the normal diesel boiling point range is 300-580 F, with a typical mid-point boiling point of about 450 F, and a normal molecular size range of C_9-C_{17}, with a typical mid-point of about C_{13}.

Heating oil, used typically in domestic oil furnaces in some parts of the country, is very similar in composition to diesel fuel. Avjet, used in aircraft jet engines, is also quite similar to diesel fuel, except for its high quality standards, particularly in regard to prevention of wax deposits at the high-altitude low temperatures typically experienced by jet aircraft.

4.6.6 OXYGENATES

Oxygenates are oxygen-containing gasoline blending components manufactured in petrochemical processes or by fermentation (ethanol). Their use is fairly recent, and has been promoted by the need for their high octane, and by regulatory requirements to reduce certain types of automobile tailpipe air emissions. The two classes of oxygenates used are ethers and alcohols.

4.6.6.1 Ethers

Ethers are molecules with two hydrocarbon groups attached to an oxygen atom. As shown on Figure 4-10, the two ethers currently used in gasoline are methyl *t*-butyl ether (MTBE) and *t*-amyl methyl ether (TAME). As described in 4.11.3.15, ethers are much more soluble in water than are hydrocarbons.

4.6.6.2 Alcohols

Alcohols are molecules with a hydrocarbon group attached to a hydroxy group; as shown on Figure 4-10, alcohols which might be used in gasoline include *t*-butyl alcohol, ethanol (or ethyl alcohol), and methanol (or methyl alcohol). Ethanol is normally made by fermentation of grain, while the other alcohols are manufactured as chemicals. All of these alcohols are very soluble in water.

4.6.7 FUEL ADDITIVES

Fuel additives are blends of various proprietary chemicals added in low concentration to gasoline to help prevent fuel system and engine deposits, and fuel system corrosion. Usually, additive packages include detergents, which can have adverse effects on water which comes in contact with products containing the additives. Most marketing terminals do not add additives to the gasoline until it leaves the terminal in the tanker trucks which supply the service stations.

4.6.8 HEAVY OILS

Although not nearly as common as the lighter transportation fuels, gasoline and diesel, heavy oils are handled by some terminals. The main uses for such fuels are power station fuel and marine engine fuel. Because of their high molecular weight and resulting high viscosity (approaching that of asphalt), such fuels are normally kept hot to enable pumping them, or are mixed with lighter products (e.g., diesel fuel), sometimes called *cutter stocks*, to reduce their viscosity.

4.7 Other Terminal Operations

In addition to transferring and storing petroleum products, most terminals also have other related operations which affect the terminal wastewater.

4.7.1 FIRE FOAM TESTING

Petroleum products terminals handle very flammable materials in large quantities, and take considerable precautions to prevent fires and to provide measures for fighting fires. For petroleum products, the most effective means for fighting fires is with foam, generated from air, water, and a foaming agent. From time to time, terminals will test their fire foam system, with the possible consequence that the testing foam will enter the wastewater system. Since the foaming agent is a detergent, and water-soluble, it may adversely affect the wastewater quality if not handled properly.

4.7.2 BOILERS

Terminals which handle very heavy products (e.g., bunker C marine fuel oil) must keep them hot so they will be fluid. As one means for doing this, some terminals use steam heat, with steam coils in the product tank, and steam generated by a boiler.

Since the water which is fed to the boiler (*boiler feed water*) becomes concentrated in non-volatile salts as the steam is generated, it is necessary in any steam system to continuously remove (*blow down*) some of the boiler water, as a stream called boiler blowdown. Since chemicals are usually added to boilers to prevent scale (hard inorganic deposits) deposition on boiler surfaces, the blowdown water will contain those chemicals (commonly, phosphates). Most small boiler systems have boiler feed water which is either untreated, or softened (not demineralized) at best. Such water commonly contains bicarbonate ions, which participate in the following reaction in the boiler:

$$HCO_3^- \rightarrow OH^-\text{(in water)} + CO_2\text{(in steam)}$$

As a result of this reaction, the boiler water (and thus the boiler blowdown water) becomes quite alkaline (high in hydroxide ions), and the steam becomes acidic (because of carbon dioxide, which dissolves in any condensed steam to make carbonic acid). Because of the acidity, the steam condensate is quite corrosive to the steel piping normally used in steam systems. In some facilities, chemicals (usually *amines*, somewhat volatile alkaline organic chemicals) will be injected in the boiler or in the steam lines to control this corrosion.

As steam is distributed in piping through the facility, some of the steam condenses as a result of cooling, even if the steam lines are well insulated. Because of this, steam distribution systems are equipped with *steam traps* along the piping network. A steam trap is a device which (when working properly) will release liquid water, but not much steam. The water which is blown down from the steam trap is of high quality, and generally not a source of wastewater contamination. However, in some cases the corrosion-control amines in this water may be a source of wastewater problems.

At the point of use, steam is placed into steam coils in the product tanks, usually with a steam trap at the other end of the coil to release the steam condensate made when the steam gives up its heat. While this process does not make contaminated water (except possibly from the amines used in the steam system), if the steam is corrosive, leaks can develop in the steam coil, and the leaked steam can make tank bottoms water in a tank which normally does not have bottoms water. The effects of this are minimized by the oil temperature, which is high enough to evaporate much of the water, but in some cases wastewater problems could be caused.

4.7.3 LABORATORY OPERATIONS

Some terminals have small analytical laboratories to conduct basic quality control tests and other tests needed for terminal operations such as wastewater treatment. As with any chemical laboratory, reagents with various potential impacts on facility wastewater are normally used in small quantities.

4.7.4 SANITARY WASTES

Sanitary waste is the general term for wastewater produced in lavatories and shower facilities. As with all facilities, terminals will make sanitary waste in proportion to the number of personnel employed. Typical production rates are 25-50 gallons/day/employee (Metcalf & Eddy, 1979).

4.7.5 PRODUCT TANK CLEANING

From time to time, most petroleum products tanks need cleaning to remove accumulated sludge. Potential byproducts from the cleaning operations include the sludge itself, cleaning water and sometimes detergent, and any storm runoff from materials placed outside the tank.

4.7.6 REMEDIATION WORK

Remediation is the general term for cleanup of an *in-situ* contamination problem. The two general types of remediation found in terminals are soil remediation, generally to remove petroleum products or other regulated materials such as leaded tank sludge, and groundwater remediation, to remove contaminants from groundwater and to prevent migration of groundwater contamination offsite. Although details of these remediation processes cannot be given in this document, it is evident that either operation can produce contaminated water. Soil remediation processes may expose contaminated soil, and thus permit generation of contaminated storm runoff water, or may use water in the remediation process (e.g., by soil washing or biotreatment). The most commonly-utilized method for groundwater remediation is pumping the contaminated water to the surface for treatment; sometimes this water is mixed with other wastewaters at the facility.

4.7.7 DIESEL ENGINE COOLING SYSTEMS

Some terminals, particularly pipeline terminals, employ large water-cooled diesel engines as the power source for pumps. The water-based coolant commonly contains corrosion inhibitors and other additives, and is a potential water contaminant when the coolant is drained for periodic renewal or for maintenance operations.

4.8 Terminal Operations

4.8.1 STAFFING

Typical classes of employees found in marketing terminals include:

- Management personnel, to supervise terminal operations, and sometimes marketing operations in the area served by a marketing terminal
- Operators, to operate and maintain terminal equipment
- Laboratory chemists and technicians (in terminals with analytical laboratories)
- Accounting personnel, to keep records on product shipments and inventory, and other facility accounts
- Truck mechanics
- Clerical and secretarial personnel
- Truck drivers (if employed by terminal)
- Custodial personnel

Although widely varying, the total number of personnel (other than truck drivers) at a typical terminal is 4-6, and some terminals have only a single employee.

4.8.2 OPERATING SCHEDULES

Some terminals are staffed 7 days/week, 24 hours/day, although most personnel are present only during the normal 40-hour work week. Other terminals are normally staffed only 40 hours/week, but are open for truck drivers to load products with automated product delivery and accounting systems. Finally, some terminals are only open during the normal work day. Probably the most common operating schedule is a normal 40 hour week, with full-time access by truck drivers.

4.9 Wastewater Sources

Types of wastewater common to almost all terminals are tank bottoms water, spill containment wastewater, and stormwater. Other types of wastewater can also be generated, depending on the nature of the terminal operation. Means for minimizing the flow or contamination of the wastewater streams are covered in Chapter 7. Table 4-3 summarizes the wastewater sources and likely contaminants.

Table 4-3

Petroleum Products Terminals Wastewater and Likely Contaminants

Wastewater Type	Oil & Grease	TPH	BOD	COD	TOC	Ammonia	pH high, low	TSS
Tank bottoms water	H	H	H	H	H	H	M	H
Spill containment wastewater	H	H	L	L	L	0	0	H
Truck wash water	H	H	M	M	M	0	H	H
Truck maintenance wastes	H	H	H	H	H	0	L	0
Ballast water	H	H	M	M	M	0	0	M
Produced groundwater	M	M	L	L	L	0	0	0
Vapor recovery water	H	H	M	M	M	0	0	0
Haulback material water bottoms	H	H	M	M	M	0	0	L
Hydrostatic test water	L/0	L/0	L/0	L/0	L/0	0	0	0
Boiler blowdown	0	0	0	0	0	0	H	L
Steam condensate	0	0	0	0	0	0	H	0
Laboratory wastes	M	M	M	M	M	?	?	?
Sanitary wastes	0	0	H	H	H	?	0	H
Detergents	L	L	H	H	H	?	H	H

Wastewater Type	Sulfide	Phenols	TDS	Naphthenic Acids	BTEX	Surfactants	Metals	Toxicity After Treat
Tank bottoms water	M	H	H	H	H	H	L	M
Spill containment wastewater	0	0	0	0	H	0	0	0
Truck wash water	0	0	M	0	0	H	0	M
Truck maintenance wastes	0	0	L	0	0	0	0	H
Ballast water	L	0	H/L	0	?	0	?	M
Produced groundwater	?	0	?	0	H	0	?	L
Vapor recovery water	0	0	0	0	H	0	0	0
Haulback material water bottoms	0	0	0	0	H	0	0	L
Hydrostatic test water	0	0	L	0	0	0	0	0
Boiler blowdown	0	0	H	0	0	0	?	L
Steam condensate	0	0	0	0	0	0	0	0
Laboratory wastes	?	?	?	0	?	?	M	?
Sanitary wastes	M	0	L	0	0	M	L	?
Detergents	0	0	H	0	0	H	0	M

H = High concentration or probability
M = Medium concentration or probability
L = Low concentration or probability
0 = Very low concentration or probability
? = Unknown concentration or probability

Table 4-4

Terminal Product Contact Water Concentrations

		Gasoline Tank Bottoms (9) *			Diesel/Fuel Oil Tank Bottoms (2) *			Terminal Wastewater (4) **		
Contaminant	**Units**	**Average**	**Maximum**	**Minimum**	**Average**	**Maximum**	**Minimum**	**Average**	**Maximum**	**Minimum**
BOD	ppm	4369	7177	1961	1305	1617	992	1412	2600	570
COD	ppm	27778	58000	8075	8688	9175	8200	3935	6000	1700
TOC	ppm	5936	12760	2741	1786	2381	1191	999	1980	290
Oil & Grease	ppm							100	240	25
TPH	ppm							42	250	2
Ammonia	ppm	1650	4300	16	1635	2500	770	22.7	116	0.1
Benzene	ppm							5.3	11	0.8
Toluene	ppm							9.3	19	0.11
Xylenes	ppm							5.6	14	0.011
Ethyl Benzene	ppb							2397	6200	180
MTBE	ppm							105	290	8.5
Methanol	ppm							143	630	<1
Ethanol	ppm							4	12	<1
Phenols	ppm							10	52	0.4
2,4 Dimethyl Phenol	ppb							603	1300	97
MBAS	ppm							6.1	16.2	1.1
CTAS	ppm							5.4	14	0.2
TSS	ppm							195	768	45
TDS	ppm							1893	3660	646
Conductivity								2260	4000	1013
Sulfide	ppm							<0.5	2	<0.01
Cyanide	ppm							<0.01	<0.01	<0.005
Arsenic	ppb	6073	20794	381	101	195	6	167	430	28
Cadmium	ppb		<3	<3	<3	<3	<3		14	<5
Chromium	ppb		62	<5		<5			90	<10
Copper	ppb	3576	8028	179	1478	2235	720		550	<20
Lead	ppb		1669	<1		<1			550	<60
Mercury	ppb		1	<0.2		<0.2				
Nickel	ppb	345	779	30	66	100	31			
Zinc	ppb	2153	9696	126	246	445	47	492	1700	20

* Samples were tank bottoms from 11 nationwide marketing terminals. Hall, J.F., et. al., "Analysis and Reduction of Toxicity in Biologically Treated Marketing Terminal Tank Bottom Water", by Texaco Inc. for API (in preparation).

** Samples were terminal wastewater (mostly tank bottoms) from 4 Gulf coast terminals. Vuong, D.C., et.al. (Texaco Inc.), "Comparative Evaluation of Biological Treatment of Petroleum Product Terminal Wastewater by the Sequencing Batch Reactor Process and the Rotating Biological Contactor Process", API Publication 4582, 7/92.

		Gasoline Tank Bottoms (13)			Diesel Tank Bottoms (2)			Jet A Tank Bottoms (4)		
Contaminant	**Units**	**Average**	**Maximum**	**Minimum**	**Average**	**Maximum**	**Minimum**	**Average**	**Maximum**	**Minimum**
TOC	ppm	1796	5570	553	923	1300	546	706	2560	54.9
Oil & Grease	ppm	12	42	2	253	265	241	35	131	2
pH		6.26	7.43	5.55	7.98	8.15	7.81	6	7.36	4.26
Benzene	ppm	27	52	12	0.435	0.46	0.41	0.28	0.52	0.034
Toluene	ppm	68	240	8	0.635	0.92	0.35	3.15	10	0.19
Xylenes	ppm	23	165	4.1	0.81	1.06	0.56	1.02	2.06	0.53
Ethyl Benzene	ppm	7	50	0.35	0.54	0.72	0.36	0.25	0.77	0.037
Naphthalene	ppb	735	2200	190	545	550	540	1361	4100	3
Phenols	ppm	29	80	1.2	23.8	42	5.6	7.47	27	0.4
2,4 Dimethyl Phenol	ppb	1550	8500	21	7700	14000	1400	191	450	4.2
TSS	ppm	144	512	7	21	36	6	36	64	12
TDS	ppm	22353	50500	3920	24750	26900	22600	20775	32800	11800
Chloride	ppm	10646	19600	1670	13350	14900	11800	10330	17600	6120
Sulfate	ppm	1424	2430	168	524	715	333	1095	2410	284
Cyanide	ppm	0.050	0.216	0.005	0.093	0.181	0.005	0.006	0.01	0.005
Arsenic	ppb	218	903	5	163	213	113	152	514	10.2
Cadmium	ppb	5	16	2	3.5	5	2	4.8	7	3
Chromium	ppb	6	12	3	6.5	7	6	163	625	3.6
Copper	ppb	33	160	3	4.5	6	3	4.8	7.3	2
Iron	ppm	42	144	1.29	4.06	6.73	1.39	19	37.1	5.29
Lead	ppb	150	754	3	3	3	3	1060	4180	3
Mercury	ppb	0	1.3	0.2	0.2	0.2	0.2	0.20	0.2	0.2
Nickel	ppb	91	645	12	15	15	15	139	515	12
Selenium	ppb	64	183	5	35.4	65.8	5	35.9	44.5	30.6
Zinc	ppb	1039	7630	24	157	312	2	876	2460	147

4.9.1 TANK BOTTOMS WATER

Although not necessarily produced in large volumes, tank bottoms water is almost always the major source of dissolved contaminants, particularly organic contaminants, in a terminal. The water which collects in the bottoms of petroleum products tanks comes from delivery with the product, from tank breathing and condensation of moisture in the air, and from rainwater which passes through floating roof seals. Generally, the throughput of water in a storage tank is much less than the throughput of product, so the water can become highly concentrated with water-soluble materials in the product. Some typical values for tank bottoms contaminants concentrations are shown in Table 4-4. Section 7.7 describes in detail how tank bottoms water flow can be minimized, how the water should be handled, and what type of treatment is appropriate for the water.

4.9.1.1 Dissolved Water

Although water is not very soluble in petroleum products, it is not totally insoluble, particularly at elevated temperature. For those facilities which receive hot water-saturated products directly from refineries, water can be generated in tankage as the product cools down. In some cases, this will be seen as a *haze*, or cloudiness, in the product. As an example, the amount of water soluble in diesel fuel at 200 F and 50 F is 952 and 38 ppm, respectively, and so the amount of water which would come out of solution as the diesel cooled between these two temperatures would be 31 gallons/1000 barrels of diesel. As another example, the solubility of water in gasoline goes from 170 ppm down to 95 ppm when it cools from 100 F to 75 F. The amount of liquid water released between these two temperatures would be 2.2 gallons water/1000 bbl gasoline. (API, 1982)

4.9.1.2 Entrained Product Water

Although obviously not an intended material, significant quantities of water can be delivered along with the hydrocarbon products entering a terminal. Water comes in contact with petroleum products in several ways. In refinery operations, gasoline and other distillate products are commonly distilled in systems which contain water and condensed steam, are frequently washed with water or aqueous solutions (e.g., caustic solutions), and are often stored in tankage which allows rainwater entry. Most of this water is separated from the product before it leaves the refinery, but small droplets of water can remain entrained in the delivered product. The product can also pick up water in the distribution system, particularly when stored in tanks which do not totally prevent rainwater entry (see below). Shipment by water (tanker ship or barge) also can result in water entrainment since empty vessels (following unloading) are commonly filled with *ballast water* to stabilize the otherwise empty vessel, and some of this water can remain in the storage compartment when it is refilled with product.

4.9.1.3 Tank Breathing and Condensation

When product is drawn out of a storage tank which has a fixed cover, air must be allowed to enter to prevent creation of a vacuum and collapse of the tank; also, air is drawn into such a tank as a result of tank breathing. This air contains water vapor (humidity), which can be partially converted to liquid water if the temperature is reduced by diurnal (day to night) temperature changes or by weather changes. Exact amounts can be calculated from psychrometric charts. As an example, if 1000 barrels of air enter a fixed-roof tank at 90 F with a relative humidity of 80 percent, and the temperature is later reduced to 60 F, then the amount of liquid water produced is about 6 lb, or 0.7 gallons. Most of this water will probably be on the inside tank walls and roof, and much of it may run down into the product, even if the tank has an internal floating roof with seals (that which does not run down may vaporize when the tank warms up again). Obviously, the amount of water generated by tank breathing and condensation is a function of tank turnover frequency, and of specific climatic conditions. Although the quantity of water produced in a given event is not large, as shown in the example, the cumulative amount over months of operation can be significant.

4.9.1.4 Rainwater

Essentially all tanks used for distillate products have covers to prevent loss of product and air pollution; these covers also keep most of the rain which falls on the tank out of the tank. If the tank has a tight fixed cover, then rainwater intrusion will not occur. Even a fixed cover which is not tight, such as some geodesic dome covers, will prevent most rain from entering the tank. Floating roofs, if used without fixed roofs, can, however, allow some rainwater intrusion, since the floating roof seals, as shown on Figure 4-4, are not perfectly tight, and a significant fraction of the rain which strikes the exposed inner tank wall can run down the wall and past the roof seal into the tank. Obviously, the amount of tank bottoms water arising from this source depends on the local rainfall amounts and on the condition of the seal. Another factor is the condition of the roof drain used to drain rainwater from the floating roof. Generally, the roof has a low point drain connected to a flexible (to accommodate up and down movement of the roof) line inside the tank, and thence to a drain nozzle in the side of the tank (Figure 4-5). If the drain should become blocked, such as by debris or leaves blown into the top of the tank, then rainwater can accumulate on the roof and overflow the roof seal at greatly accelerated rates, or the roof can be sunk by the accumulated weight of water. If the roof drain nozzle valve is kept closed, and the drain line has leaks, then rainwater can enter the tank through the leaks (even more seriously, product can leave the tank through the leaks when the drain nozzle valve is opened). Finally, leaks in roofs, particularly at joints and fittings, can obviously allow rainwater entry.

4.9.1.5 Other Sources of Tank Bottoms Water

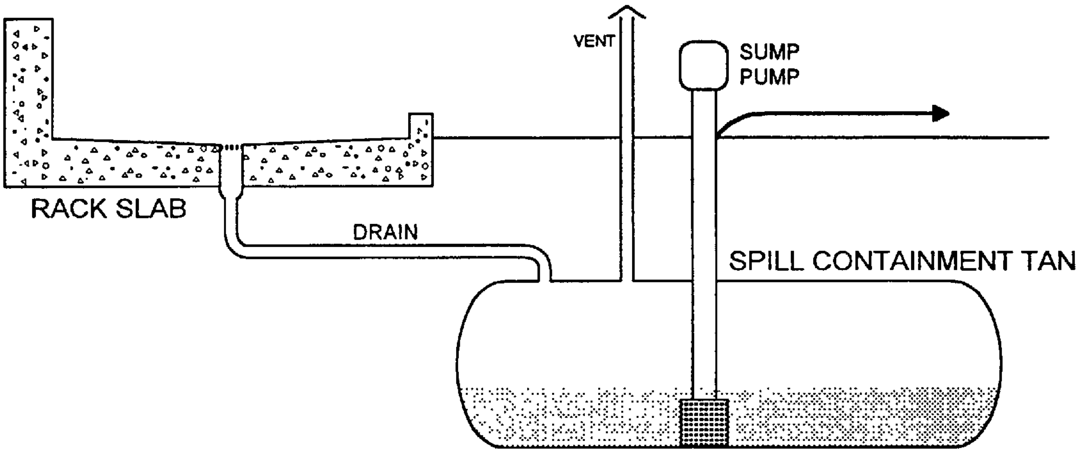
At times, terminals have a source of water, and need some place to put it before it can be treated. If the quantity is not excessive, and storage capacity allows, then some terminals will place this water into product storage tanks, and eventually draw it as tank bottoms water. Any of the low-volume streams described below could be candidates for this type of water routing.

4.9.2 SPILL CONTAINMENT WASTEWATER

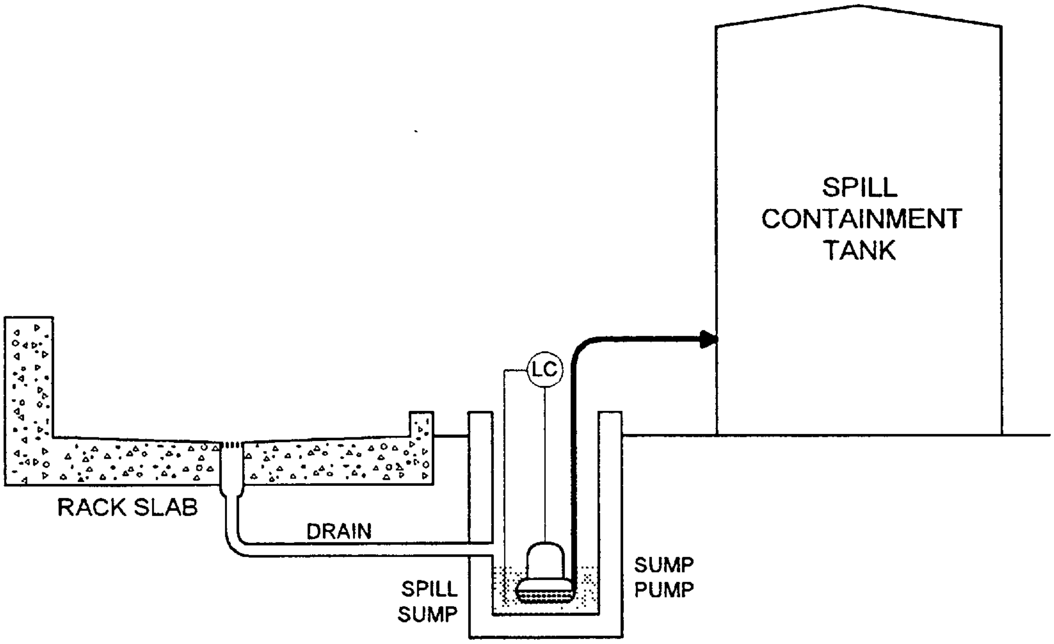
Spill containment wastewater means, in this context, water which is collected in systems designed to handle minor spills of product. Probably the most common example is collection and storage systems set up at rail or truck loading racks. In these systems, the ground is graded to deliver any

FIGURE 4-11

RACK SLAB SPILL CONTAINMENTS



UNDERGROUND SPILL CONTAINMENT



ABOVE GROUND SPILL CONTAINMENT

liquid on the surface to a drain which is connected to a tank, either direct gravity drain into an underground tank, or sump pump transfer to an above-ground tank (see Figure 4-11). By the nature of this system, water which falls on the drainage area, either as rainwater or washup water, is collected along with any spills or drips from the loading/unloading operation. Although the water will not necessarily contain high concentrations of soluble contaminants (unless detergents are used for cleanup, or product with water-soluble additives is spilled), the water should be handled as contaminated water (since oil will usually be present), and treated before discharge.

4.9.3 TRUCK WASH WATER

Many marketing terminals operate a tanker truck fleet for product delivery to service stations, and routinely wash the trucks to maintain their appearance and keep them in good condition. As would be expected, the resulting wastewater can contain detergent, and also elevated levels of fine solids. If this washing is done at the terminal, then it should be kept segregated from oily water to prevent emulsion formation, as described in 7.8.2.

4.9.4 TRUCK MAINTENANCE WASTES

As noted above, many terminals operate truck fleets, and sometimes maintain them onsite. As with any vehicle maintenance, waste streams can be generated which can adversely affect wastewater. These streams include drainage from crankcases (oil), transmissions and differentials (oil), cooling systems (antifreeze), and brake and hydraulic clutch systems (brake fluid), and parts washing fluids. Generally, as described in 7.8.3, such material should be kept out of terminal wastewater.

4.9.5 BALLAST WATER

Ships or barges which take on products at a terminal will frequently contain water, known as ballast water, in their product tanks prior to the loading; this water is used to stabilize the vessel (prevent pitching and rolling) while it is empty of product. Unless certain tank compartments are dedicated to ballast-water-only service (called clean segregated ballast), this water can be contaminated with products previously placed in the vessel (and is then called dirty ballast), and thus cannot be discharged overboard without treatment. For this reason, some terminals accept ballast water into tankage, and treat it and discharge it ashore. Contaminants include oil, and whatever was in the water (e.g., salt or silt) which was taken onboard.

4.9.6 PRODUCED GROUNDWATER

As with many industrial facilities, terminals sometimes have groundwater under their site which is contaminated either as a result of past terminal operations, or by offsite contamination which has moved downgradient to the terminal site. In order to prevent migration of contamination, this contaminated water is sometimes pumped to the surface, treated, and discharged. Contaminants can be varied, but dissolved hydrocarbons are not uncommon. If the water can be reinjected into the ground, then it does not become a facility wastewater. If this is not allowed, then the produced water must be treated to meet discharge permit standards or the standards of a POTW. The flow of such water is obviously very much case-specific, but frequently is of such a volume as to greatly exceed the flow of the other terminal wastewaters.

4.9.7 VAPOR RECOVERY WATER

As described above, many terminals have systems for removing hydrocarbon vapors from air which is displaced when filling vessels with product. In one such system, cryogenic vapor recovery, the air is chilled to condense and separate the hydrocarbons. In this operation, most of the humidity in the air is also condensed (as in an air conditioner) and becomes liquid water saturated with hydrocarbons. This material must be disposed of as contaminated water. Because of the large amounts of free hydrocarbons condensed along with the water, it is common practice to place the mixed condensate into a product tank to enable recovery of the hydrocarbons as product. When this is done, the condensed water becomes tank bottoms water.

4.9.8 HAULBACK MATERIAL

Many marketing terminals serve a central coordinating function for the service stations to whom they provide products. As part of this, some terminals accept off-specification products back from the service stations. In some cases, this is a product/water mixture which collects at the bottom of the station's underground product (gasoline or diesel) storage tanks, resulting from water in the product delivered to the station, from tank breathing condensate water, or from intrusion of water into the tank (e.g., from stormwater leakage through the on-grade fill port). When this material is placed into terminal tankage, the water which separates and is removed becomes part of the terminal wastewater stream. Its characteristics will be similar to other product tank bottoms water, except that it may contain materials normally added to gasoline only when it leaves the terminal, such as additives and oxygenates. These materials can cause significant wastewater treatment problems.

4.9.9 HYDROSTATIC TEST WATER

When maintenance work is done on equipment used for storing and transporting products, it is frequently hydrostatically tested before return to service to ensure that it will not leak under operating conditions. Hydrostatic testing involves filling the equipment (pipeline or tank) with water, placing it under pressure, searching for leaks, and observing any loss of pressure (indicating a leak). When the test is finished, the water is discharged. Since pipelines and bulk storage tanks have high volume, this large quantity of water must be discharged in a short time period, i.e., at relatively high flow rate.

4.10 Impact of Terminal Wastewater on the Environment

4.10.1 LOW FLOW OF CONTAMINATED WATER

Although terminals have considerable variability in the amount of contaminated wastewater they produce, a typical marketing terminal makes only about 1000 gallons per week of contaminated water, particularly if product tanks have fixed covers, or the terminal is located in an arid climate..

4.10.2 TREATABLE CONTAMINANTS

For the most part, the contaminants in petroleum products terminal wastewater are treatable, either onsite, or offsite in municipal treatment works. As a rule, the contaminants are organic in nature, which means that they are convertible by biological treatment or other means to harmless carbon dioxide and low-volume biosludge. Levels of non-destructible contaminants (e.g, heavy metals) are quite low.

Table 4-5

Comparison of Terminal Effluent (Before and After Biotreatment) With Other Discharges

Mass emission is based on 1000 gallon/week terminal effluent flow.

Concentrations and mass emissions after biological treatment are italicized.

Contaminant	Typical Concentration, mg/L	Pounds/ Week	Equivalent Weekly Discharge From Other Sources
Water	1000 gpw	8340	One half of a typical weekly household sanitary sewage flow *
BOD	4000	33	BOD from 10 households/week*
	80	*0.67*	*BOD from 0.2 households/week*
COD	25000	209	COD from 25 households/week*
	5000	*42*	*COD from 5 households/week*
TOC	5000	42	TOC from 17 households/week*
	1000	*8.3*	*TOC from 3 households/week*
Oil & Grease	20	0.17	5 tablespoons oil/week
	4	*0.03*	*1 tablespoon oil/week*
BTEX	90	0.75	BTEX in 0.5 gallon gasoline/week**
	<0.015	*0.00013*	*BTEX in less than 5 drops gasoline/week*
Phenols	30	0.25	
	0.6	*0.005*	*Phenol in 1/3 pint throat spray****
Surfactants	15	0.13	6 fluid ounces detergent/week
	4.5	*0.04*	*2 fluid ounces detergent/week*
Ammonia	1500	12.5	Ammonia from 30 households/week*
	20	*0.17*	*Ammonia from 0.4 households/week*
Arsenic	0.2	0.0017	
	0.2	*0.0017*	
Copper	2	0.017	
	0.2	*0.0017*	
Zinc	2	0.017	
	0.12	*0.001*	

* Metcalf & Eddy, Inc., "Wastewater Engineering: Treatment, Disposal, Reuse", Second Edition, McGraw-Hill, 1979.

** Assuming 20% BTEX in gasoline

*** At 1.4% phenol

4.10.3 COMPARISON WITH OTHER DISCHARGERS

Usually located in cities, petroleum products terminals produce, as a rule, much lower mass emissions of contaminants than other facilities in the community. Using typical flow rates and contaminant levels (Table 4-4), and typical contaminant levels after treatment (Appendix B), the mass emission rates of contaminants in a typical facility can be calculated as shown on Table 4-5, and compared with other dischargers. As can be seen, a typical terminal in a small city with a population of 100,000 would produce wastewater with about 0.1 percent of the total city wastewater load.

4.11 Characteristic Contaminants in Petroleum Products Terminal Wastewater Streams

4.11.1 SOLUBLE CONTAMINANTS FROM PRODUCTS

Most of the characteristic contaminants found in petroleum products terminal wastewaters come, not surprisingly, from the products themselves. The degree of contaminant transfer from the products depends on the nature of the contaminants, i.e., on the relative solubility in water and in hydrocarbon, and to some extent, on the concentration of the contaminant in the product, and the relative throughputs of products and water streams.

4.11.1.1 Saturation-Limited Contaminants

The first category of contaminants, *saturation limited*, covers those materials which are present at relatively high concentration in products, and are of limited solubility in water. When water contacts products, it can become saturated with materials in this class, which are hydrocarbon product constituents. The contaminants associated with soluble hydrocarbons are the soluble fraction of oil & grease and TPH, BTEX, and part of the BOD, COD, and TOC. By the nature of this category, any water which contacts a given product will tend to have the same concentration of saturation-limited contaminants, no matter what the relative quantities of water and product. Table 4-6 shows the water solubilities of various typical product hydrocarbons. Note that these are the solubilities of the pure materials, and that actual water concentrations will be determined by the percent of the material in the product. For example, water in contact with a gasoline which contains 1 percent benzene will contain 0.01 x 1791 = 18 mg/L benzene.

4.11.1.2 Extracted Contaminants

The second category of contaminants, *extracted contaminants*, are those materials which are usually minor components of products, and somewhat soluble in both product and water. Contaminants in this category are phenols, naphthenic acids, and most of the BOD, COD, and TOC in tank bottoms water. Extracted contaminants will *partition* between the hydrocarbon phase and the water phase as a function of the *partition coefficient* (essentially, the ratio of the concentrations in the two phases), and the relative amounts of the phases. Since these materials are minor components of the products, the concentrations of them in the products can be reduced by extraction into water.

> The main principle of extraction is that the ratio of the concentrations of a material in two phases will be a constant (the partition coefficient). As an example, if the partition coefficient of

Table 4-6
Solubility of Petroleum Products' Components in Water

Component	Carbons	Solubility, mg/L	Temperature, C	Ref.	Component	Carbons	Solubility, mg/L	Temperature, C	Ref.
Paraffins					**Cycloparaffins**				
n-Butane	4	61	20	1	Cyclohexane	6	54.8	20	3
Isobutane	4	49	20	1	Methyl Cyclohexane	7	14	20	1
n-Pentane	5	39.5	25	2					
Isopentane	5	48	20	2	Aromatics				
n-Hexane	6	13	20	1	Benzene	6	1791	20	3
2-Methyl Pentane	6	13	25	2	Toluene	7	535	20	3
3-Methyl Pentane	6	18	25	2	o-Xylene	8	175	20	3
2,2-Dimethyl Butane	6	24	25	2	m-Xylene	8	146	20	3
2,3-Dimethyl Butane	6	19	25	2	p-Xylene	8	156	20	3
n-Heptane	7	3	20	1	Ethylbenzene	8	161	20	3
2-Methyl Hexane	7	2.5	25	2	Naphthalene	10	31.7	20	3
3-Methyl Hexane	7	2.6	25	2	Anthracene	14	1.29	20	1
2,2-Dimethyl Pentane	7	4.4	25	2					
2,3-Dimethyl Pentane	7	5.3	25	2	Phenols				
2,4-Dimethyl Pentane	7	4.4	25	2	Phenol	6	87,000	20	3
3,3-Dimethyl Pentane	7	5.9	25	2	o-Cresol	7	30.8	20	3
n-Octane	8	0.66	20	1	m-Cresol	7	23	20	3
3-Methyl Heptane	8	0.8	25	2	p-Cresol	7	22.6	20	3
Iso-Octane	8	0.56	20	1	2,4-Dimethyl Phenol	8	6200	20	3
2,3-Dimethyl Hexane	8	0.13	20	1					
2,2,4-Trimethyl Pentane	8	0.22	25	2	Oxygenates				
2,3,4-Trimethyl Pentane	8	1.4	25	2	Methanol	1	Infinite	20	3
n-Nonane	9	0.07	20	1	Ethanol	2	Infinite	20	3
n-Decane	10	0.009	20	1	t-Butyl Alcohol	4	79	20	4
n-Dodecane	12	0.0037	20	1	MTBE	5	39,000	20	5

1 = Verschueren, Karel, "Handbook of Environmental Data on Organic Chemicals", Second Edition, Van Nostrand Reinhold, New York, 1983.
2 = Yaws, Carl L., Xiang Pan, and Xiaoyin Lin, "Water Solubility Data for 151 Hydrocarbons," Chemical Engineering, 2/93
3 = Howard, Philip H, "Handbook of Environmental Fate and Exposure Data for Organic Chemicals", Volumes I and II, Lewis Publishers, Chelsea, Michigan, 1989.
4 = Lide, David R., "CRC Handbook of Chemistry and Physics", 73rd Edition, CRC Press, Ann Arbor, Michigan, 1993.
5 = Webster, George H., personal communication, 1993

material A between product and water is 0.01, and the concentration of A in the product is 100 mg/L, then the concentration of A in water contacting the product is 100/0.01 = 10,000 mg/L. As another example for the same product, if 1000 gallons of product with an initial concentration of A of 6 mg/L contacts 2 gallons of water, then the final concentrations of A in product (C_P) and water (C_W) are calculated as follows:

1) $C_P/C_W = 0.01$; $C_W = 100C_P$
2) $1000x6 = C_P x1000 + C_W x2 = 1000C_P + 2x100C_P = 1200C_P$
3) $C_P = 6000/1200 = 5$
4) $C_W = 100C_P = 500$

For those materials whose partition coefficients favor extraction into water, very high concentrations can be accumulated in small amounts of water which contacts large amounts of product (particularly water bottoms in tanks with little water throughput). As an indication (but not direct measure) of the partition coefficients of contaminants between hydrocarbon product and water, Table 4-7 shows the *octanol-water partition coefficients* of various materials, a standard measure of extractability.

Another type of extracted contaminants is oxygenates, ethers and alcohols, which are blended with gasoline as octane and emissions improvement materials. In fuel blends, oxygenates are significant constituents (not trace components as are the other extracted contaminants), and can dissolve to very high levels in contact water.

A third type of extracted contaminants in some facilities are gasoline additives, which are placed in gasoline to reduce corrosion and deposits in automobile fuel systems. Many additives are detergents, and act to emulsify products and water. Most petroleum products terminals only mix additives with products as the products are shipped out of the terminal, and so avoid contamination of their wastewater unless significant quantities of haulback materials from service stations are brought into the terminal.

4.11.1.3 Water-Borne Contaminants

Some contaminants found in product contact water are not expected to be soluble in products: ammonia, metals, TDS, and suspended solids. For these contaminants, the most likely source is as contaminated water droplets in the delivered product. The ultimate source of the contaminated water is unknown; possibilities include the refinery and the transportation system.

Table 4-7

Octanol-Water Partition Coefficients for Common Contaminants

Contaminant	Octanol-Water Partition Coefficient
Cyclohexane	2754
Benzene	135
Toluene	537
o-Xylene	1318
m-Xylene	1584
p-Xylene	1413
Ethylbenzene	1413
Naphthalene	1995
Phenol	29
2-Cresol	89
3-Cresol	91
4-Cresol	87
2,4 Dimethyl Phenol	200
Methanol	0.17
Ethanol	0.49

The Octanol-Water partition coefficient is the ratio of the concentration of the material in octanol to its concentration in water when equilibrated between both phases

Reference: Howard, Philip H, "Handbook of Environmental Fate and Exposure Data for Organic Chemicals", Volumes I and II, Lewis Publishers, Chelsea, Michigan, 1989

4.11.2 SOLUBLE CONTAMINANTS FROM OTHER SOURCES

The most significant non-product source of soluble contaminants is purchased chemicals of various types. Perhaps the most common such materials are detergents, used to clean various equipment in the terminal. Other examples are antifreeze and brake fluid from vehicle maintenance operations, and boiler water treatment chemicals. Terminals which receive ballast water will have contaminants (e.g., salt from sea water) from the original water source. Terminals whose operations go beyond product transfer and storage, such as lube blending operations, analytical laboratories, and chemical manufacture, can obviously produce significant wastewater volumes and contamination from these sources.

4.11.3 TYPICAL CONTAMINANTS

4.11.3.1 Oil and Grease

Oil and grease, measured by the standard technique (extraction with Freon or other solvent of an acidified water sample, followed by evaporation of the solvent and weighing the residue), has two components. The first component is "real" or "free" oil, insoluble material suspended in, or floating on, the water. The second component is water-soluble material extractable with Freon from an acidified sample, and can include organic acids and inorganic sulfur compounds (those which are converted to Freon-soluble elemental sulfur by acidification). In the standard, "gravimetric", oil and grease test, gasoline components in water will not be detected, since they will evaporate along with the Freon. In the "IR" variation of the standard method, the unevaporated Freon is subjected to infrared spectroscopy, and the oil content determined by the size of those peaks which are characteristic of hydrocarbons; this method *does* measure gasoline components, but does not measure elemental sulfur. As part of the oil industry, almost all petroleum products terminals will have oil and grease limits in their discharge permits.

The regulatory intent of oil and grease limits is prevention of discharge of free oil, since it is slow to degrade in the natural environment, and has adverse esthetic and toxicity effects on the receiving water. Since the oil and grease test measures both free oil and other components, it is not an ideal test for controlling the material of concern (a crystal-clear sample can have high oil and grease concentration). In order to better measure free oil, the total petroleum hydrocarbons test, described next, was developed.

4.11.3.2 Total Petroleum Hydrocarbons

The Total Petroleum Hydrocarbons (TPH) test is intended to specifically measure hydrocarbons, the principal components of petroleum products. At this time, it is not a standard EPA test, and several analytical methods are called TPH. Which method (if any) is used depends on the state or local regulatory agency which imposes the regulations. One TPH method is a variant on the oil and grease test, in which the Freon extract is passed through a silica gel column to remove the non-hydrocarbon constituents (silica gel has a high affinity for "polar" constituents, but little for "nonpolar" hydrocarbons). Following the silica gel treatment, the Freon is treated as in the oil and grease test: evaporated or subjected to IR spectroscopy. Another TPH method involves gas chromatographic analysis of the Freon, and integrates the hydrocarbon peaks to obtain a total hydrocarbon concentration. Because gas chromatography separates components in their vapor state, the method is useful only for measuring the lighter (e.g., gasoline and diesel) hydrocarbons.

4.11.3.3 Biochemical Oxygen Demand

Biochemical oxygen demand (BOD_5), is a measure of how much oxygen will be consumed in the receiving water as a result of a wastewater discharge. This is of regulatory concern since aquatic animals need dissolved oxygen to survive. The test is performed by diluting a sample with oxygen-saturated water, inoculating the sample with bacteria ("seed culture"), measuring the dissolved oxygen level, incubating (holding at controlled temperature) the sealed sample for five days, and measuring the dissolved oxygen again. The oxygen consumption and the dilution ratio are used to calculated the BOD_5. BOD_5 is a measure of biodegradable organic material concentration (carbonaceous BOD, or CBOD). If the sample contains ammonia, and the seed culture contains bacteria capable of nitrifying ammonia (converting it to nitrate), then nitrogenous BOD can also be measured. If it is desired only to measure carbonaceous BOD, nitrification inhibitors can be added to the sample before analysis.

4.11.3.4 Chemical Oxygen Demand

Chemical oxygen demand (COD) is similar to BOD (both are expressed in terms of milligrams of oxygen uptake per liter of sample), but uses a powerful chemical oxidizing agent (acidified dichromate) instead of oxygen-consuming bacteria. Since it employs a more powerful oxidant, the COD of a sample is usually substantially higher than the BOD. The COD test has the advantage of being simpler, cheaper, and faster to run than the BOD test; pre-packaged test systems are available which can be run reliably by non-technical personnel. Unlike the BOD test, COD does not measure ammonia. However, in samples with high chloride levels (e.g., water which contains seawater), then falsely high readings can be obtained as part of the chloride is oxidized to chlorine.

4.11.3.5 Total Organic Carbon

Total organic carbon (TOC) is distinguished from *inorganic carbon*, which is various forms of carbon dioxide: carbonic acid, bicarbonate, and carbonate. TOC is a good indicator of total amounts of soluble organic contaminants, although not a direct indicator of harmful organics, which are determined by specific chemical tests. Generally, TOC in products terminal wastewater arises from extraction of water-soluble materials from the products.

4.11.3.6 Ammonia

Ammonia, NH_3, is a highly water-soluble byproduct of oil refining which probably is carried as contaminated water drops in refined product streams. Ammonia is essentially harmless to plants and terrestrial animals, but is toxic to aquatic animals at elevated concentrations.

4.11.3.7 pH, Acidity, Alkalinity

pH is a measure of the acid or alkaline character of water. It is defined as the negative logarithm of the hydrogen ion (H+) concentration (strictly speaking, *activity*), and ranges from <1 for extremely acidic water (e.g., strong sulfuric acid solutions) to >14 for extremely alkaline water (e.g., strong caustic solutions), with neutral pH being 7.0. Table 4-8 gives pH values for common materials. Acidic and alkaline pH values must be distinguished from *acidity* and *alkalinity*, which measure *how much* acid or base are present, as determined by the amount of base or acid, respectively, needed to make the sample neutral. A sample can, for instance, have moderately acidic pH (e.g., 6.0), but still have very high acidity. pH has a strong effect on many aqueous chemical reactions, and also on aquatic life. As a general rule, pH in the range of 6-9 is acceptable for wastewater discharges. It is worth noting that the pH of uncontaminated stormwater can be more acidic than pH 6 as a result of dissolving atmospheric carbon dioxide.

Table 4-8

pH Levels of Common Solutions

Solution	pH Range
Gastric juices	1.0 - 3.0
Vinegar	2.4 - 3.4
Soda water	2.0 - 4.0
Lemon juice	2.2 - 2.4
Tomato juice	4.0 - 4.4
Cows milk	6.3 - 6.6
Egg white	7.6 - 8.0
Limestone slurry	9.4
Ammonia water	10.6 - 11.6
Lime water	12.4

Reference: Hodgman, Charles D., "Handbook of Chemistry and Physics", 41st Edition, Chemical Rubber Publishing, Cleveland, 1959.

4.11.3.8 Total Suspended Solids and Volatile/Non-Volatile Suspended Solids

Total suspended solids (TSS) is a measure of the quantity of undissolved solids in water. It is directly measured by filtering a known quantity of water, and weighing the solids (after drying) collected on the filter paper. Although not directly harmful to aquatic life, it is usually controlled as an aesthetic nuisance, and as an indicator of wastewater treatment performance. Suspended solids can be inorganic (e.g., silt or clay particles) or organic (bacteria, plant residues, oil). To distinguish these, the filtered solids are burned in a furnace, and the weight of the ash residue is the *nonvolatile suspended solids* (NVSS, inorganics). The amount of weight lost in the burning is the *volatile suspended solids* (VSS, organics).

4.11.3.9 Total Dissolved Solids and Conductivity

Total dissolved solids (TDS) is the weighed amount of residue which remains when filtered water is evaporated to dryness. It is generally taken as an indication of inorganic salt content, but also includes dissolved, non-volatile, organic matter. It is related to electrical *conductivity* (expressed in electrical units, µmho/cm), since salts are generally electrically conductive. Of the two terms, however, TDS is the better quantitative measure of actual salt content. TDS can appear in tank bottoms water either as carried in refinery product stream water droplets, or as the result of salty water contact with the product (e.g., sea water in products delivered by marine transport).

4.11.3.10 Sulfide

Sulfide is the general term for the three forms of dissolved sulfide: hydrogen sulfide (H_2S), bisulfide (HS-), and sulfide (S=). Sulfide is produced as a byproduct of oil refining, and is also easily formed by anaerobic bacterial action in the presence of sulfate (a common water constituent). Sulfide is highly toxic to terrestrial and aquatic life.

4.11.3.11 Phenols

Phenols are derivatives of the common parent compound, phenol, also known as carbolic acid, or hydroxybenzene. Phenols are formed during refining processes (particularly cracking operations) used to make gasoline, and, being soluble in both hydrocarbons and water, are generally found in water which contacts gasoline. Although phenols are somewhat toxic to aquatic life, their main adverse effect is found when they are chlorinated in drinking water treatment: chlorophenols are very odorous and foul tasting. Phenol itself and phenolic compounds ("phenols") have their own test methods. Simple phenol is usually determined by gas chromatography, while phenolic compounds are determined by the regulatory standard method, known as the 4-amino antipyrine test.

4.11.3.12 Naphthenic Acids

Naphthenic acids are a family of water-soluble organic acids (cycloparaffinic derivatives of acetic acid, or vinegar) which are naturally found in crude oils and refined products. They are somewhat toxic to aquatic life.

4.11.3.13 Aromatics: Benzene, Toluene, Ethylbenzene, and Xylenes

These materials, known collectively as BTEX, are all simple derivatives of benzene, and are all normal constituents of crude oil and gasoline. Known chemically as *aromatics*, they are more water-soluble than *paraffins* (the other main constituent of gasoline), and are generally considered to be more harmful to aquatic and terrestrial life.

4.11.3.14 Light Non-Aromatic Hydrocarbons

Light non-aromatic hydrocarbons are paraffinic, olefinic, and cycloparaffinic hydrocarbons with 5 - 9 carbon atoms. They are the main constituent (along with aromatics) of gasoline, and dissolve in water to a small extent. There is no standard test method for these materials (except as constituents of non-gravimetric oil & grease or TPH).

4.11.3.15 Oxygenates: Ethers and Alcohols

Oxygenates are chemicals added to gasoline to improve its octane and reduce certain types of air emissions of automobiles. They are not produced from oil refining, but made in petrochemical processes or by fermentation (ethanol). Since they are much more *polar* (contain areas of opposite electrical charge density) than hydrocarbons, they are somewhat more soluble in water (the simple alcohols, methanol, ethanol, and propanol, are infinitely soluble in water, and *t*-butyl alcohol is very soluble). Ethers are alcohol derivatives; those found in gasoline are usually methyl *t*-butyl ether (MTBE), ethyl *t*-butyl ether (ETBE), and *t*-amyl methyl ether (TAME).

4.11.3.16 Surfactants

Surfactants (surface-active agents) are materials which accumulate at phase interfaces as a consequence of their dual nature: part of the molecule is oil soluble and another part is water soluble. Surfactants are very common materials: household soaps and detergents are the largest class of these materials. Surfactants stabilize oil/water emulsions, and thus inhibit oil separation, and also are known toxicants. Common sources of surfactants in terminal wastewater are naphthenic acids (see above), detergents purchased for cleaning purposes, and fuel additives. Also, fire foam testing can result in wastewater contamination by foaming agent surfactants.

4.11.3.17 Metals

Metals of environmental concern (“toxic” or “heavy” metals) are not found at high concentrations in petroleum products terminal wastewaters, and most are not found at all. Those which may be present in some terminal wastewaters at levels of concern include lead, arsenic, copper, and zinc.

Although increasingly rare due to phaseout of leaded gasoline, at one time most terminals handled gasoline with the octane-enhancing additive, tetraethyl lead. This organo-metallic material is not water soluble as such, but it can be degraded over time into the inorganic form, lead oxide (PbO), and dissolve to a small extent in tank bottoms water.

Arsenic is a natural constituent of some crude oils, and possibly of some petroleum products. Arsenic has been found in gasoline tank bottoms waters, although it is not known if it was delivered as an organo-arsenic compound (soluble in gasoline) or as an inorganic component in entrained water with the gasoline. The most likely species of arsenic in the water is the arsenate anion (AsO_4-), unusual in that the anion is quite water-soluble (other heavy metals are very insoluble in water), and in that it is anionic (negatively charged), while most dissolved metals are cationic (positively charged). In some cases, arsenic has been found at higher levels in activated *carbon effluent water than in the feed water, leading to the suspicion that at least some activated* carbons contain water-leachable arsenic.

Copper and zinc are not found in crude oil, nor used in refinery processing. Their presence at low levels in some terminal wastewaters is thought to possibly arise from corrosion reactions, since both metals are commonly used in metal alloys.

4.11.3.18 Toxicity

Toxicity is not, of course, a material *per se*, but is a property of water resulting from the presence of toxic materials (*toxicants*). Wastewater toxicity refers to the toxic effects on aquatic animals (sometimes, aquatic plants such as algae) as measured in *bioassays*. A bioassay is a test of aquatic toxicity which involves exposing a group of test animals to the water being tested (at various dilutions with clean water) under specified conditions and for a specified time, and observing the effects. The effects (*end points*) being observed include death (lethality and survival are related terms), growth (increase in animal body weight), and reproduction (or fecundity, the number of offspring from the test animals). Although any aquatic animal could be used in bioassays, the most common species are *Daphnia magna* (daphnia), *Ceriodaphnia dubia* (ceriodaphnia), *Mysidopsis bahia* (mysid shrimp), *Pimephales promelas* (fathead minnow), and *Cyprinodon variegatus* (sheepshead minnow).

There are two basic types of bioassay: acute and chronic. Acute toxicity means "immediate toxicity", and is therefore determined in a short-term test (usually, 48-96 hours), and is usually measured by survival of the test animals. An acute bioassay is run as a series of dilutions, and the percent of the test animals surviving at each dilution level is recorded. From those data, the LC_{50} is calculated as the *concentration of effluent which will kill half of the test animals under the test conditions.*

Chronic toxicity means "long-term toxicity", and is usually determined in a longer test (usually, 7 days) than the acute bioassay; the end points being determined can include any of the possible effects (lethality is generally included, since determination of the other effects requires survival of the animals). Chronic bioassays are also run as series of dilutions, with the effects at each dilution level being quantified. The test results are expressed differently from those of the acute test, and involve two terms: NOEC and LOEC. NOEC (No Observed Effects Concentration) is the ***highest concentration*** (lowest dilution) *of effluent at which **no effects** were seen in the test.* LOEC (Lowest Observed Effects Concentration) is the ***lowest concentration*** (highest dilution) *of effluent at which **any effects** were seen in the test.*

> As tests which involve the use of living organisms, bioassays are subject to analytical problems not found with chemical analyses. Properly done, bioassays involve a full suite of quality control measures, including running standards, performing duplicate testing , and running controls (simultaneous bioassays with 0 percent effluent water). The results from the tests and the quality control methods are interpreted statistically to ensure that valid test conditions were used (a test can be invalidated, for instance, if too many of the control animals die). A potential problem with bioassays is that adverse effects can be measured which are not caused by toxicants as the term is normally used. For example, a clean (toxin-free) low-salinity sample can have adverse effects on marine test animals which need salinity to survive. For these reasons, bioassay laboratories should be chosen with care, and interpretation of results should be done by

experienced technical personnel (usually biologists) who are familiar with the details and ramifications of bioassay testing.

Several of the contaminants found in petroleum products wastewater are known toxicants at certain concentrations, including ammonia, sulfide, naphthenic acids, surfactants, phenols, and metals. Table 4-9 shows conservative threshold toxic levels for these materials. In addition, any wastewater may contain other toxic materials not detectable by specific chemical analysis; this fact is the main justification for the use of bioassay testing as an effluent discharge standard.

Table 4-9

Estimated Aquatic Chronic Toxicity Threshholds

Contaminant	Safe Level	Units
Ammonia	10	ppm
Surfactants	0.2 - 28	ppm
Naphthenic Acids	2.5 - 25	ppm
Phenols	2.5	ppm
Arsenic	250	ppb
Cadmium	40	ppb
Chromium	500	ppb
Copper	200	ppb
Mercury	3	ppb
Lead	125	ppb
Nickel	100	ppb
Zinc	100	ppb

Values are conservative levels of NOEC's for common bioassay animals obtained from technical literature, and from limited testing on naphthenic acids.

Chapter 5

DESIGN OF WASTEWATER HANDLING AND TREATMENT: OVERALL PERSPECTIVE

5.1 Introduction

This section provides an overview of the process of selecting, designing and operating wastewater handling and treatment methods as a guide to the following sections which deal with specific options for these practices. The first part of this section deals with disposal options, since the choice of the final disposal technique strongly influences the required upstream water handling. The next part presents a "model system" as an indication of the direction of design for cost-effective treatment to meet various discharge standards. The final part discusses the factors which enter into design decisions to provide an indication of how these need to be integrated in development of a system design.

5.2 Disposal Options for Contaminated Water

As a facility which has the option of reducing its contaminated wastewater flow significantly, a petroleum products terminal often has several options for final disposal of the water. The option chosen can significantly affect the costs and risks of wastewater handling. These options, discussed below and summarized on Table 5-1, include disposal to public waters, disposal to a municipal treatment works (POTW), and hauling off to a refinery, an outside disposal company, or a regional treatment center.

It should be noted that this discussion is limited to contaminated water, which is relatively low-flow product-contact water such as tank bottoms water or spill containment water or contaminant-added water such as truck wash water. However, the main flow of wastewater at any terminal is likely to be stormwater, which has very limited disposal options because of its high volume. Stormwater, both clean and potentially contaminated (when clean), generally will be sent to storm sewers or public waters. Although still rare, and clearly unreasonable, some locations impose such strict limitations on *any* discharged water that even clean stormwater will have to be treated in some fashion.

5.2.1 DISPOSAL TO PUBLIC WATERS

Disposal to public waters (streams, rivers, lakes, estuaries, bays, ocean) under an NPDES permit, the most common option for major industrial dischargers, is likely to entail the strictest limits on contaminants as set by EPA and other authorities. In addition, public water discharge limits continue to become stricter and broader. This option requires experienced personnel to keep records, manage facility wastewater operations, and operate treatment equipment.

Table 5-1
Comparison of Disposal Options

Option	Advantages	Disadvantages
NPDES	Generally available	Strict limits, getting stricter Severe noncompliance penalties Possibly expensive treatment Expensive water analyses
POTW	Less restrictive than NPDES Usually available	Limits getting stricter Charges for discharge Cost of pretreatment
Refinery	No quality limits	May not be available Transportation charges
Disposal Company	No quality limits	High disposal charges Transportation charges Long-term liability
Evaporation Pond	Few quality limits	Requires arid climate Requires land area Limits on air emissions, odors Cost of pond, any treatment

5.2.2 DISPOSAL TO MUNICIPAL TREATMENT WORKS

As small dischargers often located in cities, petroleum products terminals often have the option of discharging their wastewater to city sewers (POTWs). Since a POTW has its own treatment system (usually biological treatment), limits on contaminants are usually less strict than for NPDES discharges. On the other hand, there are usually various charges, including connect charges, piping costs, flow charges, and various surcharges based on contaminant emission rates. Also, since POTWs are themselves subject to NPDES limits, limits on their customers are becoming stricter, and charges higher.

5.2.3 HAULBACK TO REFINERY

The quantity and quality of wastewater generated at the downstream pipeline and marketing terminals supplied by a refinery's products is generally quite small in comparison with the quantity and quality of wastewater produced by the refinery, which means that the refinery could accept all of these wastewaters with no noticeable impairment of its effluent quality or increase in its treatment cost. On the other hand, equivalent treatment at the terminal sites would have greater risk (of non-compliance) and much greater expense. These facts, combined with the fact that many of the most difficult contaminants in terminal wastewater are delivered as entrained water from the refinery (i.e., should not have been in the product to start with), make return of the terminal wastewater to the originating refinery a very appealing option. However, there are institutional and legal barriers to this economically favored practice, and some financial considerations.

5.2.3.1 Institutional Barriers to Haulback

When the various terminals and refinery are owned by the same company, an institutional barrier can arise from the fact that some companies have separate refining, pipeline, and marketing divisions, and that these do not necessarily cooperate in such matters because they are each organized to optimize their individual operations. Clearly, there are means for eliminating this type of barrier.

In other cases, the downstream pipeline and marketing terminals may not belong to the same company as the refinery which supplies them. Again, agreements can be worked out between the companies, unless legal barriers obstruct this, as discussed below.

5.2.3.2 Legal Barriers to Haulback

Most of the legal barriers to haulback are caused by the fact that wastewater from gasoline storage tanks from which no more product is being recovered is usually hazardous by EPA RCRA standards because it exceeds the TCLP limit for benzene (see 3.3). When wastewater of this type is transferred *within* a company, then legal problems can be minimized by the refinery stating on their RCRA TSD permit (or possibly, their NPDES permit) that *in-company* hazardous waste of this type will be accepted and treated. On the other hand, when the transfer is *between* companies, then the legal requirement is that the refinery RCRA TSD permit state that hazardous waste of this type will be accepted from *outside* the company.

Another legal problem arises from the unlikely, but possible, chance that material being hauled on public roads could spill in the event of an accident to the tanker truck. Legal liabilities and remediation costs for a hazardous waste spill could be significant.

Most of the above legal problems can be ameliorated by making the water non-hazardous prior to shipment by removing the excess levels of benzene. As described in Section 3.3, this can be done so long as the waste storage and treatment do not exceed 90 days.

Another technique for avoiding the legal problems is not to ship water *per se*, but to ship a mixture of off-spec product and water back to the refinery for processing. As described in Section 3.3.2.2, this avoids the classification of the mixture as a waste, and thus avoids RCRA involvement. For this to be a legitimate option, the following should apply:

- The mixture should contain recoverable product (to ensure this, it should not have been subjected to product separation at the terminal).

- Product *must* be recovered from the mixture after it is delivered to the refinery.

- The mixture should be handled the same as any product with regard to classification, transportation manifesting, and so forth.

- The mixture received at the refinery should *not* be handled or classified as a waste.

5.2.3.3 Financial Considerations With Haulback

The main cost of haulback is transportation cost, which can be significant if large quantities of wastewater are hauled long distances. Clearly, this can be minimized if the water flow is minimized as described in Chapter 7.

5.2.4 HAUL OFFSITE

5.2.4.1 Waste Disposal Companies

The most common destination for offsite disposal is commercial waste disposal companies, who accept the material as hazardous waste (as a rule, due to benzene content in excess of the RCRA TCLP criterion) for a disposal fee. In addition to the costs of disposal, this option also has the disadvantage of potential EPA Superfund liabilities, current and future, if final disposal is done improperly (or if the disposal company disposes of *any* wastes improperly). Also, there is at least some risk involved with shipping hazardous waste on public roads. Much of this cost and these risks can be reduced if the wastewater is rendered non-hazardous prior to shipment, as described above for haulback. Also as with haulback, the cost can be significantly reduced if the wastewater flow can be minimized.

5.2.4.2 Regional Treatment Centers

Another potential hauloff option would be to establish regional wastewater treatment centers, either within a company, or as consortia of several companies. Although technically and economically appealing, the regulatory ramifications of this option are not certain.

5.2.5 EVAPORATION PONDS OR TANKS

In arid climates, where pond evaporation is significantly greater than rainfall, evaporation ponds or tanks can be used for final disposal of wastewater. The ponds must be lined to protect groundwater and soil, and must be properly sized to achieve adequate evaporation rates (pond evaporation rates differ from the commonly-available pan evaporation rates). Enhanced evaporation can be achieved by using spray evaporation, but the degree of enhancement needs to be carefully calculated based on heat and mass transfer relationships for year-round climate conditions (solar heat input, sensible heat transfer from air, air/water interfacial area, air humidity, and change in air temperature and humidity as wind blows across the spray). Potential problems with evaporation systems include air emissions and odor emissions, which may require that the water to evaporated be pretreated. To avoid the need for RCRA implications, hazardous constituents should be removed from the water before placing it in the pond or tank.

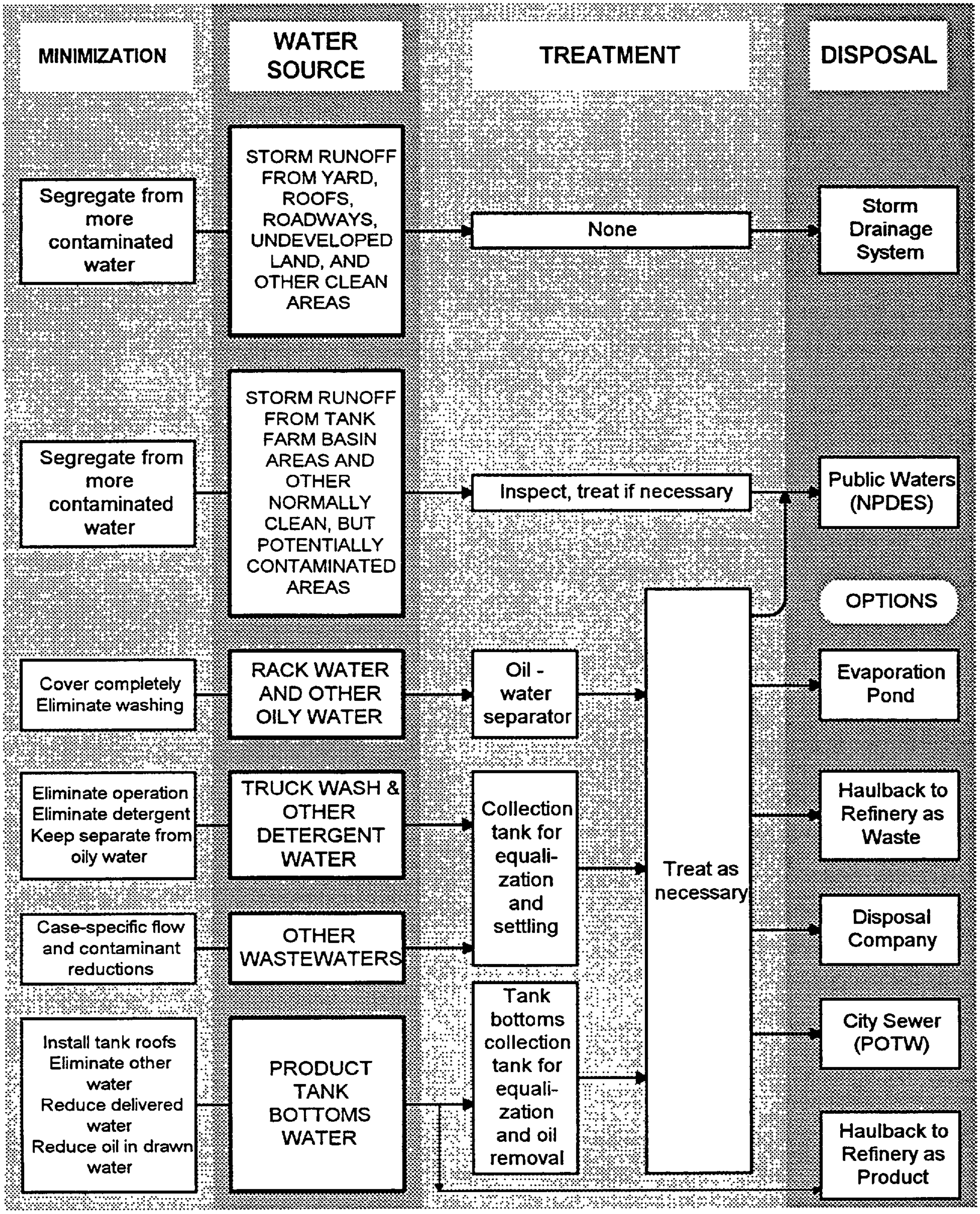
5.3 Model System

5.3.1 DEFINITION AND DISCUSSION

As used in this context, a model system is a standard for comparison, and represents the optimum system for handling and treating petroleum products terminal wastewater which could be achieved with available technology. In a real-world context, it could be thought of as the design to be applied to a new “grassroots” terminal, with minimized wastewater flow and contamination as its goal. In existing terminals, the degree to which this optimum can be approached depends on a multitude of site-specific factors, not the least of which is the capital cost of retrofitting existing equipment. The discussion of specific procedures for wastewater flow and contaminant reduction

FIGURE 5-1

OPTIMIZED TERMINAL WATER MINIMIZATION, HANDLING, AND TREATMENT SYSTEM



in Chapter 7, and of specific treatment methods in Chapter 9, should provide a better picture of the achievability of the optimum system in a given facility, and provide some guidance as to which of several techniques can best be used to achieve an improvement goal. Figure 5-1 depicts an optimum water handling system.

5.3.2 STORMWATER CLEAN AND SEGREGATED

As described in 7.2, in a model system, no stormwater would be included in the wastewater normally needing treatment. This would be done by rigorously keeping stormwater out of products tanks by providing them with fixed covers, and by thoroughly covering any loading racks or pump stations which collect spilled material. In addition, the potential for contaminating potentially contaminated stormwater would be minimized by taking appropriate measures against leaks and other accidental releases. To the extent possible, the terminal property would be classified as clean, and so allow discharge of stormwater offsite without inspection or treatment (note, however, that new stormwater regulations may reduce the benefit of this practice).

5.3.3 OILY WATER SYSTEM OPTIMIZED

Oil entry into the oily water sewer would be minimized in a model system as described in 7.4, 7.5 and 7.6 by providing measures to minimize the oil drawn with tank bottoms water, and by designing equipment to enable equipment maintenance and product sampling without discharge of oil to sewers. Tank bottoms water would all be hard-piped to a collection tank. Water draws from various product tanks would be scheduled to spread contaminant mass flows evenly over the year. The tank bottoms water collection tank would be made sufficiently large to enable equalizing contaminant levels in water sent to treatment. The collection tank would be gently mixed to optimize equalization but not harm oil separation. Oil separation from the collection tank would be optimized by providing equipment for periodically removing the oil layer. Non-separable oil/water emulsions would be minimized by not allowing detergents or solids into the oily water sewer, and by minimizing turbulence in the transfer of oily water.

5.3.4 TANK BOTTOMS WATER MINIMIZED

In addition to covering products tanks to keep out rainwater, other sources of water into the tanks would be minimized as much as possible as described in 7.7.

5.3.5 NON-OILY WASTEWATERS MINIMIZED AND SEGREGATED

As described in 7.8, if the facility made any non-oily wastewater, then its flow and contamination would be minimized to the extent practical. To maximize oil/water separation and prevent formation of emulsions, the non-oily streams would be kept segregated from oily water until oil had been separated from it. The use of water-soluble chemicals in the facility would be minimized as much as practical. Possibly, if free of regulated contaminants, the non-oily wastewater could be discharged without treatment.

5.3.6 APPROPRIATE TREATMENT APPLIED

Each of the various contaminated wastewater streams would have the type and degree of treatment applied to reliably meet discharge standards (9.3). Streams routed to treatment for removal of organic material (e.g., biological treatment) would not be mixed with organics-free streams, unless the latter had low flows or no adverse effect on the treatment. Secondary treatment would be optimized, and tertiary treatment (e.g., carbon adsorption) would be applied only if needed to meet discharge standards.

5.3.7 TREATED AND POTENTIALLY CONTAMINATED WATERS COMBINED IN FINAL BASIN, SAMPLED, AND DISCHARGED

Effluents from various wastewater treatment processes would be combined with potentially contaminated stormwater in a final mixed basin to provide polishing treatment, equalize discharge flows, and ensure that all discharged water met effluent standards.

5.4 Design Factors

5.4.1 FUTURE EXPECTATIONS

A design is made to be used in the future, and so must take into account expected changes in the facility or in the discharge requirements. Most (but not all) design features are fixed in capacity, with the consequence that it will be much less expensive to build a somewhat larger unit currently than to try to expand, or supplement, an undersized unit at a later date. The degree of anticipation (how far ahead to plan for) depends on the certainty of anticipation (how likely are expected changes to occur), and to some extent on cost analysis (earlier investment is worth more than later investment). One approach to facilitating future expansion is to use modular systems, with connections provided for future modules.

5.4.1.1 Facility Expansions, Contractions, and Changes

If a facility has plans to expand or contract the size of operations, or to make significant changes in operations, then these facts should be taken into account in the wastewater design. Some of the relevant factors are as follows:

- Changes in product throughput
- Changes in products, particularly products such as oxygenates which potentially have strong effects on wastewater
- Changes in operating practices (e.g., switching from 7-day/week to 5 day/week operation)

5.4.1.2 Tighter Regulations

Effluent regulations, whether imposed directly on the facility in an NPDES permit, or indirectly as regulations on the facility to which the wastewater is sent, determine the degree of treatment which must be designed for. Regrettably, predicting future regulations is almost impossible, and is a major problem with trying to design a wastewater system which will not become quickly outmoded. Some guidelines which may provide some help are as follows:

- If the facility is discharging under an NPDES permit, then significant design work should not be done until the permit comes up for renewal. Once a permit is granted, the discharge standards will be set at least for the duration of the permit, typically 5 years.

- If the terminal is discharging to another facility, then personnel at that facility should be contacted to determine their anticipated quality requirements, and, if possible, charges.
- Consultation should be done with experts in the area of environmental law and regulation. To avoid conflict of interest, these consultants, or their companies, should not have a financial stake in design or construction of the wastewater system. Frequently, in-house environmental consultants, if knowledgeable and customer-oriented, will be the best resources.
- Although they cannot provide guarantees on future regulations, regulatory agency personnel will frequently be able to provide sound advice on expected changes.
- If possible, and if other resources are not available, the design personnel should keep abreast of regulatory changes by reading technical literature which covers such subjects.
- Although not to be taken as absolute guides, trends in regulations should be followed. For example, if several EPA Regions are imposing effluent toxicity standards, then it may be advisable to recognize this in developing a design, even if the local Region has not yet adopted such standards in writing permits.

5.4.2 SOURCE REDUCTION VS. TREATMENT

Quite often, an effluent goal could be met by either reducing the production of a contaminant, or by providing treatment to remove it, or by various degrees of the two options. As an example, would it be better to retrofit all tank bottoms draw systems with hydrocarbon detectors, or to provide better oil/water separation equipment? The following analyzes the factors in making decisions on these issues.

5.4.2.1 Source Reduction Advantages and Disadvantages

The potential advantages of reducing flow and contaminants at their source (and thus the disadvantages of using treatment) include the following:

- Flow reduction reduces the size of all downstream equipment, including that which may have to be built at a later date.
- Source reduction of contaminants provides a permanent solution. Once a contaminant has been eliminated from the wastewater stream, treatment for it will not be needed, even if effluent regulations become stricter.
- Generally, flow and contaminant reduction measures have low operating cost.
- Source control measures are generally more reliable (less likely to malfunction) than treatment measures, mostly because they are “low-tech”, as opposed to “high-tech” treatment. As an example, eliminating use of detergents is a much more reliable method for keeping surfactants out of effluent than is operating a “surfactants removal system”.

The potential disadvantages of flow and contaminant source reduction, and thus the advantages of treatment, include the following:

- The capital cost of source reduction can be (but is not necessarily) higher than that of treatment. This determination needs to be made on a case-by-case basis.
- Source reduction is often dispersed throughout the facility, while treatment occurs at a single location.
- Installation of source reduction will probably disrupt operations more than installation of treatment. By its nature, source reduction is intimately involved with the wastewater generating operations, while treatment is a "stand-alone" process. Most changes on product tanks, for example, require taking the tank out of service, which can be a major cost and inconvenience. One way around this factor, if scheduling allows, is to make source correction changes on a piece of equipment only when that equipment is out of service for maintenance.
- Practice of some reduction measures can adversely affect operations. Elimination of use of detergents, for example, may result in operation of dirtier equipment, and could even jeopardize safety if slick oil were left on concrete slabs as a result. The effects of source reduction measures on facility operations and personnel should be examined and discussed with personnel before deciding to implement them.

An overview of which source reduction measures are most likely to be cost-effective when compared with treatment is given in 7.9.

5.4.3 COSTS

Although listed because it is an essential factor, design personnel do not need reminding that capital and operating costs will be key factors in selecting wastewater handling and treatment designs. It is perhaps worth noting that, although terminals are essential elements of the petroleum products distribution chain, they are not normally considered to be profit centers, and that any investment or increase in operating cost can be difficult to justify to company management since payback on investment cannot be directly demonstrated.

5.4.3.1 Operating Cost Elements

Typical elements of operating costs for wastewater handling and treatment systems at petroleum products terminals include:

- Manpower. Since most terminals do not have many employees, this can be a significant cost item. Moreover, if the treatment system is complex, or local regulations require it, the operators have to be well-trained in handling normal operations and upsets, which means that (1) more expensive qualified personnel may have to be utilized, and (2) training costs have to be included.

- Analyses. Analytical costs for discharged wastewater can be very high, particularly if specialized tests such as priority pollutants or bioassays are required. Also, experienced personnel will be needed to interpret the analytical results in those cases where non-compliance with permit limits is indicated.

- Electric power. Electric power is used for pumping, mixing, aeration, and specialized functions such as ozone generation, and can be a significant cost item in some systems.

- Chemicals. The main treatment designs with significant chemicals costs are those which use chemicals, such as hydrogen peroxide, as a main reagent. Other typical chemicals include acids and bases, and flocculating agents.

5.5 Wastewater Handling and Treatment Investigation and Design Procedure

This section provides an overview of procedures which can be used to determine the optimum wastewater handling and treatment methods for a given terminal's situation. The procedure is outlined on Figure 5-2.

5.5.1 DEVELOP BASIC WASTEWATER CHARACTERIZATION DATA

As with any investigation, the first step is to determine the relevant facts about the existing situation. This includes the material in sections 6.1 - 6.4 on the basic terminal equipment layout and the flow of water from inputs through routings through collections down to the current discharges. In addition, the basic terminal design and operating information on the Terminal Fact Sheets as described in 6.7 and included in Appendix A should be collected.

5.5.2 IDENTIFY POTENTIAL DISPOSAL METHODS FOR WASTEWATER

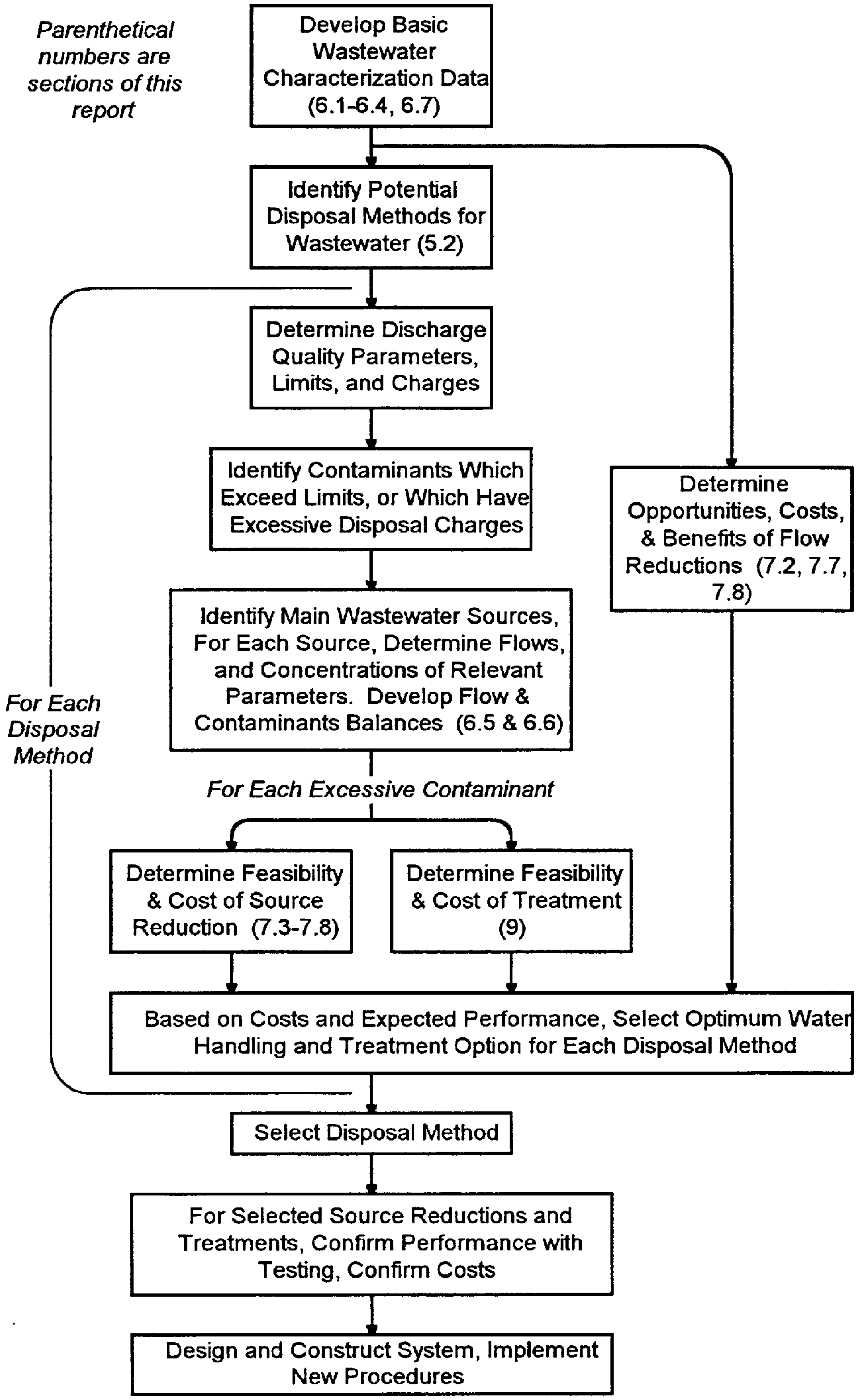
Most terminals, particularly those with low flow of contaminated water, have several options available for the final disposal of their wastewater. The selection of this option is perhaps the most important decision in the design process, since it strongly affects the degree of source reduction and wastewater treatment which will be needed, and thus the cost and reliability of the final system. At this point in the investigation, all reasonably likely disposal options should be listed. Section 5.2 lists the commonly available disposal options, along with their advantages and disadvantages.

5.5.3 DETERMINE OPPORTUNITIES, COSTS, AND BENEFITS OF FLOW REDUCTIONS

To some extent, any terminal will potentially benefit (have lower wastewater handling, treatment, and disposal costs) from reducing the flow of its contaminated water. At this point in the investigation, at least the more cost-beneficial opportunities for flow reductions (see 7.2, 7.7, and 7.8) should be investigated with regard to approximate cost and degree of flow reduction. At the very least, this should include determination of the feasibility and cost of segregating all storm water from contaminated water. It should be noted that some flow reductions also result in contaminants flow reductions, so this step should be integrated with 5.5.7.

FIGURE 5-2

OUTLINE OF WASTEWATER HANDLING AND TREATMENT INVESTIGATION



Parenthetical numbers are sections of this report

5.5.4 FOR EACH DISPOSAL OPTION, DETERMINE DISCHARGE QUALITY PARAMETERS, LIMITS, AND CHARGES

Every disposal option will have its own requirements on the quality of the water which is sent to that disposal, ranging from extremely broad and strict requirements for some NPDES permit discharges to public waters to essentially no quality requirements for some disposal companies or refineries to which the water can be hauled. All of the regulated parameters for each disposal option should be identified, along with the numerical limits on the concentrations. For any option other than NPDES discharge, there may be disposal fees, to some extent proportional to the amount of water and contaminants levels in the water, which should be determined.

5.5.5 IDENTIFY CONTAMINANTS WHICH EXCEED LIMITS, OR WHICH HAVE EXCESSIVE DISPOSAL CHARGES

From the various disposal options of 5.5.4, a master list of contaminants of concern (those regulated or charged for) can be assembled. Since some disposal option restrictions will include irrelevant parameters (e.g., pesticides in an NPDES permit), the list should be pruned to include only those contaminants reasonably likely to be present (Table 4-4 may provide some guidance on this). Once the list is finalized, the next step is determining which contaminants are actually present at the terminal at levels of concern. If the terminal already has a combined wastewater discharge, this can be done by analyzing it. If the terminal has multiple discharges, then each will have to be analyzed.

5.5.6 IDENTIFY MAIN WASTEWATER SOURCES. FOR EACH SOURCE, DETERMINE FLOWS AND CONCENTRATIONS OF RELEVANT PARAMETERS. DEVELOP FLOW AND CONTAMINANTS BALANCES.

Once the above analysis has shown which contaminants are of concern (i.e., exceed disposal option limits, or are charged for at rates of concern), the next step is determining from where in the terminal the contaminants are coming. This is done by developing a *contaminants balance*, which is the flow (e.g., pounds per week) of each contaminant from each in-plant source. To develop a contaminants balance, it is necessary to measure (or accurately estimate) the volumetric water flow from each source, to analyze the source water for the contaminants of concern, and by multiplying these, to obtain the contaminant mass flows. As a check, the balance can be developed, which means that the sum of the sources should add up to the contaminant mass flow in the combined water discharge. Sections 6.5 and 6.6 can provide guidance on this procedure.

5.5.7 FOR EACH EXCESSIVE CONTAMINANT, DETERMINE FEASIBILITY AND COST OF SOURCE REDUCTION

Up to this point in the investigation analysis, the activities have been relatively straightforward. For this step, and the next parallel step, the analysis becomes considerably more complex, since it is necessary to examine a multitude (in most cases) of contaminants with regard to the opportunities for source reduction and treatment. The source reduction examination requires broad knowledge of the nature of the sources to see if they are reducible (for example, eliminating detergent contaminants can be as simple as stopping their use in the terminal, whereas eliminating benzene in gasoline tank bottoms water is essentially impossible). Sections 7.3 through 7.8 should be consulted for guidance on this. Note that flow reductions investigated in step 5.5.3 will result in reductions of some contaminant flows. Once reduction methods have been identified, the costs of the reductions should be estimated.

5.5.8 FOR EACH EXCESSIVE CONTAMINANT, DETERMINE FEASIBILITY AND COST OF TREATMENT

In parallel with determining the opportunities for source reduction, the alternative of treatment for removal of the various contaminants of concern should be examined. Since there are a multitude of treatment methods for each contaminant, and many treatments which remove more than one type of contaminant, this is even more complex than determination of source reductions. Chapter 9 includes an overview of available treatment methods, along with some guidance as to which treatments are appropriate for individual contaminants. Once potential treatment methods have been identified, approximate costs should be estimated.

5.5.9 FOR EACH DISPOSAL METHOD, SELECT OPTIMUM WATER HANDLING AND TREATMENT OPTION BASED ON COSTS AND EXPECTED PERFORMANCE

At this point in the investigation, the options are narrowed by determining the most cost-effective means (combination of water flow reductions, contaminant flow reductions, and wastewater treatments; see 5.4.2) for handling the requirements of each disposal option. The investigation at this point can be summarized as a table with three columns: disposal option, capital cost to meet requirements, and operating costs to meet requirements.

5.5.10 SELECT DISPOSAL METHOD

From the foregoing investigation and the summary in step 5.5.9, it should be obvious as to which disposal method is to be preferred on a cost basis. In making the final decision, non-financial factors such as not wishing to be dependent on outside disposal companies, or not wishing to deal with arbitrary NPDES regulation, can also be taken into account.

5.5.11 FOR THE SELECTED SOURCE REDUCTIONS AND TREATMENTS, CONFIRM PERFORMANCE WITH TESTING, AND CONFIRM COSTS

At this point, it should be recognized that most of the above evaluations of the effects of source reduction practices, and of wastewater treatment performance, are only estimates. As noted in Chapter 9, application of identical treatments to nominally similar wastewaters from various terminals has shown highly variable degrees of treatment, with the implication that no treatment method should be adopted without testing (see 9.4.7). For this reason, laboratory or pilot testing should be done on any treatment included in the 5.5.9 plan selected for the 5.5.10 disposal method. The results of the testing should be used to refine, and if necessary, modify, the treatment plan. The testing will show not only treatment performance, but will also provide treatment sizing, and therefore cost, values, which should be used to refine the cost estimate. Although some flow and contaminant reduction methods will have clear-cut results, others may be less certain, and testing should be done, if possible, to confirm that the planned reduction methods will achieve the planned reductions.

5.5.12 DESIGN AND CONSTRUCT THE SYSTEM, AND IMPLEMENT NEW PROCEDURES

As the culmination of the investigation and design procedure, the final conceptual design developed and confirmed in 5.5.11 can be expanded into a detail design, to be followed by equipment procurement and construction. Since the plan may include changes in terminal operating procedures, these should be phased in as the design and construction proceed.

Chapter 6

SOURCE IDENTIFICATION

6.1 Overview

Every facility should have a basic understanding of its water and wastewater systems, including the significant sources of water entering the facility, the routing of the intake water to various destinations, including wastewater, characterization of significant wastewater sources, wastewater collection system, and wastewater disposal. For most terminals, such systems are relatively uncomplicated.

The elements of a water system assessment are a water system process flow diagram, a supply water system map, a wastewater sewer diagram, and a wastewater flow and contaminants characterization. Although the information need not necessarily be obtained to the degree of detail illustrated herein, depending on the specific facility design requirements, at least basic information of each type should be obtained for each facility. It should be noted that many NPDES permit applications require that some of this type of information be provided.

6.2 Water System Process Flow Diagram

A water system process flow diagram is a schematic which shows all significant streams of water entering and leaving the facility, and all the routing through pipes, sewers, ditches, vessels, and ponds in between. Figure 6-1 is an example of such a diagram for a marketing terminal. Such a diagram is essential for understanding the complete water system, and seeing how the various parts interact.

6.3 Supply Water System Map

The supply water system map shows the physical location of supply water and steam lines on a facility map. Figure 6-2 shows an example of a general arrangement plan, with supply water lines included. The function of the map is a reference for locating supply lines for maintenance, upgrading, sampling, and so forth.

6.4 Wastewater Sewer Diagram

The wastewater sewer diagram shows the physical location of all wastewater piping, sewers, ditches, and ponds in the wastewater collection system, and is needed for such activities as sampling and flow measurement. An example for a marketing terminal is shown on Figure 6-2.

6.5 Wastewater Flow Characterization

In order to design wastewater handling and treatment equipment, it is necessary to have a reasonably accurate picture of the flow of the streams being handled and treated, and the level

FIGURE 6-1

EXAMPLE OF MARKETING TERMINAL WASTEWATER PROCESS FLOW DIAGRAM

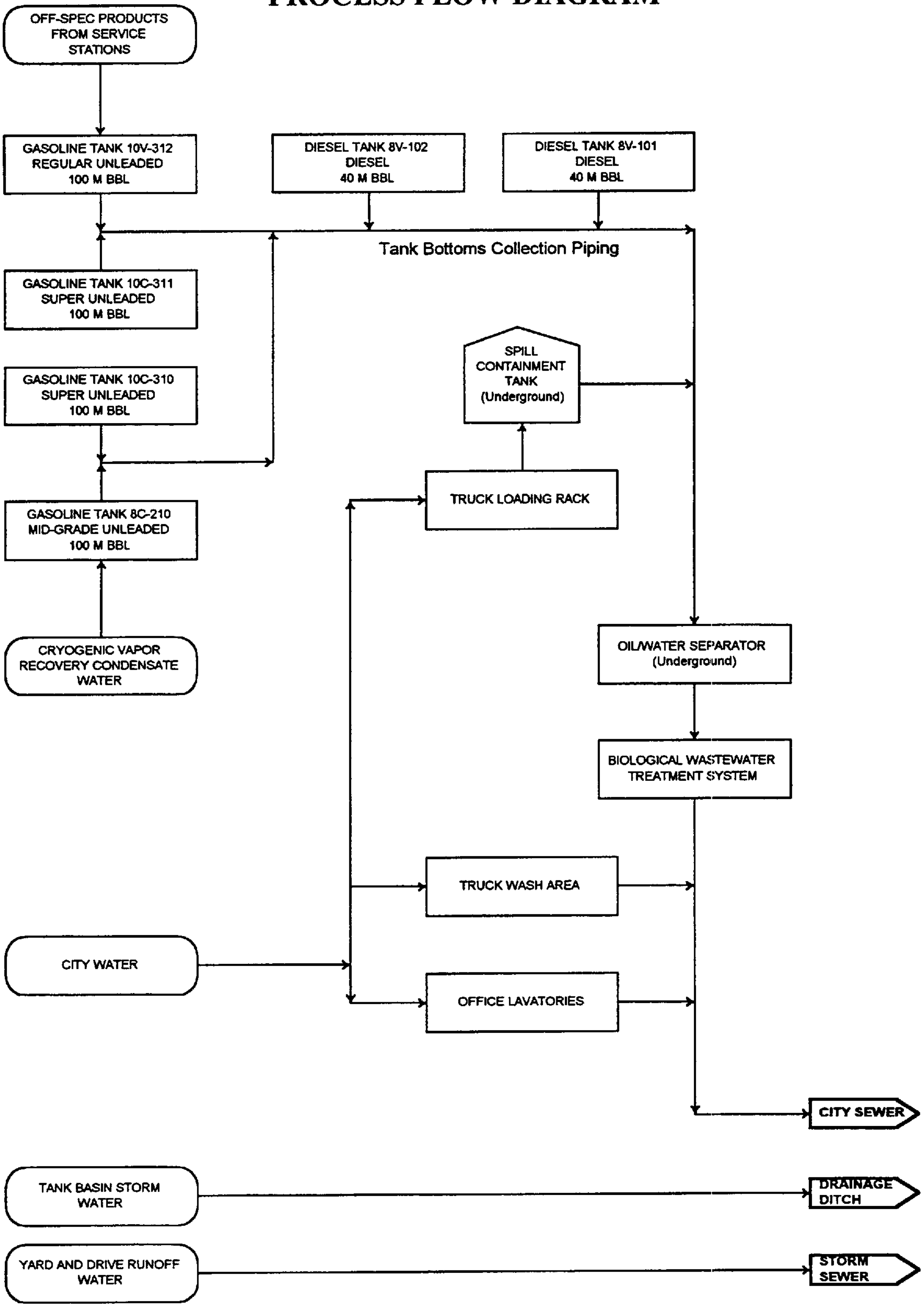
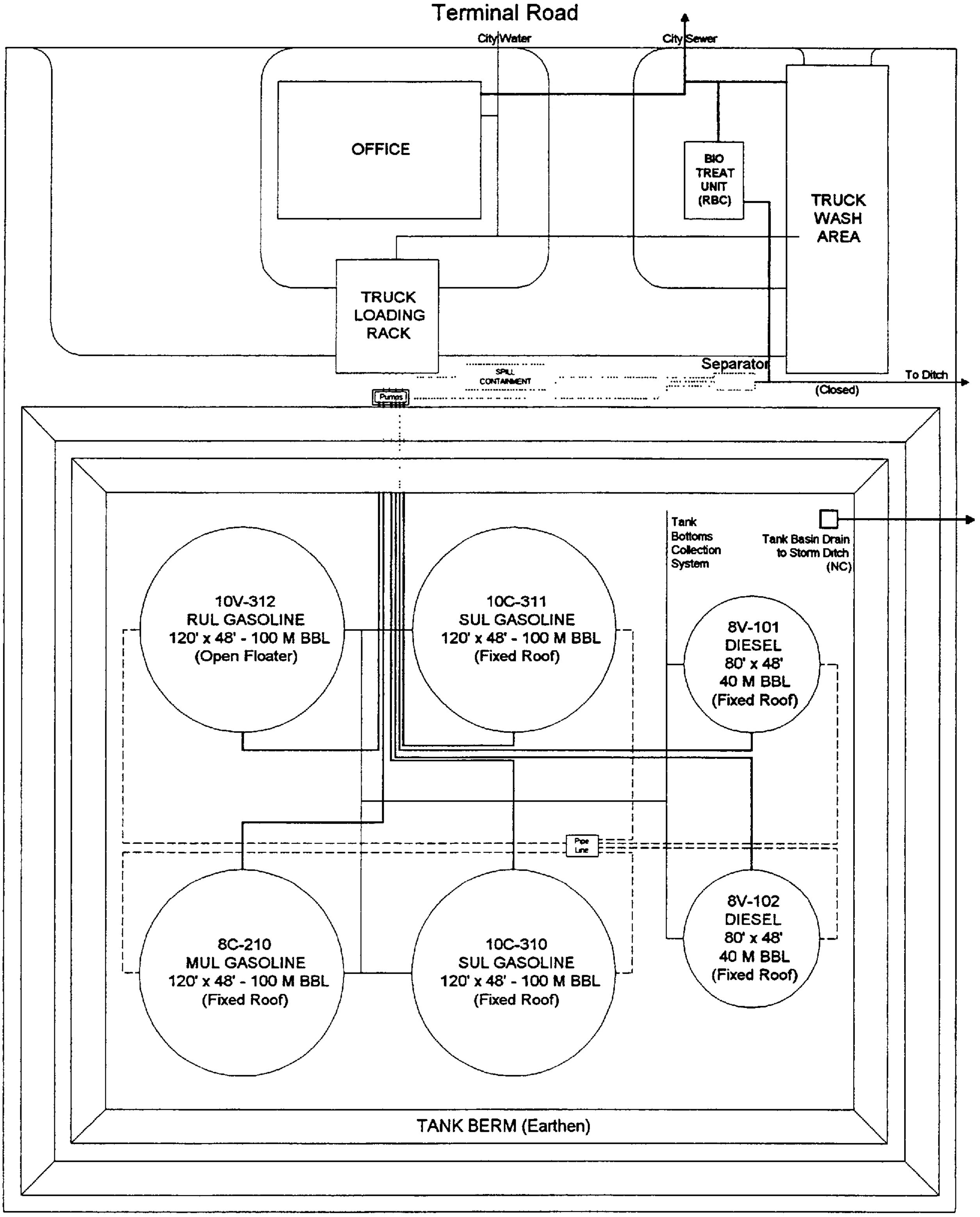


FIGURE 6-2
EXAMPLE OF MARKETING TERMINAL GENERAL ARRANGEMENT PLAN WITH WATER SUPPLY LINES AND WASTEWATER LINES



of various contaminants in the streams being treated. Unfortunately, obtaining this picture for petroleum products terminals is not simple, since the individual flow sources are sporadic (unlike, for instance, refinery process unit flows). The major contaminated water stream, tank bottoms water, flows only when the tank bottoms are drawn, which may be only once a year for a given tank, and the normal high-volume wastewater stream, storm water, flows only during storms. Techniques for characterizing a terminal's wastewater are outlined below.

6.5.1 FLOW BALANCE DIAGRAM

A flow balance diagram, shown by example in Figure 6-3, is a useful tool for quantifying the sources of wastewater in a terminal. As shown, each significant process source of wastewater is shown as a block, with water inputs of various types as vertical lines to the left of the sources, and transfer systems as vertical lines to the right of the sources. Each stream has a flow with common units; for a high-flow terminal, gpm may be the appropriate flow unit, while for a low-flow terminal, in which tanks are drawn infrequently, gallons per year (gpy) may be more appropriate. The following sections describe how flow measurements can be done for various sources.

6.5.2 TANK BOTTOMS FLOW

6.5.2.1 Tank Bottoms Wastewater Generation

The only reliable method for determining the overall production of tank bottom draws is measuring and recording the quantities of water from each draw (see 7.4.1.1 on tank water volume measurement) over a sufficient length of time (at least long enough to obtain records for each tank) to develop reliable measurements. To determine the contaminants production, each tank bottoms water should be sampled and analyzed for all contaminants of concern (those regulated on the existing discharge permit, expected to be regulated on a future discharge permit, or needed for design) at the time of water drawing (best), or at any other time. If tank bottoms draw records are not available, and tank bottoms production rates are needed quickly, then the next-best alternative is to gauge the amount of water in each tank (see 7.4.1.1), and to re-gauge it after enough time has elapsed to allow significant water accumulation.

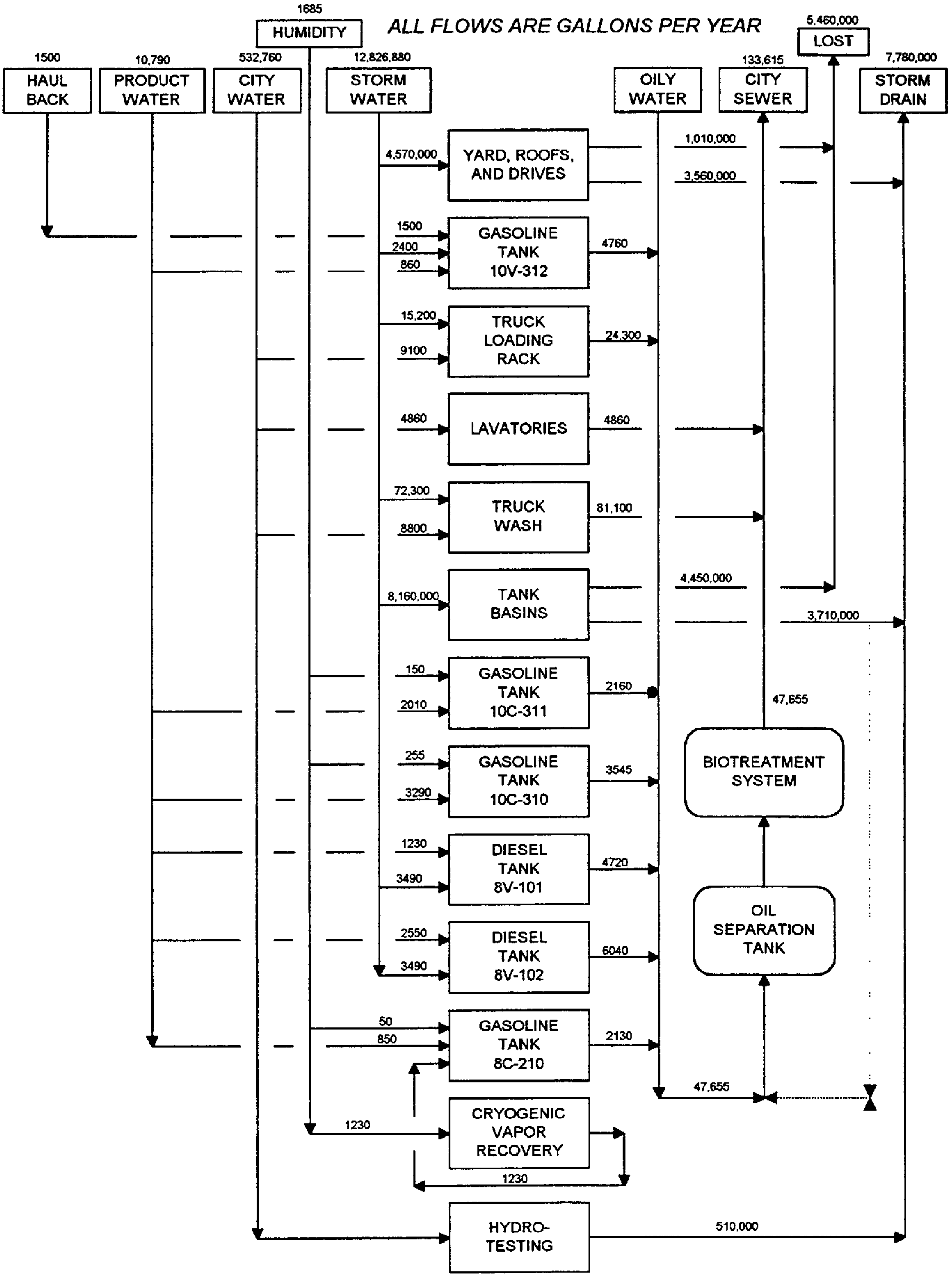
Determining the *sources* of water to each tank is more difficult, but may be important if flow reduction is planned.

6.5.2.2 Storm Water Flow Into Open Floater Tank

Probably the best means for determining the storm water flow into an open floater tank is to accurately gauge the tank bottoms volume before and after a storm, and to measure the amount of rainfall for the storm, and to ratio these to give a "gallons of tank bottoms per inch of rain" coefficient for the tank. Since rain penetration into an open floater is a function of rain hitting the inner tank shell and running down past the floating roof seal, the *angle* of the rainfall, as influenced by wind, may be significant. For this reason, the rainfall coefficient for the tank may have to be determined several times to obtain an average figure.

FIGURE 6-3

EXAMPLE OF MARKETING TERMINAL WATER FLOW BALANCE



6.5.2.3 Tank Breathing and Condensation in a Covered Tank

Condensation of water resulting from cooling of humid air entering a covered tank is probably not a major source of tank bottoms water, and can best be estimated by calculating annual air input into a tank (should equal annual tank product draw volume plus calculated breathing input [REA Staff]) and estimating the average change in absolute air humidity resulting from average tank air temperature changes.

6.5.2.4 External Sources of Tank Bottoms Water

If water is placed into a tank from outside sources (e.g., haulback of offspec product from service stations), then the amount can either be measured directly from the volume or flow of outside water source, or can be determined by accurately gauging the water volume in the tank before and after a water delivery (for sporadic water inputs), or by measuring the rate of water accumulation in the tank (by timed gauging of tank water volume) with and without the external source being on (for continuous water inputs).

6.5.2.5 Water Delivered With Product

Water delivery with product can be a significant source of tank bottoms water flow and also contamination, and so is an important volume to determine. Unfortunately, it is also a difficult measurement to make. If the volume is significant, then it can best be determined by measuring the tank water volume before and after a product delivery, and either shutting off, or taking into account, other water sources for the same time period. If, as is typical, the water content of the delivered product is not large (but still significant in annual accumulation, and in contaminant load), then it cannot be measured in this way, both because the amount of water in a delivery is too small to accurately measure, and because the water is likely to be in the form of small water droplets which take a long time to settle to the bottom of the tank.

If the tank has a fixed cover, and no other sources of water (or sources whose flow is accurately known), then the amount of water delivered with product can be obtained by difference: the annual product water flow equals the annual tank wastewater accumulation minus the other known water source flows (if any).

As another approach, and assuming that the incoming product has a uniform water composition (i.e., is the same at the start and end of the delivery), the water content of the product can be measured by sampling the delivered product, and performing a Karl Fischer water analysis on it (this determines water content in the ppm range).

6.5.3 STORM WATER FLOW

The best technique for predicting storm water flow from a given drainage area is to determine a *runoff coefficient* for the drainage area. The runoff coefficient is the fraction of rainfall on an area which becomes runoff water (i.e., the fraction which does not evaporate or percolate into the ground during and after a rain). For any given rainfall situation (annual average, 10-year storm, etc.) it can be used to calculate the number of gallons of runoff water to be expected from the area. In order to determine the runoff coefficient, the volume of water running off an area during and immediately after a storm should be measured, and compared with rainfall as measured by an onsite rain gauge (any open-top straight-sided container will do, if set well away from obstructions). Measuring the volume of the runoff can be difficult. The most reliable method is collection of all the runoff in a tank or pond, and measuring the collected volume directly. If this is not possible, then channeling all the runoff flow through a recording flow meter (e.g., a Parshall flume with detector and recorder), and integrating the flow over time, will enable calculating the volume. In a tank farm, the drains from the containments can be shut off during the storm (as they should be anyway), and the depth of water in each containment measured after the storm before draining the water. Since many tank farms have irregular shapes and contours, determining the volume this way may be difficult. If direct measurement of runoff cannot be done, the runoff coefficient can be calculated based on estimated values for various types of surface.

6.5.4 PRODUCED GROUNDWATER FLOW

Unlike most terminal streams, groundwater production is usually continuous, and its flow can be measured with a flowmeter in the pump discharge collection line, or by running the water into a tank for a measured time period, and determining the volume collected by measuring the water depth and multiplying by the tank cross-sectional area.

6.5.5 WASTEWATER FLOWS RESULTING DIRECTLY FROM INTAKE WATER USE

Many wastewater streams may result directly from use of intake water; examples include loading rack slab washup water, sanitary water, boiler feed water, and laboratory water. To measure these streams, a very accurate means is available: metering intake water. Using the facility intake totalizing turbine water meter (installed, if not already existing for municipal water), the volume of a sporadic water use can be directly measured if other water uses are discontinued during the test, or the flow of a continuous water use can be measured by timed volume of water consumption (if other uses cannot be turned off, then the continuous use can be measured by the *drop* in water consumption when the stream in question is turned off).

6.5.6 FLOW OF OTHER STREAMS

Flows of other, usually minor, streams can be measured with a flowmeter (if continuous) or by volume accumulation (if sent to a tank normally, or during a flow test). The flow of some streams may be determined indirectly. Steam condensate flow from a tank heating system can be determined by metering steam production, or boiler makeup water consumption.

6.6 Wastewater Contaminants Characterization

In addition to determining flow, it is also critical in a wastewater handling and treatment design to quantify the amount (mass flux, e.g., lb/day or lb/year) of contaminants from various significant sources. This is normally done by measuring the water flow from a source, analyzing the water for the contaminants of concern, and multiplying these. Another approach for some contaminants and sources is direct measure of contaminant input to the plant before it enters the wastewater.

6.6.1 SELECTION OF CONTAMINANTS

Chemical analyses are expensive, and it is desirable to limit the contaminants source investigation to significant contaminants. The criteria for significance are

- the contaminant is on, or expected to be on, the facility discharge permit or other discharge criterion document
- the contaminant is known to be present in facility wastewater at levels of concern, i.e., at levels which could cause non-compliance with limits, or result in contaminant charges
- the contaminant is possibly present in the wastewater source in question
- the contaminant is one which will affect the existing or proposed treatment system (for example, it is necessary to know BOD and COD for wastewater fed to a biological treatment unit even if these parameters are not on the discharge permit).

6.6.2 SAMPLING

Although samples for some wastewater contaminants can simply be taken by running them into a container, many require specialized techniques. One general rule on sampling through nozzles on tanks or lines is that the sample needs to be run long enough to purge the nozzle contents before the sample is collected.

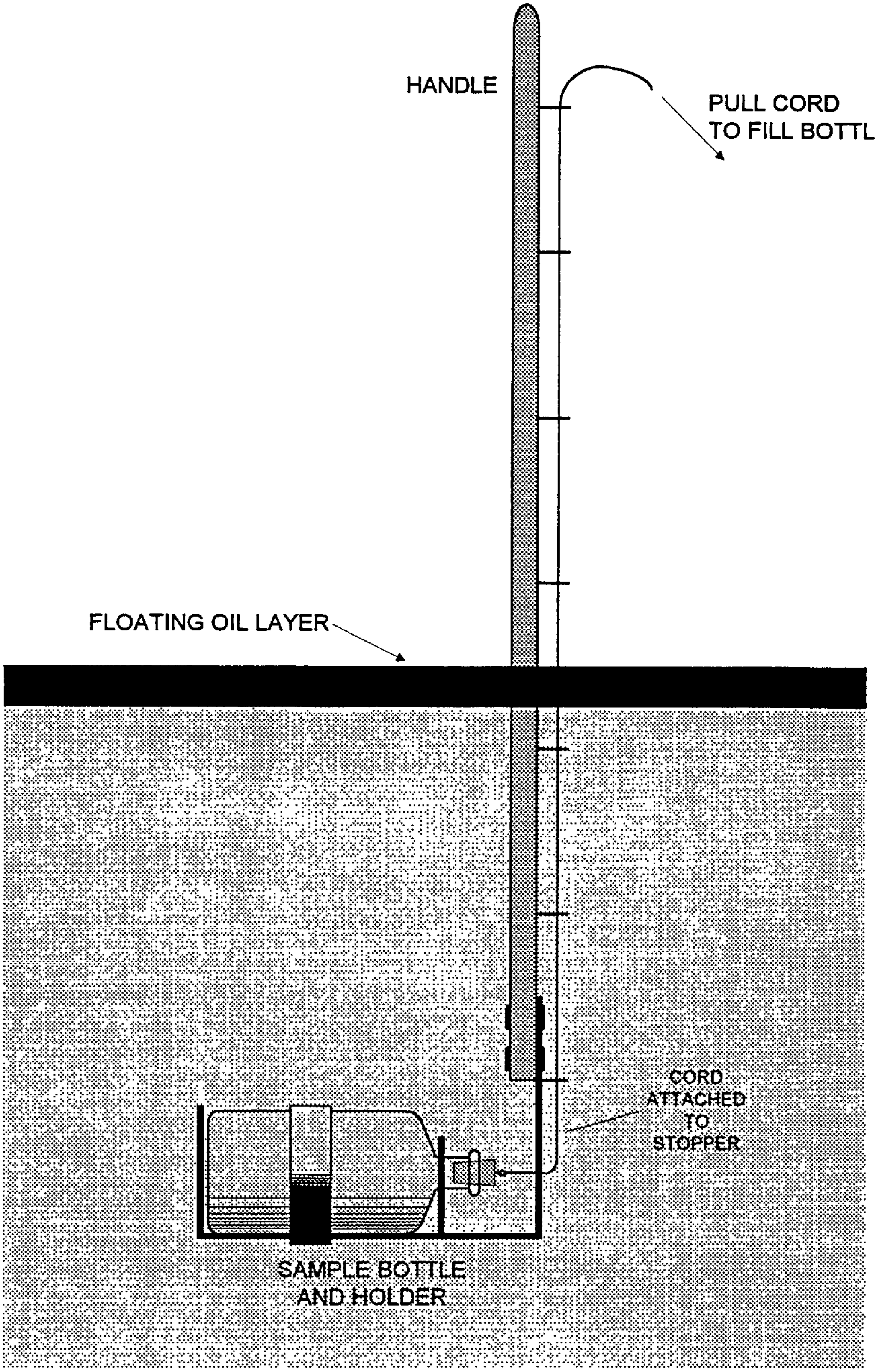
6.6.2.1 Oil & Grease and TPH Sampling

Oil & grease samples need to be taken only in clean glass 1 quart (or one liter) bottles, and need to be taken directly into the bottle (not transferred from one container to another). The reason for this is that oil adsorbs readily on container surfaces, and so would be lost if transferred from one container to another. Glass must be used, because oil would adsorb too strongly on plastic to be washed out by the extraction Freon (part of the test procedure).

Obtaining *representative* (containing the same amount of oil as the water stream being sampled) samples of oil & grease can be very difficult unless the oil is well homogenized (dispersed evenly throughout the water stream); more commonly, however, the oil is at least partially floating on the wastewater surface. If there is a floating oil layer, the only way to obtain a representative sample for oil & grease is to collect the entire wastewater stream into the sample bottle. Obviously, to collect an entire stream into a one-quart bottle requires that the stream have low flow; in addition, the entire stream must be accessible: there is no practical means, for instance, to collect the entire flow of wastewater in an underground sewer line. The best resolution of this problem is to assume that floating oil will be readily separated in downstream oil/water separation equipment (a good assumption, unless the oil and water are emulsified on their way to the separator), and so to try to obtain a sample of the water underneath the floating oil (the water will contain emulsified oil, which is much more critical, since it is not readily separated downstream).

To obtain a water-under-oil sample from an open channel (ditch or part-filled sewer), the sample bottle should be corked, immersed under the water surface, and then uncorked to allow the water to run in. A simple device for doing this is shown on Figure 6-4; commercial devices can also be obtained.

FIGURE 6-4
SUBSURFACE SAMPLER



To obtain a water-under-oil sample from a flowing pipe, the sample should be run into the sample bottle from a nozzle on the bottom of the pipe (best), or the side of the pipe (next best), but never from the top of the pipe.

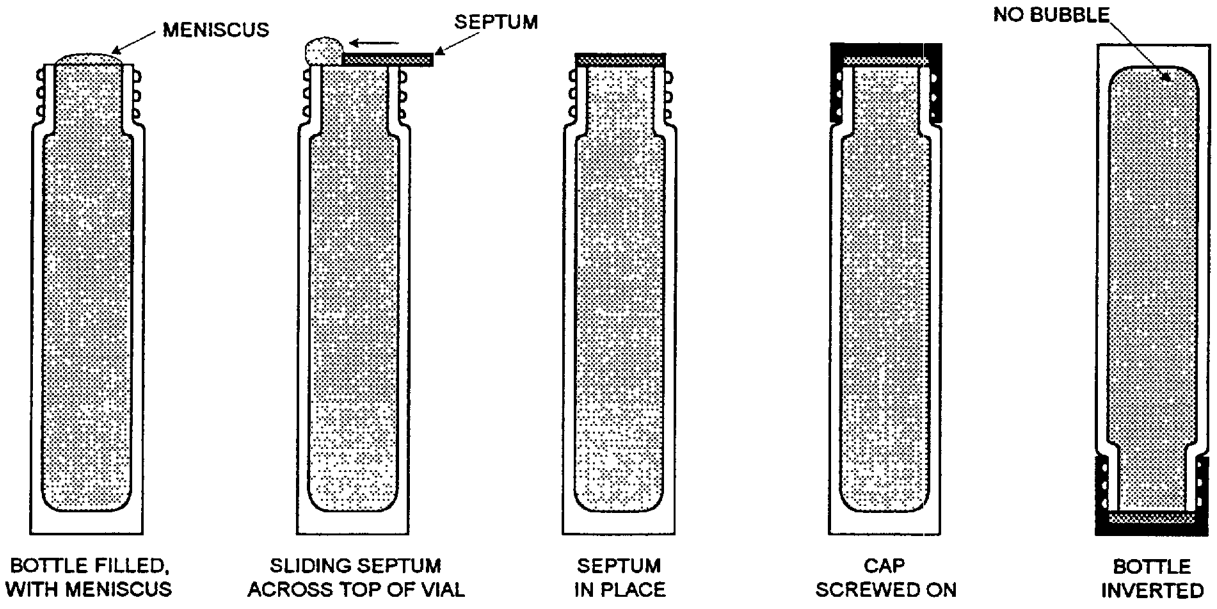
The oil content of water drawn from a product tank will change as the water draw progresses, probably from initially low to pure product at the end of the draw. In this case, the sampling should be done multiple times throughout the draw period, or alternately, taken only during the initial part of the draw as an indication of suspended oil content.

6.6.2.2 Volatiles Sampling

Sampling volatile materials such as BTEX and other volatile materials such as ethers requires special sample bottles known as VOA bottles. The technique for using such bottles, shown on Figure 6-5, is to slowly fill the bottle so full that a *meniscus* (upwardly bowing water surface) appears, carefully sliding the Teflon-lined septum across the bottle top, and then tightening the plastic cap over the septum. The bottle then needs to be inverted to make sure that no air bubble is in it. This technique, known as *zero headspace*, is done to make sure that none of the volatile contaminant is lost into an air bubble.

FIGURE 6-5

FILLING VOA BOTTLES



6.6.2.3 TSS and VSS Sampling

Although, like oil & grease, suspended solids can separate (settle) from water when it stands, there is not the same concern with adherence to sample container walls. For this reason, it is allowable to make multiple sample transfers in obtaining a TSS sample, so long as the sample is *well mixed* prior to each transfer.

Sampling for suspended solids, like sampling for oil & grease, requires some care in obtaining a representative sample, since solids can settle. Sampling techniques are similar to those for oil & grease, but with the opposite concern: samples should not be pulled off the *bottom* of a line, or open channel, and should not be obtained in the *initial* part of a tank water draw.

6.6.2.4 Sampling for Other Contaminants

Many contaminants have both soluble and insoluble fractions; BOD, COD, and TOC, for example, are present in both oil phases and solid phases, as well as being dissolved. Metals are commonly found both as suspended solids and as dissolved in water. Because of this factor, it is desirable to avoid floating oil and settled solids in samples for these contaminants, and the precautions noted above for sampling for oil & grease and for TSS should be followed.

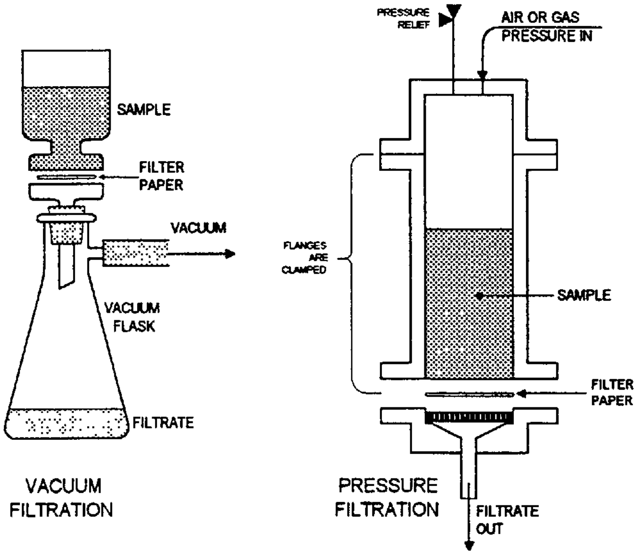
6.6.2.5 Sample Filtration

For those contaminants which, as noted above, have both soluble and insoluble components, it is often very useful to know how much contaminant is in each phase. To determine this, part of the sample should be filtered, to obtain a "soluble" analysis to accompany the "total" analysis (the "insoluble" fraction will be obtained by difference). Since solubilities change with time, and since some preservation techniques (see below) drastically change the solubilities (e.g., many samples are preserved with acid, which dissolves metals and other materials), the fresh sample should be filtered as soon as possible. Sample filtration involves a very specific technique, using filter paper with very small pores (about 0.5 micron), and some means for forcing the water through the filter paper (either by placing the filtrate under vacuum or the water to be filtered under pressure). Samples with volatile materials of interest (e.g., dissolved ethers), should only be pressure-filtered, since vacuum filtration will cause significant loss of such materials. Options for filtration, pictured on Figure 6-6, are as follows:

- Vacuum filtration using a water aspirator as a vacuum source. Aspirators are available from laboratory supply houses.
- Vacuum filtration using a vacuum pump (obtainable from laboratory supply houses) as a vacuum source. It is best to use a water trap to make sure that water does not get into the vacuum pump oil.
- Pressure filtration using air or nitrogen pressure (about 15 psi is required); air can be obtained from compressor, and both air and nitrogen can be obtained

FIGURE 6-6

SAMPLE FILTRATION



from commercial pressure cylinders (NOTE: pressurized oxygen should *not* be used, since detonation of the pressure filter could occur.)

6.6.2.6 Field Blanks

A *field blank* is a sample taken in the field in the same manner as wastewater samples, but instead of wastewater, clean water (distilled or deionized water) is used. The field blank sample is analyzed for the same constituents as the wastewater samples. The purpose of the field blank is to detect impurities resulting from sources extraneous to the wastewater, such as the sample container, preservative materials, or the atmosphere. It is particularly useful for trace contaminants, i.e., those contaminants present at low, but significant, concentrations. Whenever such materials are being sampled for, field blanks should be taken on every sampling occasion.

6.6.3 PRESERVATION

Almost all wastewater samples require special types of preservation as summarized on Table 6-1. Note that most samples require refrigeration, so either a sufficiently sized refrigerator, or an ample supply of ice, should be available. In addition, the samples must be iced while being transported to the analytical laboratory. If filtered samples are being obtained, the filtration should be done before the preservation is applied. Also note that each type of sample has a specified maximum holding time before it is analyzed. Samples which exceed this time should be discarded, and the sampling repeated.

6.6.4 ANALYTICAL METHODS

Table 6-1 summarizes the analytical techniques for most of the contaminants likely to be of concern to petroleum products terminals.

6.6.5 RECORDS OF PURCHASED MATERIALS

For contaminants found in purchased materials, the best technique for determining the amount to be expected in wastewater is often not to analyze the wastewater, but to determine how much material is being used. A good example of this is detergents, since it is easier to keep track of detergent usage, or purchase, than to analyze for surfactants in wastewater. Other materials in this category include boiler water chemicals and laboratory chemicals.

6.7 Terminal Survey/Checklist Form

A checklist of those design and operational aspects of terminals which affect wastewater generation is a very useful technique for recording relevant data and for making sure that all possible significant factors have been examined. A blank form for this purpose is attached as Appendix A.

The checklist can be used as a survey form, mailed to the facility for terminal personnel to fill out, or can be used by the team (including terminal personnel) involved with developing a wastewater characterization for a terminal. It is useful in some cases to combine these, with the form mailed out initially to be filled out by terminal with as much information as is readily available, and with the wastewater team meeting later to fill in the missing information.

Table 6-1a

Common Petroleum Industry Wastewater Analyses

Test	Abbr.	Reference*		Vol., mL	Container	Preservation**	Hold Time	Description	Interferences
		SM	EPA						
Biochemical Oxygen Demand	BOD-5	5210 B	405.1	1000	P,G	4 C	24 H	Oxygen uptake from biologically seeded samples at various dilutions	Ammonia may or may not nitrify to show nitrogenous BOD; to suppress, use nitrification inhibitors
Chemical Oxygen Demand	COD	5220 B 5220 C 5220 D	405.1 410.1 410.3 410.4	50	P,G	SA to pH <2	7 D	Consumption of strong chemical oxidizing agent	High chloride levels can show up as COD
Total Organic Carbon	TOC	5310 B 5310 C 5310 D	415.1	25	P,G	4 C SA to pH <2	24 H	Combustion and measurement of CO2 evolved	None
Oil and Grease, Gravimetric	O&G	5520 B	413.1	1000	G	4 C SA to pH <2	24 H	Extraction of oil from acidified sample with Freon, evaporation of Freon and weight of residue	Elemental sulfur is extracted by Freon, and shows up as O&G; soluble material such as organic acids are also extracted
Oil and Grease, Infrared	O&G IR	5520 C	413.2	1000	G	4 C SA to pH <2	24 H	Extraction of oil from acidified sample with Freon, determination of extract infrared spectrum in hydrocarbon bands	Soluble material such as organic acids are also extracted, but can be quantified as carbonyl bands in IR spectrum
Total Petroleum Hydrocarbons	TPH	5520 F		1000	G	4 C SA to pH <2	24 H	Same as gravimetric or IR oil & grease, except that Freon is treated with silica gel to remove polar organic compounds.	Sulfur may be detected in gravimetric procedure.
Phenolics	Phenols	5530 C 5530 D	420.1 420.2 420.3	500	G	4 C PA to pH <4 CuSO4	24 H	Distillation, Chloroform extraction of colored complex made from 4-aminoantipyrine and K3Fe(CN)6. Colorimetric or photometric finish.	
Anionic Surfactants - Methylene Blue Active Substances	MBAS	5540 C	425.1	250	P,G	4 C	24 H	Extraction of surfactant-methylene blue dye complex into chloroform, spectrophotometric finish.	Soaps (long-chain organic acid salts), although anionic surfactants, do not show up. Use sublation to purify and concentrate sample.
Nonionic Surfactants - Cobalt Thiocyanate Active Substances	CTAS	5540 D		250	P,G	4 C	24 H	Extraction of cobalt thiocyanate into chloroform, spectrophotometric finish.	Use sublation to purify and concentrate sample.
Benzene, Toluene, Ethylbenzene, Xylenes	BTEX	6210 B/E 6220 B/D		40	G VOA Bottle	4 C 4 drops 6N HCl	14 D	Inert gas purging of water and collection of vaporized organics on a carbon trap, followed by heating the trap to drive vapors into a gas chromatograph, with various detectors	

* References: SM = Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition
EPA = U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes", 3rd Edition

** Preservatives: SA = sulfuric acid; NA = nitric acid; PA = phosphoric acid

Table 6-1b

Common Petroleum Industry Wastewater Analyses

Test	Abbr.	Reference*		Vol., mL	Container	Preservation**	Hold Time	Description	Interferences
		SM	EPA						
Naphthenic Acids	NA			1000	G	4 C SA to pH <2	24 H	Run the same as oil & grease infrared method, except that naphthenic acid carbonyl peaks are used to make quantitative determination vs. standard naphthenic acids	Other carboxylic acids (such as soaps) may interfere.
Ammonia	NH3	4500-NH3 A/H	350.1 350.2 350.3	400	P,G	4 C SA to pH <2	24 H	Colorimetric phenate, colorimetric nessler, alkaline distillation and titration, ion-specific electrode	Amines are a positive interference.
pH	pH	4500-H+ B	150.1	25	P,G	On-Site		pH electrode.	None
Acidity		2310 B	305.1	100	P,G	None	24 H	Titration with standard NaOH solution to pH endpoint.	None
Alkalinity		2320 B	310.1 310.2	100	P,G	4 C	24 H	Titration with standard acid solution to pH endpoint.	None
Sulfide	S=	4500 S2- D/E	376.1 376.2	500	P,G	2 mL zinc acetate	24 H	Methylene blue colorimetric or iodometric	Reducing agents interfere. To isolate sulfide, precipitate with zinc acetate, discard water, and analyze precipitate.
Arsenic	As	3113 3114 3120	206.2 206.3 206.4 206.5	200	P,G	NA to pH <2	6 Mo	Electrothermal atomic absorption. Hydride generation atomic absorption Inductively coupled plasma.	
Selenium	Se	3113 3114 3120	270.2 270.3	200	P,G	NA to pH <2	6 Mo	Same as arsenic.	
Copper	Cu	3111 3113 3120	220.1 220.2	200	P,G	NA to pH <2	6 Mo	Flame atomic absorption. Electrothermal atomic absorption. Inductively coupled plasma.	
Lead	Pb	3111 3113 3120	239.1 239.2	200	P,G	NA to pH <2	6 Mo	Same as Cu	
Zinc	Zn	3111 3120	289.1 289.2	200	P,G	NA to pH <2	6 Mo	Flame atomic absorption. Inductively coupled plasma.	
Total Dissolved Solids	TDS	2540 A	160.2	100	P,G	4 C	7 D	Evaporate 0.45 micron filtrate to dryness @105 C, weigh.	
Total Suspended Solids	TSS	2540 D	160.2	100	P,G	4 C	7 D	Filter through 0.45 micron filter, dry filter paper @105 C, weigh	
Volatile Suspended Solids	VSS	2540 E	160.4	100	P,G	4 C	7 D	Ignite TSS filter paper @ 550 C, weigh	

- References: SM = Standard Methods for the Examination of Water and Wastewater, APHA, AWWA, WEF, 18th Edition
  EPA = U.S. Environmental Protection Agency, "Methods for Chemical Analysis of Water and Wastes", 3rd Editio

Chapter 7

SOURCE REDUCTION

7.1 Introduction

As described in 5.4.4, there are several reasons for eliminating contamination at its source rather than removing it in a downstream wastewater treatment system. As also described, there are other reasons for preferring the treatment option, including the capital cost of (some) source reduction techniques. The following analysis covers means for minimizing wastewater flow and contamination in petroleum products terminals, and is followed by an overview as to which techniques are likely to be cost-effective.

7.2 Stormwater

Stormwater is that portion of rainfall which becomes surface runoff water; e.g., that portion which does not evaporate or percolate into the ground. In many facilities, particularly terminals, stormwater is the major source of wastewater, and the type which inherently needs the least treatment.

7.2.1 STORMWATER CATEGORIZATION

For purposes of water handling, stormwater is divided into three categories: *uncontaminated, potentially contaminated, and contaminated.* The categorization is done on the basis of the type of area from which the stormwater is generated.

7.2.1.1 Uncontaminated Stormwater

Uncontaminated stormwater is that which has essentially no chance of being contaminated by industrial operations. Examples of this type of water are runoff from parking lots, building roof drains, roadways, and undeveloped or unused property. Stormwater which is classified as uncontaminated can be discharged off the facility site without collection, inspection, analysis, or treatment.

7.2.1.2 Potentially Contaminated Stormwater

Potentially contaminated stormwater is that which is normally clean, but which comes from areas in which industrial operations are done which might cause contamination. The main example of this type of water is runoff from a tank farm which has a tank bottoms water collection system. Normally, this water will be clean, but accidental discharge of tank bottoms water, or product leaks from pipe flanges, or accidental tank product overflow, could lead to contamination. In large industrial facilities, the general rule for handling stormwater from potentially contaminated areas is to collect it, inspect it (for floating oil or sheen) and analyze it to determine if contamination has occurred, and discharge it without treatment if it is clean (the normal situation). If contamination is detected, then the water is appropriately treated (e.g., subjected to oil/water separation) before discharge. For small facilities such as petroleum products terminals which have limited operating staff and no facilities for onsite chemical analysis, a preferred procedure may be to collect and store potentially contaminated stormwater in a basin or tank with sufficient retention time to permit separation of any spilled product, and to combine its discharge with other facility treated effluents for compliance analysis as a means for ensuring that accidental contamination is detected.

7.2.1.3 Contaminated Stormwater

Contaminated stormwater is that which is known always to be contaminated, or known to be very likely to be contaminated. Any stormwater which contacts crude oil or petroleum products, or which mixes with water which has been in contact with these materials, is contaminated. An example of contaminated storm water is runoff from truck loading rack slabs. Also, runoff from soil known to be contaminated (e.g., oily sludge disposal areas) should be assumed to be contaminated. The general rule for handling contaminated stormwater is that it should always be treated before discharge.

The types and distinguishing characteristics of the various types of stormwater are summarized on Table 7-1.

Table 7-1

Stormwater Characteristics

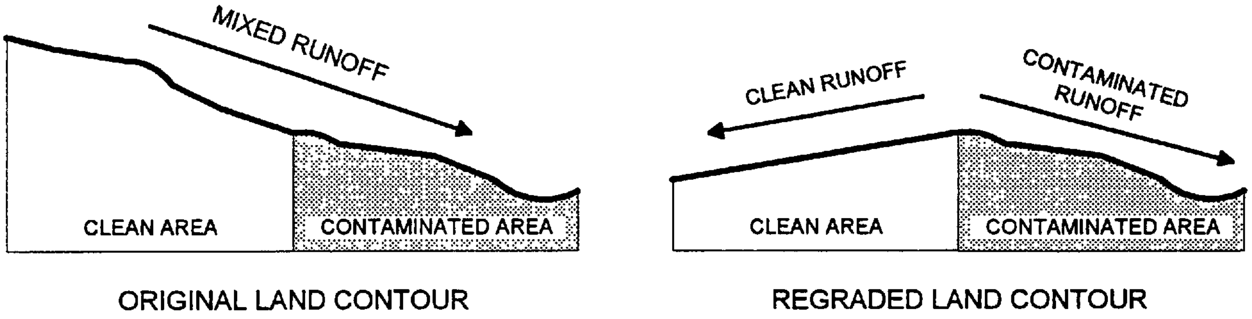
Type of Stormwater	Area Characteristics	Typical Areas	Handling
Uncontaminated	No chance of product contact No chance of other contamination	Lawns Driveways Building roofs Parking lots Undeveloped land	Route offsite without inspection or treatment
Potentially Contaminated	Possible contact with product Possible mixing with contaminated water	Tank Farms Pipeways	Collect, inspect or analyze Discharge directly if clean Treat if contaminated
Contaminated	Contact with product Mixing with other contaminated water Contact with contaminated surface Mixing with soluble contaminants	Tank water Rack water Contaminated soil	Treat as needed Haul off

7.2.2 STORMWATER SEGREGATION PRINCIPLES

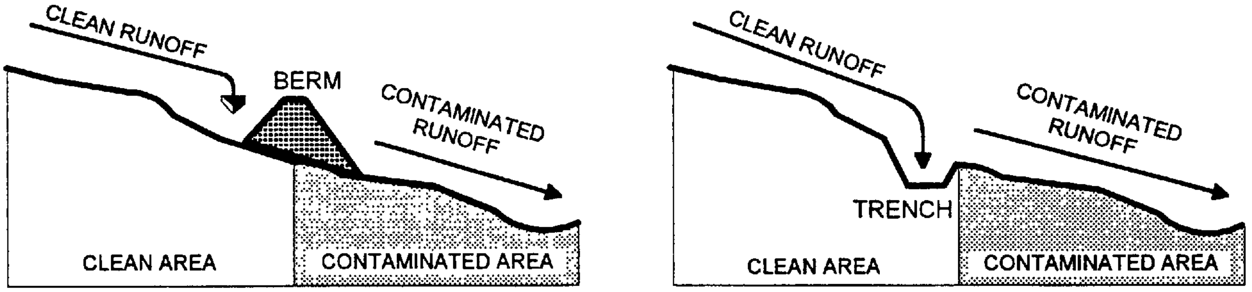
Stormwater is, at most locations, a major source of wastewater volume, and thus a significant factor in sizing wastewater treatment systems. It is also, as a rule, relatively free of contamination. The combination of these two factors leads to the general principle: *as much as possible, stormwater should be segregated from contamination to enable discharging it with minimal treatment.* Full implementation of this principle can lead to significant savings in building and operating wastewater collection and treatment systems, and to overall improvement in the impact of facility wastewater on the receiving water. Since achieving segregation is usually not cost-free, the degree to which this is done should be based on a cost analysis: is the cost of the

FIGURE 7-1

GEOGRAPHICAL STORMWATER SEGREGATION

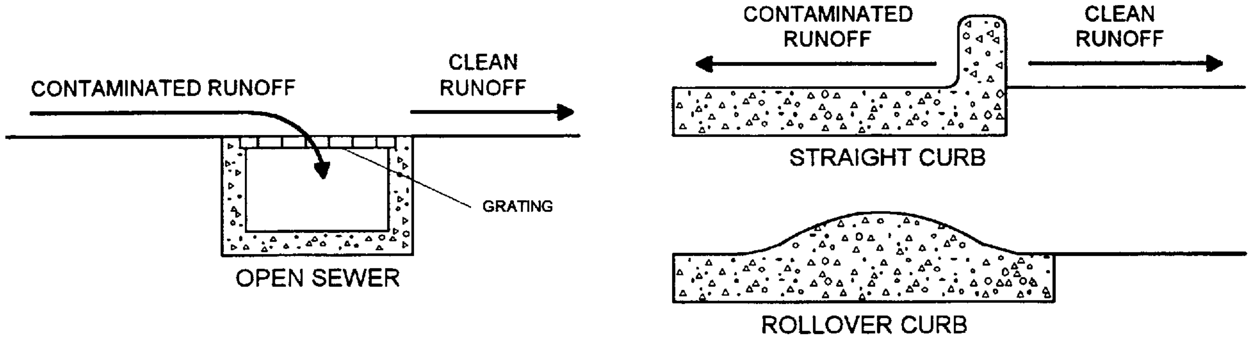


(A) RUNOFF SEGREGATION BY LAND REGRADING



(B) RUNOFF SEGREGATION BY BERM

(C) RUNOFF SEGREGATION BY INTERCEPTOR TRENCH



(D) RUNOFF SEGREGATION BY INTERCEPTOR SEWER

(E) RUNOFF SEGREGATION BY CURBS

segregation construction (usually an investment cost, rather than an operating cost) justified by the reduced cost of treating wastewater (both investment and operating).

There are two basic principles for storm water segregation: geographical segregation and roofs. Both are aimed at preventing contamination of clean storm water and dilution of contaminated water.

7.2.3 GEOGRAPHICAL SEGREGATION

Geographical segregation is prevention of mixing of runoff from one type (uncontaminated, potentially contaminated, and contaminated) of area with runoff from another type of area. This can be done with a combination of grading, berms, interceptor drains, or curbs.

7.2.3.1 Grading

Grading is arranging of land slopes such that water flows in the desired direction. As shown on Figure 7-1a, an area in which both uncontaminated and potentially contaminated runoff were mixed could be regraded to allow separation of the two.

7.2.3.2 Berms

Berms are elevated barriers to surface water movement, usually made of earth, although constructed walls (e.g., of concrete) are also used as shown on Figure 7-1b.

7.2.3.3 Interceptor Drains

Interceptor drains are collection channels (ditches or sewers) which capture a type of runoff before it can mix with another type; this is illustrated on Figure 7-1c&d.

7.2.3.4 Curbs

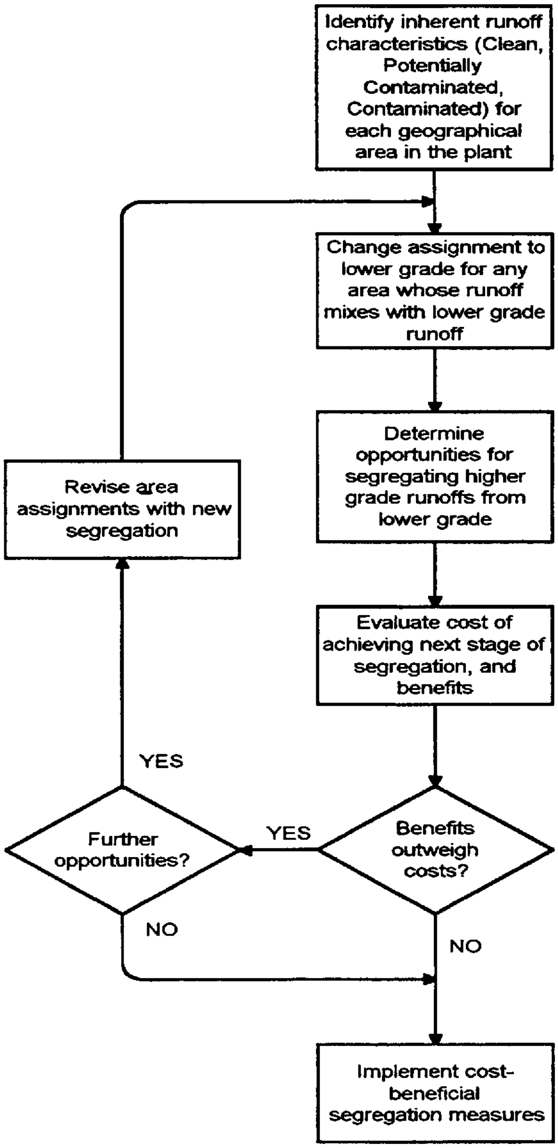
Curbs, like berms, are physical barriers to water movement, distinguished by being low enough to enable movement of personnel and equipment over them; they are usually used around process areas. As shown on Figure 7-1e, curbs can be simple low walls, or can, preferably, be rollover curbs, which are curbs widened and sloped to allow rolling equipment to travel over them without hindrance, and which also minimize tripping hazards for personnel.

7.2.3.5 Identification of Area Types

A key step in devising geographical stormwater segregation is identification of which plant areas generate each of the three types of stormwater. This is commonly done with a facility map, with each drainage area color-coded for uncontaminated, potentially contaminated, and contaminated stormwaters. The main issue at this stage is determining the boundaries between the areas. The rule to follow is to maximize the area which is less contaminated, consistent with the practicality of achieving the physical separation by the means noted above.

The first step is to identify the areas which are inherently a certain type of stormwater, using the criteria described above for stormwater characterization. Since the existing plant drainage pattern may result in commingling of runoff from different types of areas, the next step is determining the feasibility of preventing this by use of the segregation techniques. A mixture rule should be followed: whenever a higher class of runoff (less contaminated type) mixes with a lower class in a drainage area, then all runoff from that area must be assigned the lower class. The cost and difficulty of maximizing segregation in a given case must be balanced against the cost of having to handle and treat the corresponding larger volumes of water for that case. The final step in the plant runoff classification is reassignment of the plant drainage areas in light of the segregation achieved and the mixture rule. In cases where the runoff collection system is to be revised or constructed, the collection system will then be designed to bring together the runoff waters of each type. The steps in performing the geographical runoff segregation procedure are shown schematically on Figure 7-2. Stormwater flow estimation techniques are described in 6.5.3.

FIGURE 7-2
STORM SEGREGATION PROCEDURE



7.2.4 ROOFS

The second basic means for achieving storm water segregation is use of roofs over contaminated areas, with runoff from the roofs sent to a less-contaminated area — in effect, an umbrella over the contaminated area. Since roofs are expensive, this technique is normally used only when considerable savings in treatment costs can be achieved, usually at facilities which do not generate much process wastewater, and so can achieve very large percentage savings in wastewater flow by storm water segregation. This situation is usually found in petroleum products terminals.

7.2.4.1 Storage Tanks

The prime use of roofs is on storage tanks, since the tank bottoms water is highly contaminated, and has very low flow if stormwater is kept out. Tank roofs are described in 4.5.1.2.

7.2.4.2 Water-Soluble Materials Tanks

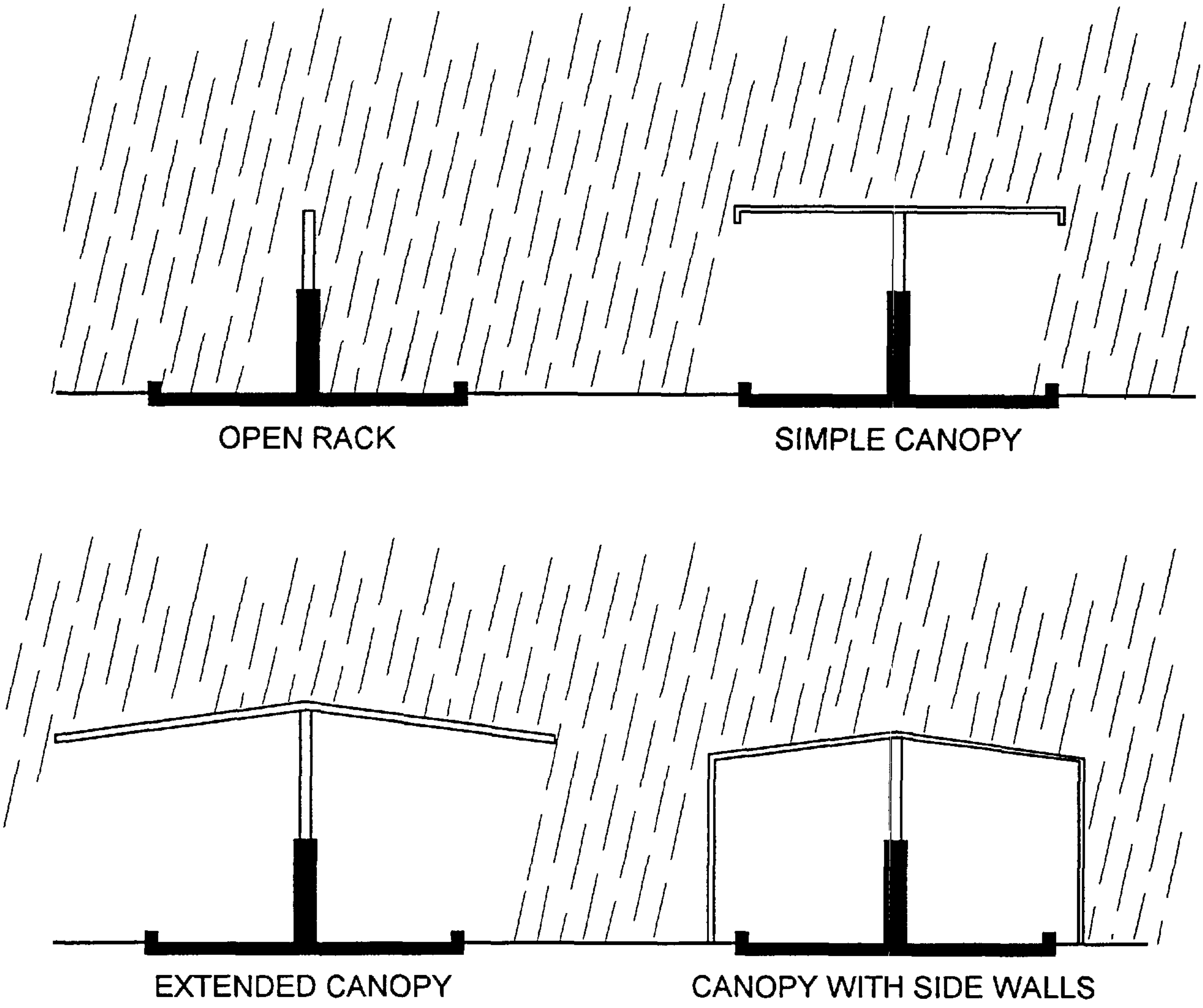
A special case of tank covers is for tanks which contain, either as pure materials or mixtures, water-soluble materials such as gasoline oxygenates (ethers and alcohols), fuel and lubricant additives, and other water-soluble chemicals. Since water mixing with such materials can result in significant water contamination, as well as product quality degradation, the recommended practice is to always provide fixed roofs on tanks which contain significant amounts of water-soluble materials, and to operate the tanks in such a manner as to keep all water out the tanks.

7.2.4.3 Transfer Racks

Another type of commonly used roof is that used over transfer racks (truck, rail, and barge loading and unloading racks), since making and breaking hose connections to the transport vessel may result in small product spills onto the facility slab. Roofs, commonly called canopies, are often used in these areas to protect personnel making the transfers, and to keep water out of the transport vessel (e.g., top loading trucks or rail cars). As shown on Figure 7-3, the main design point with these roofs is the right combination of height and width to keep significant amounts of rain from blowing in from the side. Although often overlooked since it does not affect personnel and product protection, the roof drains should be routed away from the facility slab. To keep stormwater from running onto the facility slab, the slab should be surrounded by curbs, obviously rollover curbs (see Figure 7-1) in the case of truck loading/unloading racks.

FIGURE 7-3

RACK CANOPY RAIN PROTECTION



7.2.4.4 Pump Stations

"Clean" tank farms (those equipped with tank bottoms collection systems) frequently contain pump stations, which are rated as contaminated areas due to pump seal leaks and pump maintenance discharges. Rather than collect and treat the water from the pump station slab, it is preferable to place a roof over it, or enclose the whole area in a pumphouse. Design factors are the same as those for loading rack canopies.

7.3 Minimizing Contamination of Potentially Contaminated Stormwater

As described above, potentially contaminated stormwater is collected and subjected to minimal treatment before discharge; if it becomes contaminated, it must be treated more thoroughly. Clearly, in order to reduce the load on the treatment system, it will be desirable to minimize the probability that such contamination will occur. This section describes means for improving the odds of keeping the potentially contaminated stormwater clean.

7.3.1 TANK FARMS

Tank farms may be contaminated by accidental release of materials to the ground, including leaks in piping or the tanks, overfilling the tanks, accidentally opening tank nozzles, or tank cleanout activities. For all of these releases, means are available to minimize the likelihood of contamination.

7.3.1.1 Leak Control

Leaks in tanks or piping are controlled by proper maintenance of the equipment. Clearly, no facility will allow major leaks to go unfixed, but it should be noted that even minor leaks (constant drips) can result in significant, and costly, contamination of runoff water. Maintenance procedures (painting, periodic inspection and repair) should be employed to prevent any leak, however small, from going unfixed for long.

7.3.1.2 Tank Overfilling

Tank overfilling has obvious adverse consequences (danger of fire and loss of product) beyond those associated with water contamination, and procedures are generally followed to make this a rare occurrence. To recap these procedures: tanks should be gauged before filling and tank filling operations should be monitored. The use of tank high-level alarms and automatic shutoffs should also be encouraged.

7.3.1.3 Accidental Releases

Accidental opening of tank nozzles resulting in product discharge to the ground is probably quite rare; problems are most likely to occur in complex piping systems. To minimize the chances of this occurring, a policy can be established to keep blind flanges or caps over all pipe openings and unconnected valve ends.

7.3.1.4 Tank Cleaning

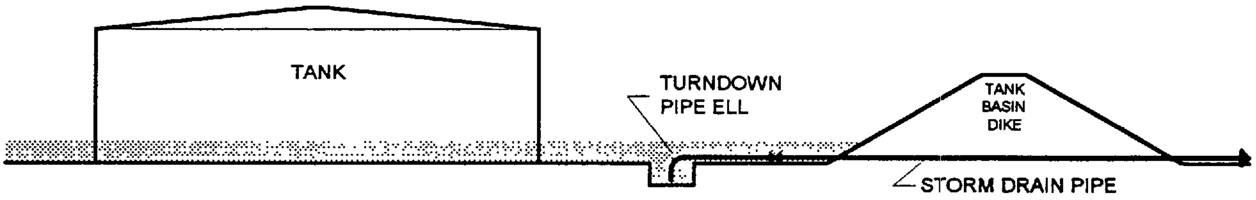
Tanks usually accumulate sludge on their bottoms over time, which needs to be periodically removed in a cleaning procedure. As a rule, the cleaning should be done in such a manner that none of the oily sludge comes in contact with the ground around the tank.

7.3.1.5 Containment Dike Operation

As a spill containment measure, petroleum tanks are generally surrounded by a containment area, bounded by dikes or walls. The general rule is that the area will hold the contents of the largest tank in the area without spillover. To allow removal of rainwater from the contained area, drainage pipes with shutoff valves are placed through the dikes or walls. To prevent discharge of spills through the drain lines, the policy is generally followed to keep the shutoff valves closed at all times except during attended rainwater drainage. If there is an oil spill at the same time that rainwater accumulates in the tank basin, then drainage of clean water can be facilitated by having "turndown ells" on the basin end of the pipe as shown on Figure 7-4. These devices allow drainage of the water while minimizing the entrainment of floating oil. Note that in spills of water-soluble materials such as oxygenates, or of products containing these materials, the entire mixture of product and rainwater must be collected and treated, since the water will contain large amounts of soluble contaminants.

FIGURE 7-4

TANK BASIN STORM DRAIN

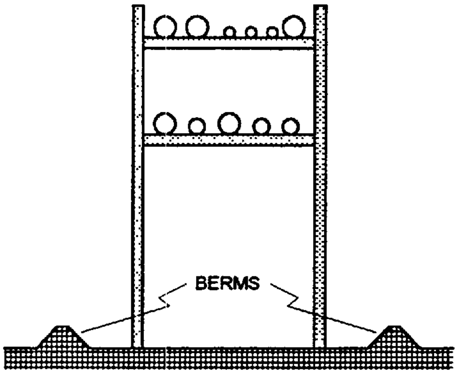


7.3.2 OTHER POTENTIALLY CONTAMINATED AREAS

In addition to tank farms, other potentially contaminated areas are generally those where leaks or spills could be discharged to the ground, and subsequently mixed with stormwater. Obviously, the main preventative measure is operation of the equipment in such a manner as to prevent leaks or spills. Another technique which should be applied where feasible is division of the area into isolatable zones in order to limit the spread of the contamination. It may be advisable, for instance, to place low berms on either side of a pipeway as shown on Figure 7-5.

FIGURE 7-5

PIPEWAY SPILL BERMS



7.4 Minimizing Oil Discharge Contamination of Wastewater

As discussed below, oil becomes mixed with wastewater in a variety of ways. By the use of proper equipment design and proper operating procedures, wastewater contamination with oil can be minimized.

Oil discharges are the means by which oil, the product, becomes oil, the wastewater contaminant. This occurs in petroleum product tank bottoms draws, from leaks, from occasional drainage of equipment, from sampling stations, and from spills.

7.4.1 PRODUCT TANK BOTTOMS DRAWS

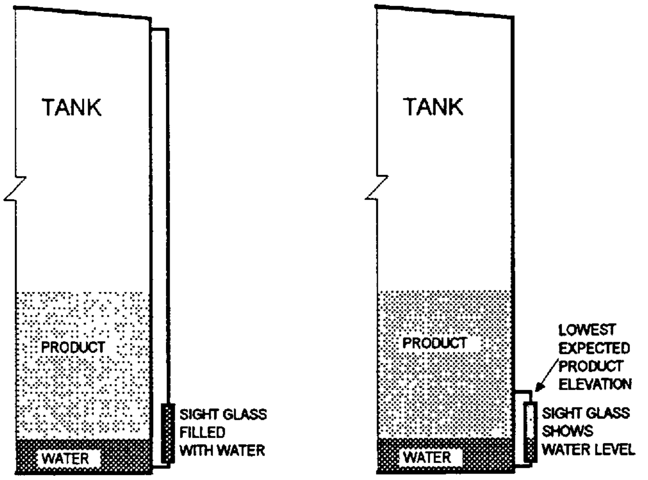
Product tank bottoms draws are the means by which water which collects in the bottoms of petroleum product tanks are periodically withdrawn to prevent the water from being mixed with product delivered from the tank. Tank water draws should always be routed to a collection tank for oil separation and appropriate treatment. Probably the main challenge in designing and operating tank draw systems is devising a method to enable maximum withdrawal of water while achieving minimal withdrawal of product. Some guidelines on means for achieving this are as follows.

7.4.1.1 Water Volume Determination

Determining the amount of water in a tank to be drawn is often useful in controlling the water draw. One means for doing this is to gauge the tank with a tape or stick coated on its lower end with *water indicating paste*. The paste changes color in the presence of water, and thus shows the water depth when the gauging device is withdrawn and inspected.

FIGURE 7-6

TANK BOTTOMS SIGHT GLASS CONNECTION



INCORRECT SIGHT GLASS CONNECTION

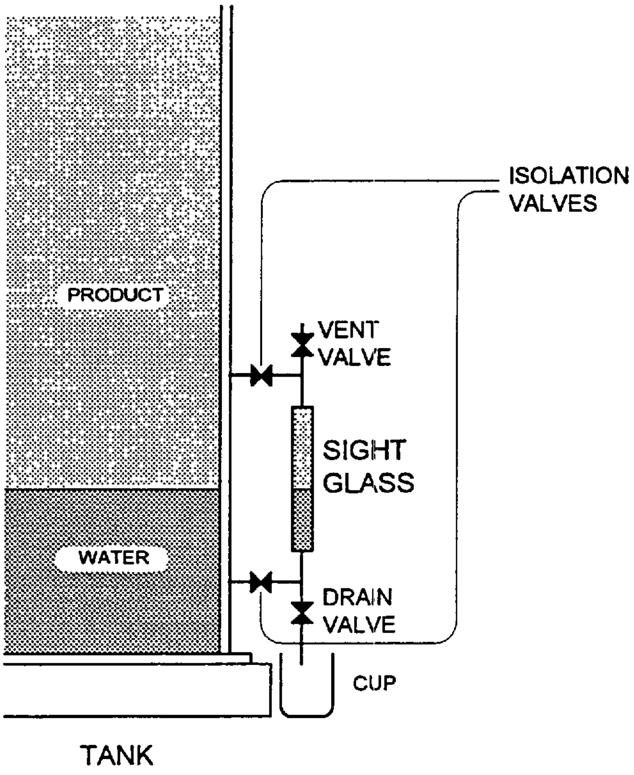
CORRECT SIGHT GLASS CONNECTION

Another means for determining interface level is to place closely-spaced trycocks on the tank wall across the range of elevations (usually, 0 - 2 feet) above the tank bottom expected for water accumulation. The operator opens the trycocks (draining into a pail or collecting sink) until the highest one which delivers water is found.

Sight glasses mounted on the side of the tank can also be used to find the water/product interface level, *but only if the upper end is lower than the product/air interface or floating roof (in tanks so equipped) elevation.* The reason for this requirement is that there will otherwise be no relation between the interface level in the sight glass and the interface level in the tank, as shown on Figure 7-6. Probably the best means for

FIGURE 7-7

TANK BOTTOMS SIGHT GLASS PIPING



achieving the requirement is to place the lower sight glass nozzle at the bottom of the tank, and the upper sight glass nozzle at an elevation closely above the highest expected water level (e.g., 2 feet above bottom). As shown on Figure 7-7, the upper and lower tank nozzles should have shutoff valves, normally kept shut, to guard against spills in the event of sight glass breakage. Also, the sight glass should have a drain valve on the bottom and a vent valve on the top so it can be drained after each reading to prevent freeze rupture (in winter) and to assist in keeping the glass clean.

For each tank, it is often useful to have a calibration curve showing the relation between tank water level and tank water volume. In many facilities, this certified calibration (known as *tank strappings*) is already available and used for product accounting purposes. Those facilities whose tanks do not have strappings can obtain them, or can develop them by placing known volumes of water in the tank and recording the water level. Note that they cannot be accurately calculated from tank dimensions, since the total volume is relatively small, and the bottoms of tanks are often not perfectly level (i.e., the water depth at one location in a tank is not necessarily the same as the depth at another location).

7.4.1.2 Prevention of Product Entrainment

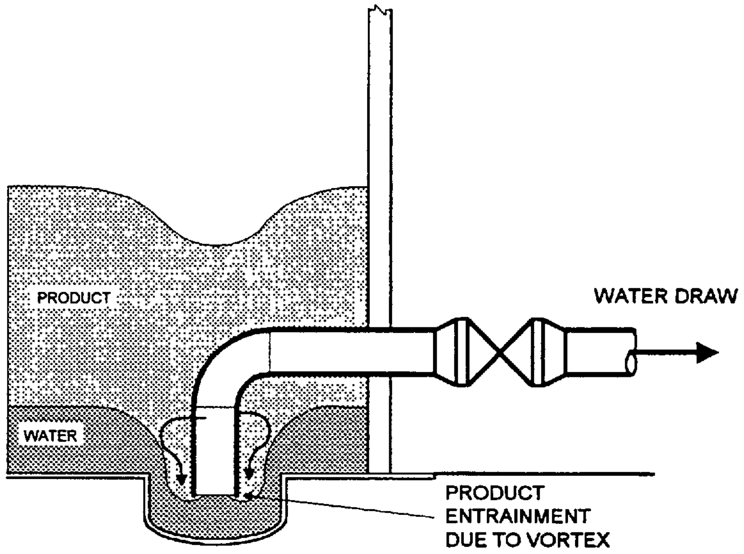
Product entrainment is the carryover of droplets of product in a water draw flow. There are several design guidelines and operating procedures to minimize entrainment.

The first design element, commonly employed, is to place a water sump in the tank bottom next to the water drain nozzle, and to connect the nozzle to the tank interior with a turndown ell. As shown on Figure 7-8a, this design ensures that water is being drawn from as low an elevation as possible, i.e., as far away from the water/product interface as possible.

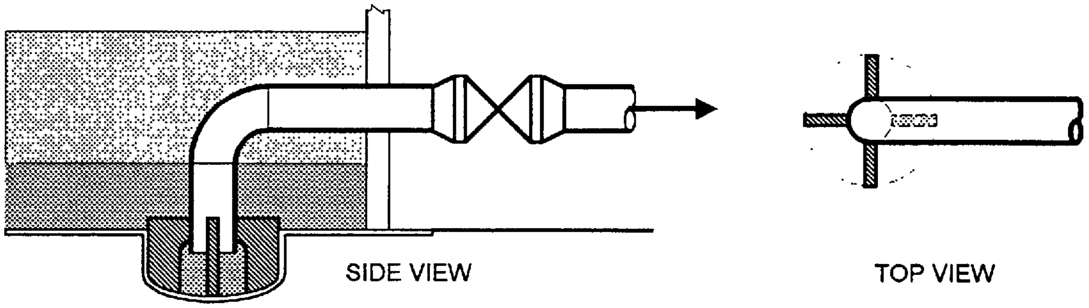
When liquid is drawn from a tank through a nozzle, it will tend to establish a swirling vortex, which can pull the product layer down to the water draw elevation. As shown on Figure 7-8b, *vortex eliminators* (vertical barriers to prevent liquid swirling), or *vortex barriers* (Figure 7-8c, horizontal barriers to vortex penetration) can be used near the water drain nozzles to minimize product entrainment.

FIGURE 7-8

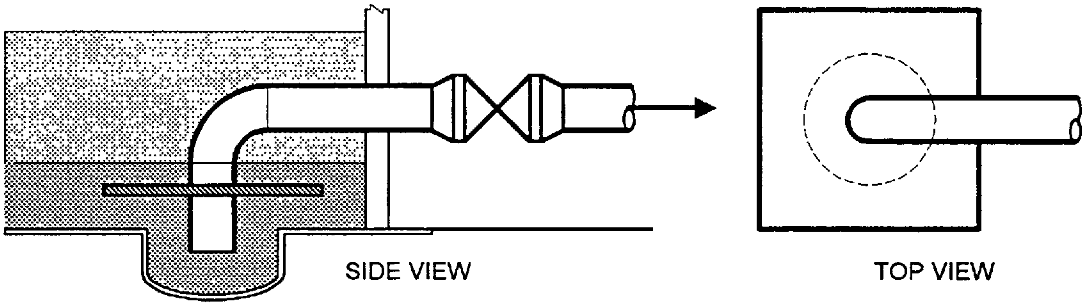
TANK WATER DRAW PRODUCT ENTRAINMENT CONTROL



(A) WATER DRAW NOZZLE WITH TURNDOWN ELL
(VORTEX SHOWN)



(B) VORTEX ELIMINATOR



(C) VORTEX BARRIER

Another good design practice is to raise the product draw nozzle elevation as much as is economically feasible (useful tank product volume is correspondingly reduced). A large separation in the elevations of the two types of draws will enable drawing only the lower layer of water each time (i.e., enable leaving some water in the tank at the end of the draw), thus avoiding drawing down to the interface, and drawing some product along with the water.

The main operating procedure to minimize product entrainment is control of the water draw rate. At higher water flow rates, entrainment is more likely, and it is more probable that the interface will be overshot. A compromise must be achieved between minimizing the time taken to draw water from a tank, and minimizing the probability that product will be drawn along with the water.

A related measure is reduction of water draw frequency. Each time water is drawn, a certain amount of product will be drawn along with the water (at the end of the draw period as the water/product interface approaches the draw nozzle). Other factors being equal, it is better to draw a given volume of water at one time, rather than dividing the draw into several periods. In addition, reducing the amount of water to be drawn in a given period (as described in 7.7) will enable less frequent water drawing.

7.4.1.3 Water/Product Interface Detection

It can be surprisingly difficult to distinguish drawn water from drawn product, in that they can have similar appearance (unless the water is discolored by contaminants), and similar odor.

The simplest procedure is manual control, in which the water draw valve is manually opened, the drawn material is periodically sampled, and the valve is manually closed when product appears. Since water drawing can take several hours, and is inherently a boring operation, many operators prefer to make periodic sampling and inspection visits to the tank during the draw. To help ensure that only water is drawn, some facilities require that the operator be stationed full time at the tank during the draw to periodically sample the material being drawn. The latter practice requires extra manpower, and does not guarantee that product will not be drawn because of the similarity in appearance of water and products. Clearly, it would be desirable to have a reliable automatic method or device to shut off the draw valve when product appears. Some possible means by which this could be done are as follows.

The electrical properties of water and product are quite different, which should allow devising a detector based on electrical conductivity or capacitance. A possible problem with this approach is fouling of the electrodes or sensors.

Water is obviously somewhat denser than product, which is the basis for some control devices using a float of exact specific gravity to control a shutoff valve. Such a device can be wholly mechanical (and thus simpler than an electronic system), but may be prone to fouling since the working parts are wetted by the contaminated water.

If the volume of water in the tank has been determined with some accuracy (see above), then a device to meter the draw volume, and to shut off the valve when a set volume had been reached, could be effective. This could be done with a totalizing flow meter (similar to a common household water meter) with mechanical or electrical connection to the shutoff valve; again, fouling of the flow-measuring turbine may be a problem. Another, somewhat more elaborate technique, would be to route the water into a collection tank with a level shutoff valve (e.g., a float valve) on the fill line set at the desired elevation (volume).

Another technique is to route the drawn fluid through a canister of material which swells in the presence of hydrocarbon, and thus blocks the flow when product is drawn. This would be a use-once, throwaway, device, but might shut off prematurely if minor entrainment of product in the water occurred.

7.4.2 LEAKS

Leaks, although not necessarily common, can be a major source of oil in wastewater. Leaks are sometimes tolerated since the oil thus discharged is eventually collected in a downstream oil/water separator. However, it is still desirable to control leaks as much as practical since this will avoid having to reprocess the oil carried by the wastewater, and will also usually reduce the generation of unseparable oil.

There are various types of leaks, including pump seal leakage, valve seal leakage, pipe flange leakage, and leaks in vessels and piping.

7.4.2.1 Pump Seal Leaks

Pump seals are located on the rotating shaft in rotating pumps (centrifugal pumps, gear pumps), and on the piston in piston pumps. Some pumps (e.g., magnetic drive rotating pumps and diaphragm pumps) do not have seals. Many rotating seals require a certain amount of leakage to lubricate the seal; sometimes the lubricant is the process fluid, and sometimes seal water. The main recommendations on pump seals are (1) to consider oil leaks as a factor in pump selection, tending towards selection of mechanical seals over packing seals, and of sealless pumps over those which use seals, and (2) to maintain the pump seals in good condition, and repair, replace, or tighten (in the case of packing) the seals when oil leakage becomes excessive.

7.4.2.2 Valve Stem Packing

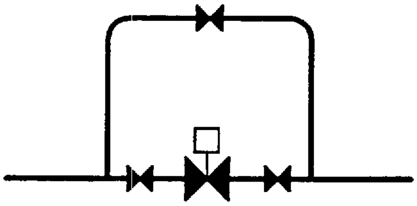
Almost all valves have stems to connect the internal parts with the external actuator, and seals, usually packing, to minimize leakage of process fluid along the stem. Some valves (e.g., bellows valves) do not need stem seals. As with pump sealing, the main recommendations with valves are to choose designs least likely to leak, and to maintain valve seals in good condition.

7.4.2.3 Maintenance on Pumps and Valves

To encourage performing maintenance on pumps and valves (particularly control valves), the process design should enable doing maintenance without shutting down the operation. For pumps, this means having spare pumps to switch to (or piping to enable temporary installation of a standby pump), and for control valves, having a manual valve bypass arrangement as shown on Figure 7-9.

FIGURE 7-9

CONTROL VALVE BYPASS AND ISOLATION LOOP



7.4.2.4 Piping Leaks

For many pumps and valves, a certain amount of leakage is considered inherent to the operation of the device. On the other hand, leaks in pipe flanges or screwed fittings, piping, and vessels are not inherent, but usually result from improper assembly, or corrosion, and should not be allowed to continue if the leakage is significant. To check for leaks, it is recommended that equipment taken down for maintenance be hydrotested before return to service.

7.4.3 DRAINAGE OF EQUIPMENT

Drainage of equipment is usually done when the equipment is taken out of service for maintenance. Since vessels, lines, and associated equipment normally contain large amounts of oil, drainage of this oil into sewers is potentially a very large source of wastewater oil contamination. Most of the techniques for minimizing oil drainage into sewers are process design factors (not operations procedures).

7.4.3.1 Avoid Pocketing

Specific guidelines cannot be given to cover the multitude of process arrangements, but the general principle to be followed is that *when the process (or segment of a process) is shut off, the oil in the equipment should, as much as possible, flow out of the system through existing equipment.* A few specific design recommendations are as follows (see Figure 7-10). Vessels should have drain lines at their low points with connections to enable pumping or gravity draining of the vessel contents to other parts of the system. As much as possible, piping should not have *pockets*, i.e., low points in the pipe run which cannot gravity drain in either direction. Check valves should either be arranged to not block line and vessel drainage, or should have bypasses.

7.4.3.2 Use Drain Nozzles

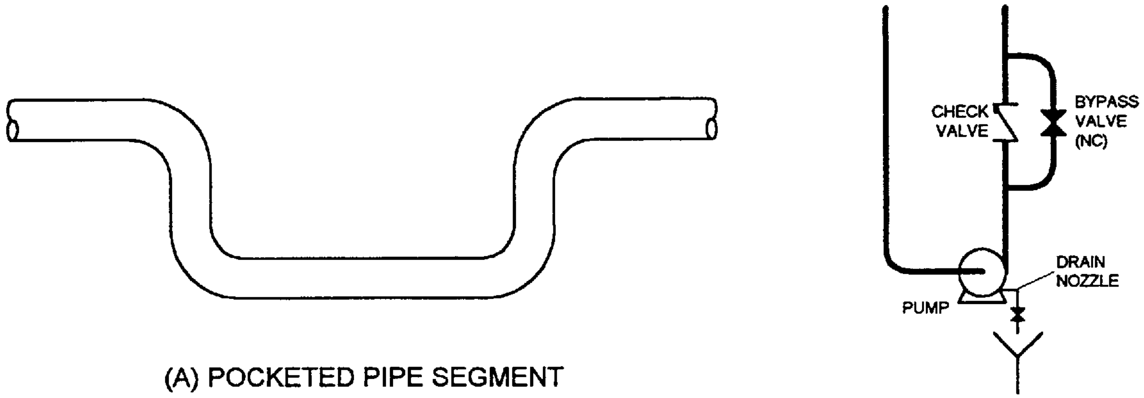
Even in well-designed systems there will be zones which cannot be readily drained within the process; examples include pumps and control valves which are generally located at grade, and thus inherently pocketed (Figure 7-10b). The general principle to be followed for these parts of the system is that *a drain nozzle with a shutoff valve should be located at the low point of the zone, with venting at the high end of the zone, and provision should be made for accepting oil drained through the nozzle.*

7.4.3.3 Provide Collection Point

The main design challenge is making provision for accepting drained oil. One means for doing this is to provide a below-grade oil collection sump, and to run hoses from the drain nozzles to the sump. Oil can be transferred from the sump to the slop oil system (see discussion below) either by vacuum truck or with a permanently installed sump pump and piping system. If an oil sump is not available, the drain nozzle can be directly connected to a vacuum truck suction hose (after making sure that tank vacuum-relief vents are open).

FIGURE 7-10

FACILITATION OF PIPE DRAINAGE



(A) POCKETED PIPE SEGMENT (NOT DRAINABLE)

(B) PUMP LOW POINT DRAIN AND CHECK VALVE DRAIN BYPASS

7.4.4 SAMPLING NOZZLES AND STATIONS

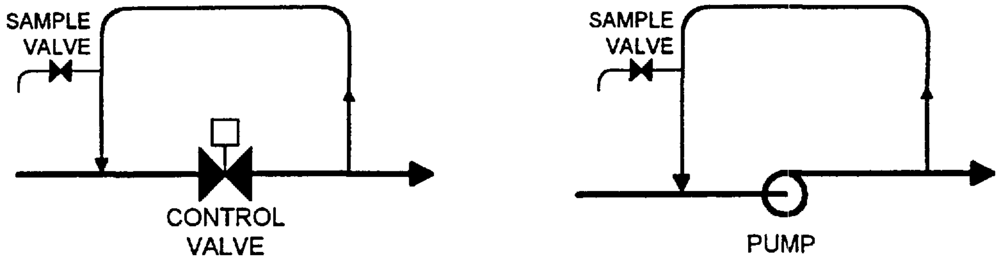
Sampling nozzles and stations are used to collect samples at various points of the petroleum products distribution system. Since the sample nozzle piping is a dead volume (no flow normally), general sampling practice is to open the sample valve and allow the material to flow for a sufficient time period to purge the piping dead volume and thus obtain a representative sample from the source line or vessel. Unfortunately, sample line purging is sometimes done by allowing the sampled liquid (oil) to discharge into the oily water sewer, with significant amounts of oil being thus placed in the wastewater. With modern design of sampling systems, discharge of this type of oil can be minimized or eliminated.

7.4.4.1 Sampling Loop

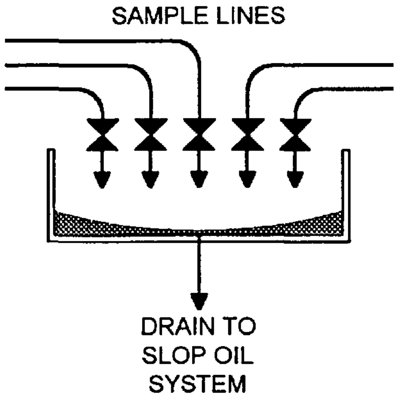
One good design practice for sampling systems is to place a *sampling loop* in the system. As shown on Figure 7-11a, the sampling loop is connected at its upstream end to the normal sample connection, and at its downstream end to a lower pressure region of the same process. The pressure differential is commonly achieved by looping around a pump or control valve as shown in Figure 7-11a. In this system, when a sample is taken, the sample loop is purged by opening the loop line valves for a sufficient time, and then the sample nozzle, located on the branch of a tee in the sample loop, is opened for collecting the sample.

FIGURE 7-11

PRODUCT SAMPLE PIPING



(A) SAMPLE LOOPS



(B) SAMPLE TROUGH

7.4.4.2 Sample Trough

In cases where installation of sample loop is not feasible (e.g., sampling a vessel which is not being pumped from), the best design practice is to provide a collection sink or trough at the sample nozzle, connected to the slop oil system (see below). To facilitate this type of arrangement, several sample nozzles can be grouped together as a sampling station above a common collection trough as shown on Figure 7-11b.

7.5 Minimizing Oil/Water Emulsion Contamination

Since oil is separated from wastewater by gravity separation, the presence of a type of oil which cannot be gravity separated has serious adverse effects on wastewater quality. Emulsions are such a type of oil, and are frequently found in petroleum industry wastewater. Emulsions are stable suspensions of one liquid phase in another; the phase composed of droplets is the dispersed phase, and the phase in which the droplets are dispersed is the continuous phase. In the petroleum industry, both oil-in-water and water-in-oil emulsions can be generated. Since their density is intermediate between the densities of oil and water, emulsions usually accumulate at the interface between floating oil and water. These emulsions are commonly known as rag or cuff.

7.5.1 EMULSION STABILIZING FACTORS

Emulsions are stabilized by three factors: small droplets, surfactants, and fine solids. Small droplets stabilize emulsions since small droplets are inherently slower than large droplets to separate from the continuous phase (see 9.5.1.3). Surfactants (surface-active agents, detergents, soaps) stabilize emulsions by collecting at the oil/water interface and reducing the surface tension which promotes phase separation. Viewed another way, surfactants hinder the coalescence of small droplets into large, easily separated, droplets. (Soaps and detergents get their cleaning power from this ability to disperse dirt and oil in water.) Fine solids are very effective at stabilizing emulsions, possibly by being wetted by both liquids simultaneously. Knowledge of the emulsion stabilizing factors can be used to minimize emulsion generation, as described below.

7.5.2 PREVENTION OF EMULSIONS

Generation of emulsion is caused by the emulsion-stabilizing factors noted above: small droplets, surfactants, and fine solids. Prevention is achieved by minimizing these factors.

7.5.2.1 Oil Droplet Control

Formation of small oil droplets is caused by agitation of oil and water, which results usually from pumping of oil/water mixtures, or turbulent flow of oil/water mixtures. Centrifugal pumps are the most common type of pumps used in the petroleum industry, and are also the type most likely to generate emulsions since the fluid is subject to high agitation in the pump body; positive displacement pumps (gear pumps, piston pumps, diaphragm pumps, Archimedes screw pumps, and so forth) produce much less agitation. Because of this, whenever excess oil in wastewater is a problem, it is better to use positive displacement pumps to pump mixtures of oil and water, particularly wastewater which contains significant amounts of oil. If possible, the use of centrifugal pumps in wastewater systems upstream of the oil/water separator should be avoided altogether.

Turbulence can also be produced by means other than pumping. High velocities of fluid flow in pipes or ditches will result in turbulence, which will cause emulsion formation if oil and water are mixed. To avoid this, it is better to avoid flow turbulence in oily water streams by keeping velocities low. In pipes, this is achieved by increasing pipe diameter. In ditches or partially filled pipes, this is achieved by restricting the gravity gradient, and by avoiding “waterfalls” or “rapids” (sudden changes in bottom elevation).

7.5.2.2 Detergents Control

Detergents, by their nature, are very good at stabilizing emulsions, and thus should be used with care. (Detergents are also generally toxic to aquatic animals at elevated concentrations, and cause foaming problems in wastewater treatment.) Crude oil contains natural surfactants (such as naphthenic acids), but the worst emulsion problems are caused by manufactured detergents, used for cleanup or as gasoline or lube oil additives.

Cleaning detergents are commonly used to clean up oily equipment of various types. Since such detergents always have a substantially adverse effect on oil/water separation, the general recommendation is to use the minimum amount of detergent necessary to perform the cleaning.

In addition, it is recommended to seek out non-detergent alternatives to detergents, such as dry cleaning methods (solvents, absorbent material for spilled oil), or steam cleaning.

Gasoline additive packages commonly contain detergents to keep vehicle fuel systems clean of deposits. Unfortunately, these detergents are also very effective at stabilizing oil/water emulsions. For this reason, it is recommended to avoid all contact of water with gasoline additives, or with gasoline which contains additives. If gasoline is mixed with additives in the terminal, it should be kept in "waterproof" tanks. If in bulk storage, the tank should have a fixed roof. If in underground storage, the tank should have in-ground fill nozzles which are leak tight, or located sufficiently high above grade to keep runoff water from entering the nozzle, and should, of course, be free of leaks which will let water in (as well as let product out).

Most marketing terminals do not mix additives with their products until the products leave the terminals, thus avoiding the storage water problem. However, some of these accept water-containing offspec products from service stations (see 4.9.8), and water from this material will always contain additives. To avoid problems from this source, the following options are available:

- Do not accept haulback material, or take steps to minimize its generation.
- Keep haulback product separate from other products until all water has separated. If the recovered product is sent to product tankage, select (if possible) a "low flow" tank (e.g., one with a fixed cover).
- Do not mix water separated from haulback material with oily water being routed to an oil/water separation device.

Testing of fire foam systems by release of the foam can result in wastewater contamination by foaming agent surfactants if the foam is dissolved in water. Means for minimizing problems from this practice include physically cleaning up (instead of washing down) the foam (where this is possible), selecting a foaming agent which is compatible with the terminal treatment system (e.g., is biodegradable if the terminal uses biotreatment), and keeping the "foam wastewater" segregated from any oily wastewater (since it can stabilize oil/water emulsions) until the latter is treated in the oil/water separation device.

7.5.2.3 Fine Solids Control

As noted above, fine solids are capable of generating stable emulsions in oil/water mixtures; some emulsions which have been stable for years have been instantly broken by filtration. Common sources of fine solids in oily wastewater are soil, powdered materials, and corrosion products.

One of the most common sources of wastewater fine solids is soil erosion, particularly erosion of clay soil, which is composed of very small (colloidal) particles. To prevent emulsion generation and stabilization, it is good practice to minimize the erosion of soil into wastewater collection systems. Means for doing this include segregation of runoff areas (see 7.2), planting of groundcover plants, paving the drainage area, and use of geofabrics.

Powdered materials such as spent blasting sand are sometimes handled in petroleum products terminals. Such materials should be stored in such a way as to prevent them from being carried by storm runoff into sewers. If they are placed on paved areas, they should be cleaned up by dry methods (sweeping) rather than by water washing.

Many corrosion processes make fine solids as corrosion products; sulfide corrosion of steel, for example, usually makes very fine iron sulfide as a byproduct. If possible, such materials should be cleaned out of process equipment by means that do not result in mixing of oil, water, and solids. If possible, for instance, the material should be physically removed rather than washed out with water.

As a general technique for keeping solids out of oily wastewater, it is recommended to use closed sewers or pipes rather than open ditches for conveying wastewater, since this enables better control of runoff solids and wind-borne solids. Design of wastewater collection systems is covered in 8.4.

Sanitary (human) wastes can also stabilize emulsions if mixed with oily water, since sanitary waste usually contains biosolids and detergents which stabilize emulsions. A rule for handling sanitary wastewater is to segregate it from oily water until the latter has been treated in the oil/water separation device. Means for doing this include (1) sending the sanitary waste to a municipal sanitary sewer (where this is accessible), (2) sending the sanitary waste to a septic tank or other dedicated sanitary treatment unit, and (3) treating the sanitary waste along with the other terminal wastewater, but only after oil separation.

7.5.3 EMULSION TREATMENT

Emulsion treatment (emulsion breaking) is not necessarily an easy process, since some emulsions are very stable, and resistant to treatment. In general, it is preferable (easier and less expensive) to prevent emulsion formation than to break emulsions. Techniques for emulsion breaking that are commonly employed, in order of ascending cost, are heat treatment (including heating to above 100 C under pressure), acid treatment (acids cause many detergents to lose their surfactant properties), and treatment with specialty proprietary chemicals. In addition, there are less commonly used, but supposedly effective, advanced (expensive) treatment methods such as filtration and electrostatic emulsion breaking, and use of membrane processes such as ultrafiltration.

7.6 Use of Slop Oil Systems to Minimize Oil Discharges

Slop oil systems are systems for collecting “waste” oil as an alternative to placing such oil into sewers. The collected oil is almost always reused in some fashion. To minimize oil contamination of wastewater, and to maximize recovery of valuable product, it can be useful to use some type of slop oil system in any petroleum handling operation, and to establish the operating guideline of never deliberately placing oil into a water sewer, or water in a slop oil system.

The components of a slop oil system are collection points, transport, and handling equipment. Because of the diversity of petroleum products terminal operations, and facility design, it is not possible to provide highly specific design criteria; however, general principles can be given as outlined below.

7.6.1 SLOP OIL COLLECTION POINTS

Slop oil collection points need to be provided at all points in the system where slop oil is generated. In other words, wherever waste oil is generated, there needs to be a place to put it. These collection points need to be as convenient as possible, since the alternative (placing oil in the water sewer) is so easy, and thus tempting, to use. The nature of the collection points is highly operation-specific. In some cases where low volumes of waste oil are produced (e.g., crankcase draining in a truck maintenance bay), a collection drum may be sufficient. In the other extreme, where large volumes of waste oil are produced, then a direct pipe connection from the system may be the optimum handling. One technique for handling intermediate volumes of waste oil is to provide an *oil sump* in the area, at lower elevation (including underground) than the points of oil release to enable gravity drainage. Connections to the sump can be direct piping, oil sinks located throughout the area with drains to the sump, or hoses which can be connected between the oil release points and the sump. Any collection system should be designed and operated to minimize collection of water along with the oil; oil sinks, for example, should have rain covers in rainy climates.

7.6.2 SLOP OIL TRANSPORT

Slop oil transport is the means by which the slop oil is conveyed from the initial collection point to the point of central handling or processing. This, too, is highly location-specific. In some cases, slop oil collection piping throughout the facility may be justified. In most cases, however, the best collection system will be periodic vacuum truck transport from a local sump to a central collection tank, or truck transport of filled slop oil drums.

7.6.3 SLOP OIL DISPOSAL

Slop oil disposal is the means employed for recovering the slop oil as a useful material. In most applications, this will include separation and removal (e.g., as tank bottoms water) of water collected along with the oil. The main element in devising slop oil handling is finding the optimum destination for the slop oil. In a products handling facility, slop oil may sometimes be acceptably blended in one or several of the products, *so long as procedures are established ahead of time to ensure that this practice will not result in making off-spec product.* One example of this would be a marketing terminal which handles only gasoline, and in which "waste" premium gasoline could acceptably be mixed with regular gasoline. In cases other than the above, the slop oil could possibly be periodically transported to a refinery, or sold as fuel.

7.7 Minimizing Tank Bottoms Water Accumulation

Product tank bottoms water is usually by far the most contaminated wastewater generated in a petroleum products terminal, and thus the most expensive water to treat. Since the cost of most treatment methods is at least partially a function of the quantity of water to be treated, it is generally quite desirable to minimize the quantity of tank bottoms water. The means for doing this are directly related to the sources of the water, described in 4.9.1.

7.7.1 EFFECTS OF TANK BOTTOMS FLOW REDUCTION ON CONTAMINANTS

Tank bottoms flow reduction will affect mass flows of tank bottoms water contaminants in different ways, depending on the solubility of the material as described in 4.11.1.

7.7.1.1 Effects On Insoluble (Entrained) Components

In tank bottoms drainage, the entrained component is product drained along with the water. Reducing the frequency of water draws, which is greatly facilitated by reducing the amount of water to be drawn over a given time period, will proportionately reduce the mass flow of entrained product.

7.7.1.2 Effects On Saturated Components

Saturated components are present at essentially fixed concentrations (saturation levels), no matter what the flow of water, so the mass flow of these components in the tank bottoms water is directly proportional to the water flow.

7.7.1.3 Effects On Extractable Components

Extractable components are those which are soluble in both water and product. Reducing the water flow (while keeping the product flow the same) will usually somewhat reduce the mass flows of extractable components, but not proportional to water flow reduction. The exact amount of reduction depends on the distribution coefficient of the component, and the amount present in the incoming product.

7.7.1.4 Effects On Water-Borne Components

The mass flows of water-borne components, which are completely water-soluble (and not soluble in products) are not affected at all by reduction in tank bottoms flow rates. The obvious exception to this is flow reduction in the water stream which carries the components into the tank. Since this stream is usually the water entrained in the incoming product, flow reduction will be difficult (see below).

7.7.2 ENTRAINED PRODUCT WATER REDUCTION: POLICIES AND PROCEDURES

Water entrained in the products received at a terminal can be a significant source of tank bottoms flow, and is often the major source of contaminants (probably the *only* source of highly water-soluble contaminants such as salts, ammonia, and other materials). Unfortunately, this is usually the source over which the terminal has the least control. The following discussion covers procedures by which such control could be gained, and the next section provides guidelines on technical means for reducing water entrainment in products.

7.7.2.1 Establish Distribution Chain Procedures

One control technique would be the establishment of procedures from the refinery down through the product distribution chain to control entrainment of water. When the same company refines, transports, and terminals the products, this can be readily done by establishing the necessary company policies and procedures. In many cases, however, multiple refineries and pipeline companies or other transport companies can serve a given terminal, which makes obtaining control over water content much more difficult.

7.7.2.2 Set Product Specifications for Water or Contaminants

Another approach would be for the terminal to establish rigorous specifications on the water content (or water-soluble contaminants content) of products received at the terminal, similar to other specifications such as octane or vapor pressure. However, the concentrations of water which can result in accumulation of significant quantities of water bottoms and associated contaminants are small (since product turnover volume commonly exceeds water accumulation volume by large factors, e.g.10,000:1), and detection of such concentrations in product samples requires specialized tests. The Karl-Fischer analysis might be usable for determining water content, but at present there is no established analytical test for water-soluble contaminants in petroleum products.

7.7.2.3 Require Take-Back of Delivered Water

Yet another approach would be to require that any water delivered with product be taken back by the originator of the product. To be workable, this would require that other sources of water into a tank be eliminated (i.e., tanks would have to have fixed covers to keep out rain, and no other water-containing material could be placed in the tank). Also, products from different sources could not be mixed in the tank, at least until all water had been drawn from the preceding batch. Regulatory (particularly RCRA) aspects would have to be worked out (see Section 3.3), as well as necessary accounting procedures and other business arrangements. Assuming that all of the above conditions could be met, this procedure would provide incentives for product suppliers to control their water entrainment, which could be done by procedures noted in the next section.

7.7.3 ENTRAINED PRODUCT WATER REDUCTION: TECHNIQUES

The following section discusses the technical means by which the entrainment of water in product delivered from a facility can be reduced or eliminated. Since reduction of water *contamination* is even more critical than reduction of water *flow*, the discussion starts with the main source of contaminated water, and the facility which can deal with it most easily: the refinery.

7.7.3.1 Reduce Refinery Process Product Water Entrainment

Most of the gasoline produced in a refinery is co-condensed with (gasoline and water are in the same boiling point range), and separated from, an extremely contaminated type of water: sour water. Sour water is generated in most gasoline-making process units: catalytic crackers, hydrotreaters, cokers, and hydrocrackers, and typically contains about 10,000 mg/L of ammonium bisulfide and also other water-soluble materials such as phenols. Since many tank bottoms samples have been found to be contaminated with ammonia, and ammonia is very much more soluble in water than in gasoline, it appears likely that the ultimate source of this ammonia is refinery sour water entrained in the gasoline shipped from refineries. There are several means by which this type of entrainment could be reduced or eliminated:

- Improve separation in the water knockout drums in the process fractionation sections. Typically, water is separated in water legs on vapor/liquid knockout drums. Means for improving water separation include installing or maintaining naphtha/water interface detectors to control the KO drum water level control and providing vortex eliminators (see 7.4.1.2) on the water draw nozzles.

- Use coalescers to separate water droplets from product. Coalescers are standard refinery equipment for this service.

- Water wash products which have separated from sour water. Water washing is commonly done for alkylate naphtha from sulfuric acid alkylation units (to prevent downstream corrosion caused by entrained acid), and could also be done for naphtha streams from other processes. Water washing will also remove some soluble contaminants such as phenols from the products.

- Dry products before shipping them out. Several means are available for removing water from products, including silica gel or zeolite adsorbents (molecular sieves), membrane processes, and salt filters (an old technique which uses beds of rock salt).

- Follow other procedures as noted below for reducing entrained water in products shipped out from tankage.

7.7.3.2 Reduce Water Entrainment in Products Delivered From Tankage

Means for reducing water entrainment in product delivered from a tank are similar in many ways to means for reducing product entrainment in water drawn from a tank (7.4.1.2), with some differences:

- Install product draw nozzles some distance above the maximum expected tank water level, and do not allow water to accumulate above the maximum elevation.

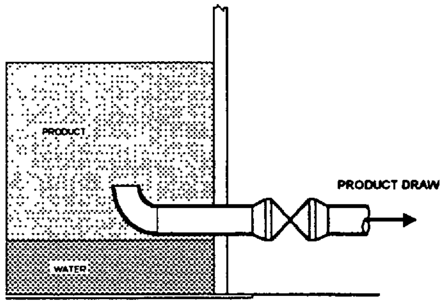
- Keep water level as low as possible. Since frequent water drawing can adversely affect water quality and scheduling in a terminal, this procedure is best adapted to a refinery, whose wastewater quality would be proportionally much less affected.

- Remove all water before drawing a product batch. This is practical only if fairly large (and relatively infrequent) product batches are drawn from a tank, which is probably the case for refineries and gathering terminals.

- Use turned-up product draw nozzles to minimize water entrainment. As shown on Figure 7-12, the openings on such nozzles will be kept away from the water layer, and the movement of fluid into the nozzle opening during product draw will be mostly downwards, instead of upwards from the water, or across the water. The disadvantage of this technique is that effective product volume in the tank is reduced.

FIGURE 7-12

TANK PRODUCT DRAW WATER ENTRAINMENT CONTROL



7.7.4 TANK BREATHING AND CONDENSATION REDUCTION

Since condensation from humid tank breathing air is normally a minor source of tank bottoms water, and control would be difficult (high-flow air dehumidifier?), it is doubtful that attempts should be made to control this source of tank bottoms water.

7.7.5 RAINWATER REDUCTION

Rainwater is probably the major source of tank bottoms water in those terminals which do not have fixed roofs on their tanks (or are not in arid climates). Positive control of this source of water can obviously be achieved, at a cost, by installing fixed roofs, or covers, on the tanks. Other procedures include repairing or replacing floating roof seals when they have become worn, and making sure that floating roof drains are kept clear of blockage.

7.7.6 REDUCTION OF OTHER SOURCES

As noted previously, some terminals place certain wastewater streams or water-containing materials into product tanks. Control of these sources is covered individually, below.

7.8 Minimizing Other Wastewater Sources

7.8.1 RACK WATER

As described in 4.9.2, rack water, or spill containment water, is that water collected in the drainage system of loading/unloading racks, along with (usually) minor amounts of spilled products. In a terminal with good geographical storm water segregation, this can be a significant source of contaminated wastewater, but one whose flow can be controlled. The two sources of rack water are stormwater and cleanup water.

7.8.1.1 Minimize Stormwater

As described in 7.2.4.3, stormwater intrusion into a transfer rack drainage system can be controlled to any degree desired by a combination of roof coverage, curbs, and roof drain routing.

7.8.1.2 Minimize Cleanup

Water is used on transfer racks to clean up (normally minor) product spills, product drips, and sometimes to clean the equipment and slab of accumulated dirt. Several means are available to reduce flow and contamination from this source.

One approach is to use dry cleaning methods. Spills can be handled by use of absorbent granules or fabrics (although this entails disposal of the used materials). Equipment can be wiped or swept clean instead of washed clean, where this is adequate.

In those cases where water must be used, then the amount used can be minimized. In many cases, operators do not realize the adverse effects of over-using water, and can be educated to use only the minimum amount needed for achieving the purpose. In addition, the water supply can be restricted (small hoses, etc.), unless this would jeopardize safety in handling major spills.

In addition, detergent use can be minimized, which is particularly important since detergents have so many adverse effects (stabilizing oil/water emulsions, causing foaming in treatment systems, and killing aquatic life), and loading rack cleaning can be a major source of detergents in a terminal. If detergents must be used, then their use should be minimized; one procedure for doing this is to establish accounting procedures for detergent use by each operator. Detergents should be selected to have minimal impact. They should, for instance, be biodegradable, particularly in facilities which have biotreatment or discharge to municipal treatment systems which use biotreatment.

If detergents are used in transfer racks, then consideration should be given to isolating the rack wastewater from the other plant oily water, particularly tank bottoms water, to help prevent emulsion formation. This may not be feasible, however, if the rack water itself contains significant amounts of oil in need of separation.

7.8.2 TRUCK WASH WATER

Probably the best technique for minimizing truck wash water is to have the trucks washed offsite at a facility designed for this purpose. Note that this is not intended to transfer contaminant discharges from one location to another, but to prevent mixing of oil, normally found in terminal wastewater, with emulsion-stabilizing detergents and fine solids. Another option in some cases is direct discharge of the truck wash water to municipal sewers; if the municipality accepts such water from similar facilities (e.g., car washes, laundries), then it should accept it from a terminal. If neither of these options are available, then the next best technique may be minimizing use of detergents at an on-site wash station, possibly by use of high pressure water wash or steam jet cleaning. If detergents are used on-site, then the resulting wastewater should be rigorously segregated from oily water until the latter has been subjected to oil/water separation.

7.8.3 TRUCK MAINTENANCE WASTES

Most vehicle oils contain additives which will stabilize emulsions, and brake fluid and antifreeze are highly concentrated sources of water-soluble organic contaminants. Therefore, as a rule, all truck (and other vehicle) maintenance wastes such as waste crankcase oil, transmission fluid, brake fluid, and antifreeze should *not* be placed in the terminal's wastewater system, and should, therefore, be hauled offsite for recovery or disposal. To facilitate this, collection drums for each type of product should be placed in the maintenance bays, and means (e.g., funnels with hoses) should be provided to facilitate proper handling. To discourage bypassing the fluid collection, maintenance bay drains could be equipped with shutoff valves under the control of terminal management.

7.8.4 VAPOR RECOVERY WATER

Condensates from cryogenic vapor recovery systems should be routed to product tanks or slop oil tanks to enable recovery of valuable product and separation of water. There is normally no need to minimize the flow of this water unless it is excessive, which would normally be caused by sizable exterior air leaks into an aspirated system. Such a problem should be corrected immediately, not only because of condensate water generation, but because of the hazard of generation of explosive air/product vapor mixtures.

Some vapor combustion systems have a water seal to prevent flame flashback into the vapor lines. To prevent freezing, the water is commonly mixed with antifreeze (ethylene glycol). If this mixture is drained for maintenance or to remove contamination, then the drained material should be disposed of as is (not mixed with facility wastewater).

7.8.5 HAULBACK MATERIAL WATER BOTTOMS

Since water may enter service station tanks through leaks, the procedure for minimizing this source of water is fixing the leaks. To encourage such repairs, the cost of hauling and treating the off-spec product/water mixture could be charged against the station.

If the water is delivered along with the product from the terminal accepting the haulback material, then the solution is to minimize entrainment of such water in the delivered product (see 7.7.1).

Water condensed from humid air as a result of tank breathing (minimal for underground tanks) and venting cannot be practically controlled, but should be a minor source anyway.

7.8.6 BALLAST WATER

Ballast water, which often has high volume, high levels of emulsified oil (due to agitation and fine solids from silty intake water), and incompatible contaminants (e.g., sea water in an inland terminal) is frequently a problem stream for a terminal to handle. Although no simple solutions are available, alternatives to discharge of the water at the terminal should definitely be explored.

7.8.7 HYDROSTATIC TEST WATER

As described in Section 4.9.9, water used to hydrostatically test vessels and pipelines for leaks is released as a large volume at high flow. To facilitate handling of this water, it should be classified as clean as possible. If the vessel or pipeline is scrupulously cleaned of oil and other material prior to the hydrotest, then possibly the water can be discharged untreated along with clean stormwater. If this is not allowed, then it should be handled the same as potentially contaminated stormwater.

7.8.8 STEAM SYSTEM

In 4.7.2, it was noted that corrosion inhibitor chemicals are sometimes added to steam systems, and that these chemicals might be a source of wastewater contamination. When this is the case, measures should be taken to collect condensate from steam traps for return to the boiler as feed water, and condensate leaks should be repaired.

7.8.9 LABORATORY OPERATIONS

In those terminals which operate analytical laboratories, there are several opportunities for reducing lab wastewater flow and contamination:

- If vacuum filtration is done by water aspiration, consider using a vacuum pump or recycle water aspirator instead.
- Place all spent solvents and test samples into collection drums for separate disposal or reprocessing.
- Avoid use of regulated (e.g., chlorinated) solvents.
- Place solids and water contaminated with regulated materials (e.g., heavy metals) into collection drums for disposal.

- Wash laboratory glassware in a water-saving dishwasher, rather than hand cleaning.
- Minimize use of detergents in cleaning glassware and other equipment.

7.8.10 TANK CLEANING OPERATIONS

Perhaps the best method for minimizing wastewater from tank cleaning operations, if this is done by a cleaning contractor, is to require the contractor to remove offsite any wastes generated during the cleaning operation. Other techniques include:

- Maximizing dry cleaning techniques: physical manipulation of sludges (shoveling, scooping, sweeping) rather than water washing.
- Avoidance of detergents (e.g., replace with steam cleaning).
- Not allowing any removed material to be exposed to rainwater (place in a closed container or enclose in a tarpaulin on an elevated location).

7.8.11 REMEDIATION ACTIVITIES

Means for minimizing water and contaminants from techniques for remediating contaminated groundwater or soil should be addressed when designing the remediation work.

7.8.12 DIESEL ENGINE COOLANT DRAINING

When diesel engine coolant systems are drained for changeout or periodic maintenance, various means are available for minimizing wastewater contamination:

- Collect the coolant in a tank for placing back in the engine.
- Collect the coolant and haul off as a waste.
- Purchase coolant chemicals with reduced contamination hazards if these are available and effective.

7.9 Overview of Source Reduction Measures

The justification of source reduction as a means for reducing wastewater treatment cost needs to be done on a case-by-case basis. The following summarizes some general rules as to which source reduction measures are likely to be justified:

- Geographical segregation of clean storm water to enable discharging it without treatment is usually worth the cost of the segregation measures.

- Cleaning up, and keeping clean, drainage areas to enable the runoff to be classified as potentially contaminated (requiring extensive treatment only if accidentally contaminated) rather than contaminated (always requiring treatment) is almost always cost-effective (and also prevents groundwater contamination).

- Reducing tank bottoms water generation by covering tanks is expensive, and needs to be justified by determining the resulting wastewater treatment cost reduction.

However, there is also an air pollution benefit in covering tanks, which may help to justify this measure.

- Reducing the amount of product in tank draw water will probably be justified in tanks which have high volumes of water to be drawn. For "low-flow" tanks, it is probably more cost-effective to use a tank bottoms collection tank as an oil separator than to take extensive measures to reduce the amount of product in the drawn water.
- Control of oily water agitation may only be justified if heavy oils are present. As a rule, with lighter products (gasoline and diesel), agitation alone will not create stable emulsions.
- Since detergents have so many adverse effects (oil emulsification, wastewater treatment foaming, and effluent toxicity), control of their use is usually justified.
- If soluble, difficult-to-remove, strictly-regulated contaminants such as ammonia or arsenic are delivered with product, then control of this source may result in very substantial savings in treatment.
- It is generally justified to avoid on-site truck washing to prevent detergent contamination and emulsion problems.
- Collection of vehicle maintenance wastes (keeping them out of wastewater) is inexpensive, and almost always justified.

Chapter 8

WASTEWATER HANDLING DESIGN

8.1 Introduction

This chapter covers the portion of the wastewater system between wastewater generation, described above, and wastewater treatment, described in the next chapter. Topics include stormwater handling (storage and disposal), flow and contaminant equalization, and wastewater conveyance systems.

8.2 Stormwater Handling in Terminals

8.2.1 INTRODUCTION

Except for terminals located in arid climates, or those with very porous soil, the main wastewater stream which must be dealt with is stormwater. Even those terminals which send their contaminated water offsite (e.g., to municipal treatment works or disposal companies) will usually have to handle and dispose of stormwater onsite, for regulatory (many municipal works will not accept stormwater) or financial reasons. In addition, most facilities will generate large quantities of potentially contaminated stormwater, and provisions must be made for occasional handling and disposal of this water when contamination occurs.

Stormwater storage has both short-term and long-term components, which are quite different. Consider, for example, a five-acre facility which normally receives 30 inches of rain per year, and which receives, as part of this, a one inch rain in an hour (not an unusual rainfall intensity). In this example, the annual average storm flow (assuming a runoff coefficient of 1.0 for simplicity) would be

30" x 1 ft/12" x 5 acre x 43,560 ft^2/acre x 7.48 gal/ft^3 x 1/365 days x 1 day/1440 min = 7.7 gallons/minute.

During the hour of the one-inch rain, the storm flow would be

1" x 1 ft/12" x 5 acre x 43,560 ft^2/acre x 7.48 gal/ft^3 x 1/60 min = **2263** gallons/minute.

The total volume of this storm would be 2263 x 60 = 135,762 gallons.

Clearly, a system designed to handle the average yearly runoff would be grossly undersized for handling individual storm flows. It is this discrepancy which leads to the need to store stormwater in any facility which in some fashion controls its stormwater, rather than allowing it to discharge off-site without control. As discussed in 7.2.1, at least some of the stormwater in a terminal (the tank farm area) will be classified as potentially contaminated, and should be controlled (at least inspected for floating oil or sheen before discharge).

Fortunately, there is an excellent match between the area whose stormwater must be controlled (the tank farm) and the location where the water can conveniently be stored (the tank farm). It is common practice in the industry to keep drain valves from tank basins closed (as a spill containment measure), and to open them only after inspecting (or analyzing) the water to make sure it is not contaminated. The chief issues, then, in storm control in a terminal are concerned with what happens to the water *after* it is stored in the tank basins:

- Where will the water drained from the tank basin be sent if it is clean (directly offsite, or to another collection basin)?
- What will be done with the water if it is contaminated by a spill of product or tank bottoms water?
- How quickly will the basins be drained if the water is (a) clean, and (b) contaminated?

(Note: As a convenient rule of thumb for purposes of storm flow calculations, one inch of rain on one acre per hour is very close to one cubic feet of water per second.)

8.2.2 ROUTING OF CLEAN TANK BASIN STORMWATER

Once it has been determined that tank basin water is clean, it can be discharged without further treatment. The options for routing this water include direct discharge offsite (to sewers, ditches, or public waters) and collection in a pond or tank for subsequent discharge, often after combining with other treated wastewaters. Each of these options has its advantages and disadvantages.

8.2.2.1 Advantages of Direct Discharge of Clean Tank Basin Stormwater

The advantages of direct discharge (i.e., discharge without combining and collecting with stormwater from other tank basins or other treated wastewater) include:

- Direct discharge may be simpler and more economical, particularly if the water can be gravity drained to the final outfall.
- Direct discharge will facilitate rapid draining of the tank basins after a storm to improve personnel access to the basin.

8.2.2.2 Advantages of Collecting Clean Tank Basin Stormwaters and Combining With Other Treated Wastewaters Before Discharge

The advantages of collecting all clean tank basin stormwaters and combining with other treated wastewaters before final discharge (compared to direct discharge) include:

- Collection and combination may be more economical in those cases where the water must be pumped out of the facility, since fewer pump stations will be needed (and smaller pumps, if flow is equalized).

- Collection of tank basin drainages and combination with other treated wastewaters before final discharge will enable sampling and analyzing the total discharge from the facility, thus providing a more certain check on the quality of the discharged water. Also, this procedure will eliminate the need to perform complete analyses on individual wastewater streams, since the combined stream will be so analyzed.

8.2.3 ROUTING AND HANDLING OF CONTAMINATED TANK BASIN STORMWATER

Although rare, at times accidental spills of product or contaminated tank bottoms water will cause accumulated tank basin water to become contaminated. As a rule, this will only happen to an individual basin (i.e., the other basins will still be clean, and can be discharged as normally done). The optimum means for handling the contaminated water will be determined mostly by the required quality of the water as specified in the discharge permit: in some cases, removal of floating oil may be adequate, while in other cases removal of dissolved contaminants (most likely to be critical in the case of a tank bottoms water spill) may be required. Means for handling spills may be specified in the facility's SPCC plan.

8.2.3.1 Removal of Floating Oil From Contaminated Tank Basin Water

For most petroleum products (fuel products without additives), product and water in a spill situation will separate cleanly, with little oil in the water phase. In such cases, it may be acceptable to *drain most of the water from the basin in such a manner as to drain water from the bottom of the pool.* A convenient means for doing this is to have the water drain line inlet terminate in a turndown ell, preferably located in a sump area, as shown on Figure 7-4. The operating procedure is to open the drain valve, and allow water to drain out of the basin in a controlled fashion (avoiding excess velocities and vortexing) until the water level (with floating product) nears the pipe entrance, but before the water surface reaches ground level (to avoid soil contamination).

Spilled product may be removed from the tank basin water surface with any of several types of portable oil skimmers (floating skimmers, rope skimmers, etc.). This could be done before draining any water, or after draining most of the water, but before draining the final portion.

8.2.3.2 Removal of Dissolved Contaminants from Contaminated Tank Basin Water

Since petroleum products are themselves not very water soluble, the main situation for contamination of tank basin stormwater by soluble materials would be a spill of tank bottoms water into the tank basin during a storm, or spill of water-soluble gasoline components such as ethers or alcohols. If permit requirements for discharged stormwater require control of soluble contaminants, or if it is desired to minimize contamination of groundwater (particularly when the tank basin is made of permeable soil), then this water should be collected and treated. To minimize groundwater contamination, it will be desirable to remove the contaminated water from the basin as quickly as possible. Possible destinations for the water include:

- Storage in a tank or basin ("spill" or "offtest" tank or basin) reserved for this purpose.

- Temporary storage in whatever product tankage happens to have volume available, if any.

The first option has the disadvantage of using expensive storage capacity which will normally not be used; however, if the facility normally routes its tank basin water through a final basin, then spare capacity could be provided in that basin at relatively low cost. The second option has several disadvantages to counteract its lower cost:

- It may not be possible to count on the terminal having spare tank volume for handling spills when they occur.

- Using a product tank for this purpose will reduce available product volume accordingly, and may even make the product in the tank inaccessible (if the resulting water layer were deeper than the tank product nozzle).

- For some products, or some spilled material, this practice may adversely affect product quality. It would not be desirable, for instance, to place water contaminated with ether or alcohol in a diesel fuel tank (since these would be extracted into the diesel). Because of rigorous quality requirements on aviation fuels, tankage used for these should not be used for storing contaminated water.

Once the contaminated water is collected, it will have to be treated to meet quality standards for discharge. Since the quality of the contaminated stormwater depends on the spill quantity and quality, and the amount of stormwater, and discharge standards vary considerably, it is difficult to determine a general optimum means for doing this treatment. Some of the options include:

- Bleed the water down at slow rate through the plant wastewater treatment system. Since the water will be dilute compared to normal wastewater (due to being mixed with stormwater), it will help to have a wastewater treatment system which is not hydraulically limited. If this approach is chosen, then it should be factored into the wastewater treatment design and sizing. As a rule of thumb, the load on the treatment system could be determined by the maximum amount of contaminants expected to be contained in any product tank bottoms water inventory divided by the acceptable time for disposing of the stored contaminated stormwater. The hydraulic load on the treatment system could be determined as being the volume of the largest expected tank bottoms spill plus the volume of the largest collected amount of tank basin water.

- Provide temporary treatment for the contained contaminated stormwater. In some cases, the water stored in a tank or a pond can be treated *in situ*. Some means for doing this include addition of hydrogen peroxide, or providing aeration (perhaps with a rental compressor) to promote biological degradation. Also, contract treatment operations could be brought in to treat the volume of contaminated water.

- If the water is being hauled off, or sent to a municipal treatment works, it can probably be disposed of at high rate, although the large volume may cause transportation costs to be high for the hauloff option, and other disposal charges to be high for municipal treatment.

One factor which enters into making provision for handling contaminated stormwater is the quantity of water to be disposed of. This varies considerably from case to case, not only because rainfall intensities vary widely (from place to place, and time to time), but also because the size of the containment area varies considerably. At one extreme, many facilities provide one tank basin per tank (capable of holding the tank contents). At the other extreme, all of the facility tanks are inside of a single basin (capable of holding the contents of the largest tank). Clearly, the amount of stormwater which can be contaminated will be greater in the latter case.

8.2.4 LIMITATIONS ON RETENTION OF WATER IN TANK BASINS

As noted above, in most terminals, tank basins will be the prime location for immediate storage of stormwater. For even extreme storm events, this immediate storage will normally not cause problems with operations of the terminal. Longer term storage, however, and accumulation of water from several storms, has its disadvantages, the chief of which is that the basin will be flooded while the water is being stored. The problems caused by basin flooding are

- Basin capacity for holding spills will be reduced by the volume of stored water.
- Personnel access to the basin will be hindered.
- Tank water draw equipment may be flooded.
- Empty tanks may be floated off their foundations.
- Product transfer pumps and motors can be damaged by water immersion.

8.2.4.1 Reduction of Basin Spill Capacity by Stored Stormwater

Although the fraction of spill capacity reduced by storm storage depends on specifics of the basin design (mostly, dike slope, and dike or wall height) and the size of the rainfall being stored, in most cases the spill capacity will not be significantly reduced by stormwater storage.

8.2.4.2 Restriction of Personnel Access to Tank Basin and Tank by Stored Stormwater

The usual reasons for personnel entering a tank basin are

- Opening and closing tank nozzle valves
- Gauging the tank product and water levels, both from the automatic gauge (located near the bottom of the tank wall) and by manual gauging from the top of the tank (reached by the tank stairway).
- Inspection of the tank and its equipment
- Draining tank water bottoms

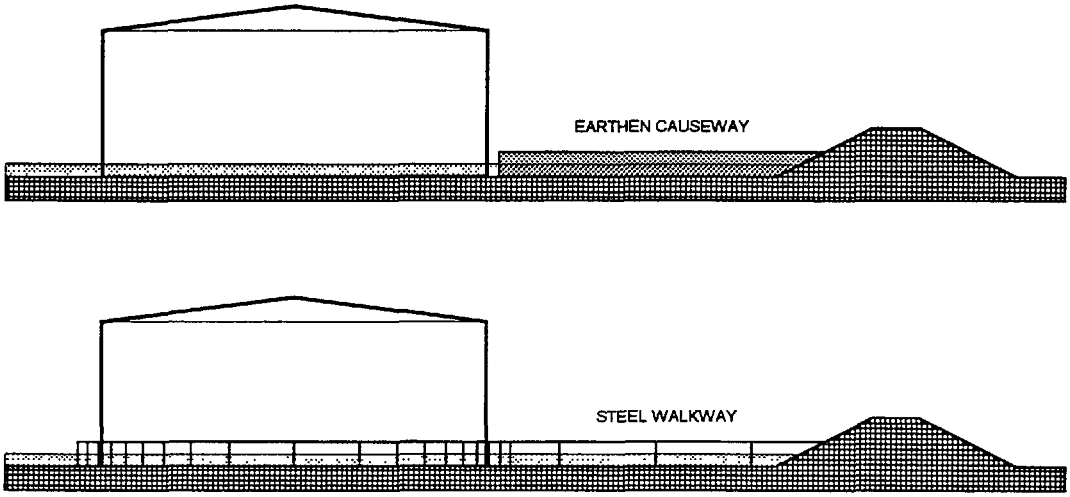
Although normal water depths may not absolutely *prevent* personnel access (if wading boots are available), certainly the presence of standing water will *inhibit* such access. The following measures (see Figure 8-1) can help to accommodate the storage of rainwater in tank basins:

- Elevated walkways from the tank dike to the tank and its stairway can be provided, either as earthen causeways, or as elevated steel walkways. If access to all sides of the tank is needed (to reach all nozzles, or to inspect all sides of the tank), then the walkway can circle the tank.

- Low-elevation valves can have valve stem extensions to enable operating the valves while they are flooded.

TABLE 8-1

FLOODED TANK BASIN ACCESS



8.2.4.3 Flooding of Tank Draw Facilities by Stored Stormwater

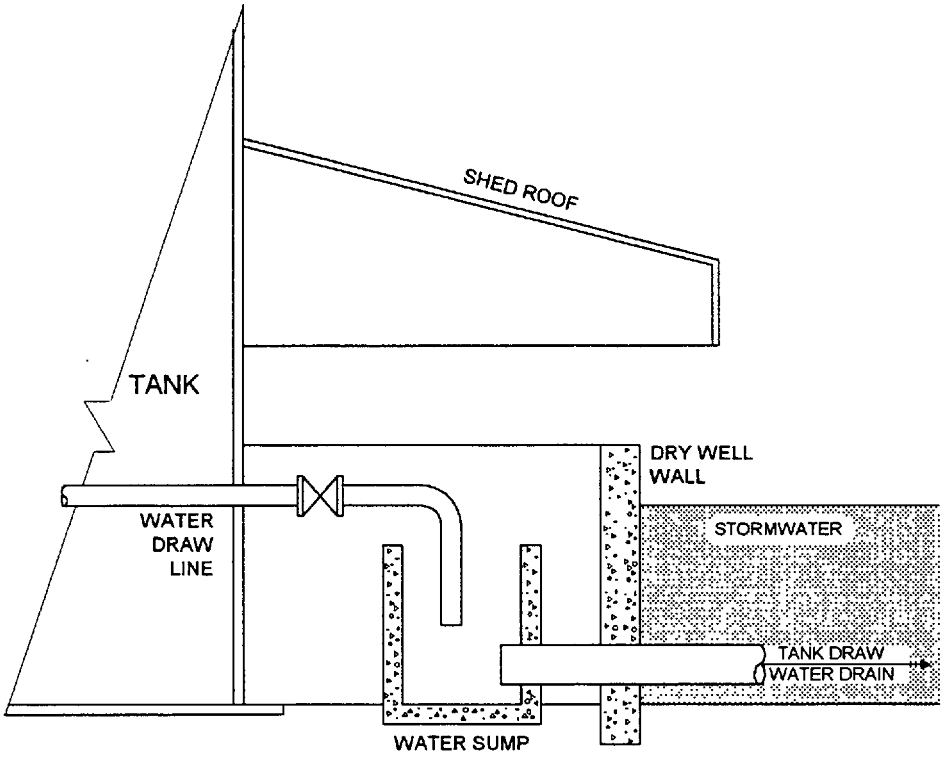
For obvious reasons, tank bottoms draw equipment of various types (see 7.4.1) is located near the bottom of tanks, and so may be flooded by stored stormwater. To overcome this problem, the general solution is to *construct dry wells around the water draw equipment.* A dry well is made by constructing a surrounding wall high enough to prevent water intrusion, and deep enough to contain stormwater falling directly into the well at a level below the equipment (or the well may be equipped with a sump pump to remove such water, or a cover may be placed over the area), as shown in Figure 8-2. In addition to dry wells around the equipment, the walls around water draw sumps can be made high enough to prevent stormwater intrusion, as shown on Figure 8-2.

8.2.4.4 Floating of Tanks by Stored Stormwater

Although it may seem unlikely that a multi-ton steel tank could be floated off its foundations by stormwater, calculation of buoyancy forces (see below) shows that this is indeed possible when product levels in the tank are low enough, and the surrounding water level is high enough. To prevent this, it is essential that water levels never be allowed to approach the buoyant limit during normal operations (during extraordinary events such as impending hurricanes, water can be pumped into the tanks to prevent floating). To reduce the effects of this factor, tanks can be built above the surrounding basin bottom, either by elevating the tank foundation (for new construction), or by excavating the bottom, as shown on Figure 8-3. Of course, engineering

FIGURE 8-2

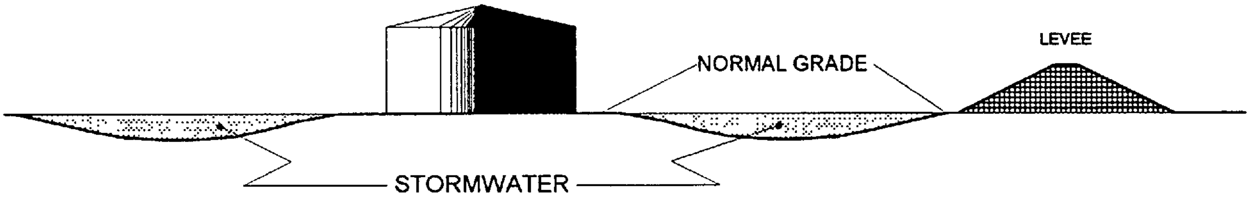
TANK WATER DRAW DRY WELL



judgment needs to be applied in determining the slope of the basin bottom near the tank foundation with regard to soil load-bearing characteristics and foundation structure.

FIGURE 8-3

STORMWATER STORAGE IN EXCAVATED TANK BASIN



Example of Tank Buoyancy Calculation. In this example, the depth of water needed to float a 250,000 bbl 200 foot diameter, 48 foot tall cone roof tank is calculated by determining the weight of the empty tank, and the depth of a corresponding volume of water. Tanks are made of stacked cylindrical rings, typically 8 foot tall, with lower rings thicker than the upper rings. In this example, the ring thicknesses from the bottom up are 1.5", 1.25", 1", 0.75", .5", and 0.25". Using a steel density of 489 lb/ft^3, the weight of the rings is 431478, 359565, 287652, 215739, 143826, and 71913 lb, respectively. Assuming the top and bottom to be 0.25" steel, the weight of each would be 320049 lb. The total weight, assuming no other fixtures, would be 2,150,273 lb. The weight of water displaced by a 1 foot depth of the tank is 1,961,296 lb. Thus, to just float the tank, 2150273/1961296 = 1.1 foot of water would suffice.

To determine the rainwater accumulation in the tank basin, assume the tank is in a 300 ft bottom square diked basin, with dikes of 1:2 slope, and 15 feet tall. The holding volume of this dike (including the tank volume) would be $15*(300^2 + 360^2 + \sqrt{300^2*360^2})/3 = 1,638,000\ ft^3$, or 292,000 bbl. A 2" rain on $360^2\ ft^2$ would make 161,560 gallons of rainwater in the basin, at a depth of 2.9 inches (calculated from $h*l^2 + 2ah^2l + 4a^2h^3/3 - V = 0$, where h = depth, l = bottom length, a = slope [1:a slope], and V = volume). To accumulate the limiting depth (1.1 ft), the amount of rainfall would be $100,459\ ft^3 / 360^2 = 0.78\ ft = 9.3$ inches.

8.2.4.5 Damage to Pumps and Motors

Tank basins commonly contain pumps and associated electric motors for effecting transfer of product and water bottoms. Although generally made to withstand weather, such equipment commonly is not made to be operated submerged, as could happen if tank basin stormwater depth were to be high enough. The problem is exacerbated by the fact that pumps are generally located at as low an elevation as possible to provide maximum suction head (to prevent developing a partial vacuum in the suction lines and pump, which would cause cavitation, or gas bubble formation). If this is a potential problem, the best solution may be to provide a waterproof sump for the pump as described above for tank draw facilities.

8.2.5 LONG-TERM RETENTION OF STORMWATER

As discussed in 8.2.2, in some facilities it will be preferable to hold uncontaminated stormwater rather than immediately discharge it. In such a case, the duration (and quantity) of the retention and the location of the retention must be determined. A number of factors enter into these determinations.

8.2.5.1 Equalization of Stormwater Discharge Flow

If stormwater is collected at a central point, the equipment used to handle the water will be sized for a certain flow. The more the drainage of stormwater out of the facility can be equalized (spread out over time), the smaller this equipment (e.g., pumps) can be. Also, equalizing storm drainage flow will provide more consistent effluent quality in those cases where the treated contaminated water and potentially contaminated stormwater are discharged as a combined effluent. In order to achieve good flow equalization, the retention volume should be made as large as economically achievable. As discussed below, the retention can either be done in the tank basins, or in a separate water holding basin or tank.

8.2.5.2 Advantages of Long-Term Stormwater Retention in Tank Basins

The relative advantages of using tank basins for long-term storage of stormwater are

- There is no cost for building a separate stormwater basin or tank.
- There is no need for high volume conveyances (or pumps) for moving the stored water downstream to central collection.
- Extra land area for the storm basin or tank is not needed

8.2.5.3 Advantages of Long-Term Stormwater Retention in a Separate Basin or Tank

The relative advantages of using a dedicated basin or tank for long-term retention of storm water include:

- The costs and disadvantages (8.2.4) of having flooded tank basins can be avoided.
- Particularly in terminals with a large number of tank basins, stormwater management in a central storage location will be easier than in a multitude of tank basins.
- The central stormwater storage facility can also be used (with some capacity expansion) to hold, and possibly treat, stormwater contaminated by spills of product or tank bottoms water (see 8.2.3).

8.2.5.4 Basin vs. Tank Stormwater Storage

If long-term storage of stormwater outside of tank basins is desired, then the decision must be made between storage in a tank or in a basin. Factors which affect this decision are

- Tank storage usually costs much more than basin storage.

- Deeper containment storage (particularly in tanks) will allow more storage volume with less land area.

- Deeper containment storage (particularly in tanks) will require more pump energy for transferring water into or out of (depending on elevations) the containment.

8.2.5.5 Sizing of Stormwater Retention

Sizing of stormwater retention is not a simple issue, since the cost and operating disadvantages of a large retention volume (and long retention time) must be balanced against the degree of flow equalization which can be achieved, all in the context of somewhat unpredictable rainfall patterns. One approach to determining design is as follows:

1. Select a worst-case year (in terms of extremes of both high and low flow periods) from historical rainfall records (either from facility records, if complete, accurate, and long-term, or from the nearest weather bureau). From the records, calculate the daily rainfall volume (gallons per day) throughout the year.

2. Assume a maximum daily stormwater discharge flow (i.e., flow out of the stormwater containment). Calculate the resulting daily volume of contained stormwater and daily discharge flows from the daily rainfall flows, and the daily volume of water placed into the containment (if rainfall exceeds the maximum allowed discharge) or taken out of the containment (if rainfall is below the maximum allowed discharge). Determine the maximum stored volume during the year. Also determine the number of zero discharge days (i.e., days when there is no rainfall, and no stored water to be discharged).

3. Repeat step (2), with other maximum daily stormwater discharge flows. Plot maximum yearly stored volume and number of zero discharge days versus assumed maximum daily

discharge flow. Generally, as the maximum daily discharge flow rises, the maximum annual stored volume decreases, and the number of zero discharge days increases (i.e., flow equalization decreases).

4. Based on the costs of containment, and the desirability of preventing zero discharge days (i.e., of equalizing storm discharge), select the design value for stormwater discharge flow, and the size of the containment.

8.3 Contaminant Load Equalization for Wastewater Treatment

Those facilities which dispose of their contaminated water offsite to municipal treatment works or other disposal facilities (disposal companies or refineries) without pretreatment do not normally need to be concerned about how evenly the contaminant load (lb/day) is distributed over the year, since the offsite disposal facility receives waste from enough sources to equalize its load. However, those terminals which treat their contaminated water for direct discharge, or pretreat their contaminated water before offsite disposal, must design and size their treatment system to handle loads for various contaminants. In most terminals, however, the contaminant load from the wastewater sources can be extremely variable, as discussed below.

8.3.1 LOAD DISTRIBUTION IN TANK BOTTOMS WATER DRAWS

Tank bottoms water is by far the major source of contaminants in most terminals, and also can be a very erratic source. For those terminals which generate relatively small quantities of tank water bottoms, tanks may be drawn quite infrequently; in some cases, only once per year. As an example, a moderate-size terminal may have seven large storage tanks, and draw 5,000 gallons of tank bottoms water from each tank annually (this would be 1.02 inches of water in a 100 ft diameter tank). If the tanks had tank bottoms water with 10,000 mg/L COD, then the contaminant loads would be 417 lb COD from each tank draw, for an annual contaminant load of 2919 lb/year. If the tanks were all drawn on the same day, the load on that day would be **2919** lb/day of COD. If spread out over the entire year, the daily load would be **8.0** lb/day of COD. Clearly, in this example, the treatment system could be made much smaller if the load were equalized. The two main ways for accomplishing this are to schedule the tank draws, and to provide load equalization containment volume.

8.3.2 LOAD DISTRIBUTION BY SCHEDULING TANK DRAWS

One means for leveling out the contaminant load from tank draws is to schedule the draws to accomplish this. In the example above, one tank could be drawn every (365/5 =) 73 days. For an actual terminal, with varying tank draw frequencies (depending on the rate of water accumulation in a particular tank, and the requirements to control water level in that tank), and varying water qualities, the procedure would be as follows:

- Determine the tank draw interval (or frequency) for each tank, as days between tank draws.
- Determine the water quantity in each draw for each tank (gallons).
- Determine, for each contaminant of concern, the average concentration of that contaminant in the water bottoms from each tank.

- From the above numbers, determine the pounds of each contaminant of concern in the water draw from each tank.
- By trial-and-error, establish a tank draw schedule for each tank which provides an approximately even distribution of the various contaminants of concern over a year's time.

8.3.3 LOAD DISTRIBUTION BY EQUALIZATION TANK

The classical means for equalizing contaminant flows into any wastewater treatment system is to provide a mixed volume upstream of the treatment. The same volume can also be used to equalize flows (by allowing water level to vary). For most terminals with treatment systems, an equalization tank is a very effective and relatively economical means for achieving even load distribution. Even if tank draws are scheduled, as described above, a tank is needed to hold water between the scheduled draws.

8.3.3.1 Equalization Tank Sizing

Sizing an equalization tank depends, obviously, on the degree of equalization required, and the demands placed on equalization (the "sporadicity" of the tank draws). Some of the factors to consider in this determination are as follows:

- As an minimum, the tank should be large enough to hold the single largest tank draw during a year.

- For terminals whose tank bottoms water flow has been minimized (7.7), it will frequently be economical to size the tank to hold an entire year's tank draws. A 25,000 gallon (600 barrel) tank will suffice for many moderate-sized flow-reduced terminals.

- As an additional factor in tank sizing, it should be considered that the tank will also be the oil/water separator for tank draw water, and accordingly will provide better oil separation if it is larger.

8.3.3.2 Equalization Tank Design

As noted above, the tank bottoms water will also serve as the oil/water separator for the tank draw water. Design of the tank, therefore, should be done to accommodate the dual functions. This is described in 9.5.2, and also below.

To accomplish contaminant equalization, the water batches placed in the tank must be mixed, and mixing is not compatible with good oil separation. The following procedure provides a means for reconciling these two requirements: after each batch placement of water in the tank, mix the tank contents gently for enough time to blend the water, and then shut off the mixer until the next batch of water is accepted. "Gentle mixing" means about 1 HP/10,000 gallons of tank water, which should enable water blending in about 30 minutes. Depending on tank design, and designer preference, mixing can be done with top-mounted or side-mounted mixers, or can be done with pump-around mixing.

Turbulence, particularly vertical movement of water, directly counteracts separation of oil. To minimize the effects of turbulence, water should be placed in the tank from the bottom (to avoid disturbing the oil layer), and withdrawal of bottoms water should not be done until several days after the last addition of significant amounts of water. To enable continuous feeding of a wastewater treatment system, a small tank between the equalization tank and the treatment system can be provided to promote quiet settling in the equalization tank, as shown on Figure 8-4. Water draw from the tank should be done with the same control measures for oil entrainment described for product tank water draws in 7.4.1.

The presence of an oil layer on the top of the water does not harm oil separation performance until it becomes thick enough to significantly reduce tank water volume, or until removal of tank water must be done near the oil/water interface. In all of the oil draw procedures, it is necessary, or at least desirable, to be able to determine the thickness of the water layer and the oil layer; means for doing this are similar to those described for product tanks in 7.4.1.1. Means for removing the oil, shown on Figure 8-4, include:

- Use of multiple draw nozzles at various elevations
- Use of a swing line to place the withdrawal elevation at any point desired
- Drawing the water completely from the bottom, and then drawing the oil

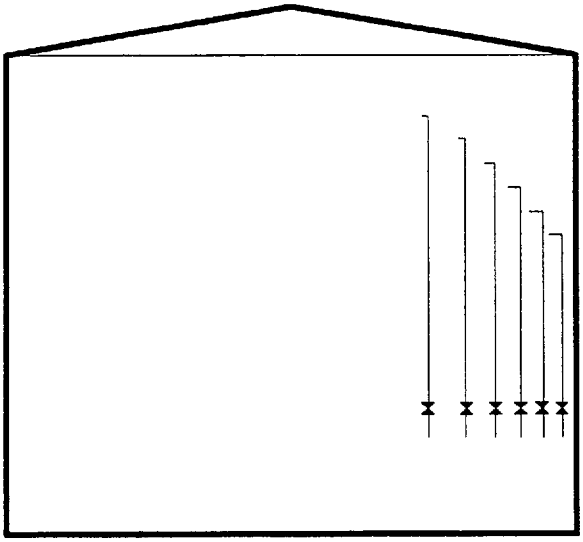
With time, any oil/water separator will accumulate settled solids; in a tank, these will accumulate in the bottom of the tank. When the height of the solids layer approaches the elevation of the water placement/draw nozzle, the solids should be removed. If the settled sludge is fluid, or can be fluidized with gentle agitation, then the solids can be removed by draining out of a low-level sump as shown on Figure 8-4. If the solids cannot be fluidized, then the tank will have to be emptied, and the solids removed by manual cleaning. More frequent removal of the solids may help to keep them in a fluid state.

8.4 Wastewater Conveyance

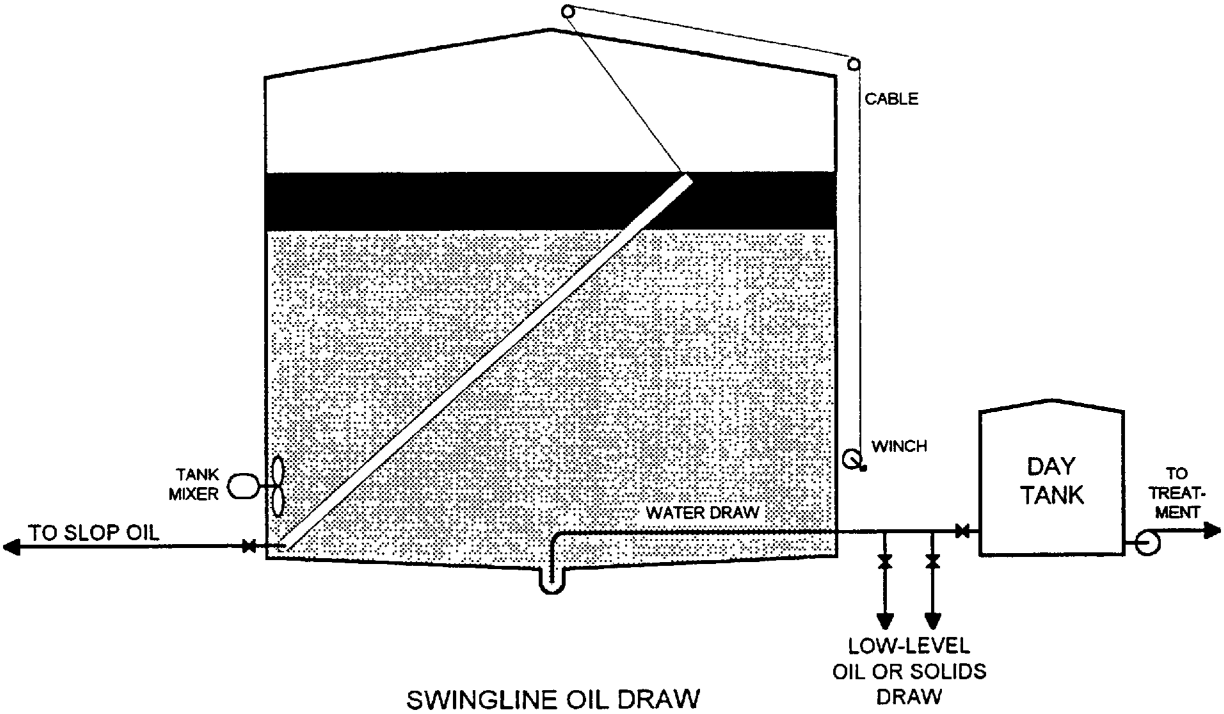
Wastewater conveyance is the general term for the means by which wastewater is moved from one point to another, and by which multiple streams are combined into single streams. The types of conveyance are familiar: pipes, sewers, ditches, and ponds. Water moves through conveyances by two means: gravity drainage (flowing downhill) and by pumping.

Pipes are distinguished from sewers by being built to withstand internal pressure, and thus by having more leak-proof joints. Although newly-constructed sewers with bell-and-spigot joints will probably not leak, sewers (which are always underground) are prone to development of leaks at their joints (groundwater infiltration into municipal sewers is a common problem). This factor affects the choice of conveyance for certain types of wastewater, as does the fact that sewer leaks are hard to detect.

FIGURE 8-4
EQUALIZATION TANK DESIGNS FOR TANK DRAW WATER



MULTIPLE OIL DRAW NOZZLES



SWINGLINE OIL DRAW

8.4.1 SELECTION OF CONVEYANCES

The choice of which type of conveyance to use depends on several factors:

- **Pumped vs. Gravity Flow** If the liquid is pumped under pressure, then only pipe can be used as a conveyance. As a variation on this, pump lift stations can be used in some cases to raise the liquid to an elevation where gravity flow by other conveyances can be used.

- **Effects of Leakage from Conveyance** If the conveyance is transporting contaminated wastewater, then there can be adverse effects if the liquid leaks from the pipe, particularly if it enters and contaminates the ground (contaminated soil and contaminated groundwater are difficult and expensive to remediate). The effects can be particularly severe if the leaks are not readily detected, and so occur over a long time period. This provides an incentive to use a conveyance which is less likely to leak, and one in which leaks can be readily detected. This criterion favors piping, preferably located above ground. If sewer pipes are used for conveying contaminated water, then it may be advisable to line them with seamless plastic pipe.

- **Effects of Leakage into Conveyance** At some locations, groundwater elevations will be high enough to cause infiltration into the conveyance if leaks are present. This is not necessarily a serious problem, but in some cases can be, e.g., if groundwater is contaminated, and the conveyance is transporting uncontaminated water. In such cases, leak-free conveyances as described above may be desirable.

- **Volume of Flow** As a rule, ditches can handle higher volume flow at lower cost than sewers, and sewers can handle higher volume at lower cost than pipes. For high volume flows, particularly stormwater, this factor favors ditches over sewers, and sewers over pipes.

- **Plant Topography** The topography (land shape) of the facility may influence which type of conveyance is the most cost-effective. Particularly for facilities with land at different elevations, and those with more complex land shape, there will generally be more flexibility of flow routing in the sequence: pipes > sewers > ditches > ponds.

- **Access to Liquid** If it is necessary to obtain samples of the liquid along the length of the conveyance, then the most convenient conveyances are ponds, ditches, and above-ground pipes with sample nozzles. The least convenient are below-ground pipes (unless special sample attachments are made) and below-ground sewers (generally accessible only at manholes, which are somewhat hazardous to enter if hydrocarbons are present).

8.5 Design of Tank Bottoms Collection Systems

Since tank bottoms water is highly contaminated, it is generally preferable to provide means for directly transporting it to the tank bottoms collection tank without possibility of its leaking onto (and into) the ground, and without dilution by other water. As a rule, this implies that the transport should be above ground, and that sewers and ditches should not be used. Within these constraints, there are several alternative methods for transferring tank bottoms water which are used.

8.5.1 SUMPS

In many cases, the water conveyance system is not directly attached to the tank water bottoms nozzle, since this prevents inspection of the drawn water during the draw process. For this reason, small sumps are often provided at each nozzle, and these are piped to *collection sumps* for further disposal of the water. Collection sumps can be located at each tank, or can be piped up to serve several adjacent tanks. Depending on the system, water can be gravitated out of the collection sump, pumped, or sucked into a vacuum truck.

A collection sump is basically a water-tight containment, and has only a few design features, which include:

- If the water is not to be continuously pumped or gravitated out of the sump, the sump volume should be comfortably above the maximum volume of water expected to be accumulated in any of the tanks served by the sump.
- The sump needs to be low enough to allow gravity flow from all the tank water nozzles which it serves.
- The sump needs to extend above ground far enough to prevent runoff intrusion, particularly stormwater which may collect in a tank basin.
- If vacuum trucks will be used to empty the sump, then access for the trucks needs to be provided.
- If the sump occupies a fairly broad area, it should be covered to keep rain from falling in it.

8.5.2 HARD-PIPED

"Hard piping" means the use of above-ground pipes to transport the tank bottoms water (note that the pipes are normally "below ground" at the point where they penetrate the tank basin dikes). In a hard-piped system, pipes are run from each nozzle sump to the collection sump. From the collection sump, the water is normally pumped (sometimes gravitated) in above-ground piping to the facility tank bottoms water collection tank.

8.5.3 FLEXIBLE HOSES

If piping is too expensive to install on every water draw nozzle, then flexible hoses can be used to connect the nozzles to collection sumps, with the cost of extra manpower (for making the hose connections) being balanced against the capital cost of piping. Particularly in the case of "low-flow" tanks which are drawn infrequently, the use of hoses may be cost-effective.

8.5.4 VACUUM TRUCKS

The capital cost of piping tank bottoms collection can be mostly avoided by using vacuum trucks to convey tank bottoms water. Particularly in cases where water flow from tanks is low, and a vacuum truck is kept onsite (or is readily available), this may be a competitive option. It will probably be desirable to provide a sump to gravitate the tank bottoms water into, in order to facilitate inspecting the drawn water, and to avoid pumping at excessive rates (which will tend to entrain product).

Chapter 9

WASTEWATER TREATMENT DESIGN

9.1 Introduction

As of 1994, regulations on most terminals are such that treatment beyond simple oil/water separation is not needed to meet discharge standards. For this reason, there are not many actual installations in terminals of the types of treatment described in this section. However, most (but not all) of the treatments described herein are widely used at other types of facilities such as refineries, and several of the treatments (as described in Appendix B) have been tested at terminals either in pilot scale or full scale demonstrations. As noted below and elsewhere in this report, all options, including source control and selection of disposal methods, should be carefully considered before deciding to employ any of the wastewater treatment technologies described below.

9.2 Selection of Treatment

9.2.1 OVERVIEW

After determining the means for disposal of the facility wastewater (5.2), the associated quality requirements and charges (5.4.1) for that disposal option, and the degree of flow reduction and contaminants source reduction (Chapter 7), the treatment requirements for the water can be determined by the difference between the predicted wastewater quality and the desired quality for the various parameters of interest. For example, if the predicted wastewater will have a maximum monthly average COD level of 1000 mg/L, and the discharge permit requires the monthly average COD to be no more than 200 mg/L, then the treatment will have to accomplish an 80+ percent removal of COD. The same analysis could then be done for all permit parameters whose limits are lower than the predicted wastewater quality.

Since contaminant reduction can be achieved by a combination of source reduction and treatment, and the decision between these will be based on the relative costs (and other relative advantages and disadvantages) of each, the above analysis may have to be done for various scenarios of source reduction/treatment combinations. This section analyzes the options for treatment for removing various contaminants, and provides some indication of design factors for these options.

9.2.2 THE EFFECT OF DISPOSAL MEANS ON TREATMENT OF TANK BOTTOMS WATER AND OTHER PRODUCT CONTACT WATER

As described in 5.2, the choice of the means for final disposal of wastewater can strongly affect the degree of treatment, and the necessity for any treatment, of the wastewater. Some general (but not universal) guidelines for treatment of tank bottoms water and other product contact water (e.g., spill containment water) are as follows, arranged in (the usual) order of degree of treatment required:

9.2.2.1 Transport Offsite With Product Mixtures

If water is included with product mixtures sent offsite, usually to a refinery, as product, then it has no quality requirements. As noted in 3.3.2.2 and 5.2.3.2, such material should not even be subjected to oil/water separation.

9.2.2.2 Transport Offsite as Hazardous Waste

Unless charges are assessed based on contaminants concentrations, there is essentially no need to pretreat water being transported offsite as hazardous waste.

9.2.2.3 Transport Offsite as Non-hazardous Waste

Since almost all products-contact water removed from product recovery operations in a petroleum products terminal will be hazardous due to benzene content, this disposal option requires removal of the benzene before transport. To remove only benzene, the best techniques are probably air stripping (9.9) or simple biological treatment (benzene is highly biodegradable). If there are charges for levels of non-hazardous constituents, this needs to be taken into account in determining treatment needs.

9.2.2.4 Evaporation Ponds or Tanks

Evaporation ponds or tanks have few quality requirements on their feed water. Tank bottoms water which is classified as hazardous waste (usually due to its benzene content) should not be placed in evaporation ponds. To enhance evaporation, there should not be any floating oil on the pond water surface. Finally, there are air emission concerns: control of air pollutants and control of odors; requirements for control on these will be very site-specific. Air emissions and benzene content can be controlled by simple air stripping, as described in 9.9. Odorous materials (concentrated tank bottoms water is *very* malodorous) may be more difficult to remove; biological treatment (9.6) is effective for this, as are other techniques for removing soluble organic contaminants.

9.2.2.5 Disposal to POTW

POTW pretreatment requirements are usually less stringent than requirements for discharge to public waters. Since these requirements and disposal costs vary widely from place to place, the degree of treatment will have to be determined on a case-by-case basis.

9.2.2.6 NPDES Disposal to Public Waters

As with POTW disposal, disposal to public waters under an NPDES permit will entail widely varying degrees of treatment, and so must be determined on a case-by-case basis.

9.3 Appropriate Treatments

As described above, petroleum products terminals contain wastewaters with widely divergent flows and characteristics. Some streams have very high levels of dissolved contaminants, and very low flow. Other streams have high flow, but low contamination, and yet others are normally free of contamination, but do become contaminated at times. Under these circumstances, the optimum wastewater procedure should be the application of what is termed "appropriate treatment". Appropriate treatment is defined to mean *the segregation of different types of* *wastewater streams, applying to each type of wastewater the kind and degree of treatment needed to remove the contaminants from the stream, and finally, combining the treated streams into the overall facility discharge stream.* It is a commonsense approach of fitting the treatment systems to the waste streams in order to minimize treatment costs (by minimizing the size of each type of treatment) while maximizing treatment effectiveness (by not diluting the feed to each type of treatment with water not needing the treatment).

The following sections provide an overview of the capabilities of various treatment methods for removing several classes of contaminants. This is followed by descriptions of the treatment technologies. Tables 9-1 and 9-2 summarize the appropriateness of source reduction methods and treatment methods for the various types of contaminants.

9.3.1 ORGANIC CONTAMINANTS

Since petroleum products terminal wastewater is characterized by relatively high levels of dissolved organic matter, and discharge requirements almost always contain specifications on one or several parameters in this category, it is likely that removal of organics will be required.

9.3.1.1 Types of Organic Contaminants

Contaminants in the soluble organics category include BTEX components, phenols, oxygenates, surfactants, and naphthenic acids, and the soluble fraction of oil & grease, TPH, BOD, COD, and TOC. In addition, many toxic components will be found in this category.

9.3.1.2 Source Reduction Potential for Organics

For most terminals, the potential for source reduction of organic contaminants is limited (since the major source is usually material extracted from the products themselves), except where major sources are purchased materials such as detergents or highly water soluble product components such as oxygenates.

9.3.1.3 Treatments for Organics

The treatments which are capable of removing dissolved organic matter are biological treatment (9.6), oxidative treatment (9.12), and activated carbon (9.10), in that approximate order of cost-effectiveness. Since the chemical (oxidation) and physical (activated carbon) treatment costs are roughly proportional to the contaminant load, it is sometimes cost-effective to meet strict limits on organic components by a combination of biotreatment (secondary treatment) followed by tertiary treatment with oxidation or activated carbon.

9.3.2 BTEX REMOVAL

Although removable with other organic contaminants, it is sometimes desired to remove only BTEX components, particularly the benzene which can make the wastewater a hazardous waste. In addition to the methods for organics removal noted above (all of which are effective for BTEX), it is also possible to remove BTEX in simpler, less-expensive air or gas stripping processes (9.9).

Table 9-1
Contaminants and Source Reduction Potentials

Numbers are the approximate order* of suitability of a source reduction for a contaminant

Source Reduction Technique	Organics	BTEX	Separable Oil	Emulsified Oil	Suspended Solids	Soluble Metals	Ammonia	pH Off	Organic Toxicity
Reduce import of product water	1					1	1	1	1
Reduce use of detergents	1			1					1
Reduce tank water volume	2	1		2					
Improve tank draws			1	2					
Reduce rack spills			1						
Eliminate erosion				3	1				

* 1 = most suitable, 2 = next most suitable, etc. Blanks mean not suitable.

Table 9-2
Contaminants and Appropriate Treatments

Numbers are the approximate order of suitability* of a treatment for a contaminant

Treatment Technology	Organics	BTEX	Separable Oil	Emulsified Oil	Suspended Solids	Soluble Metals	Ammonia	pH Off	Organic Toxicity
Oil Separation Tank			1						
Oil-Water Separator			2						
Air Flotation				2	3				
Biotreatment	1	1		1	1	1	1		1
Chemical Oxidation	2	2							2
Activated Carbon	2	2		3		3			2
Air Stripper		1							
Filtration				4	2				
Precipitation						2			
Alkaline Stripping							2		
Chlorination							3		
pH Control								1	
Biological Polishing	3			5	4	3	4		3

* 1 = most suitable, 2 = next most suitable, etc. Blanks mean not suitable.

9.3.3 OILY CONTAMINANTS

All petroleum products terminals will have oily material in their untreated wastewater, and all can expect to have limits on these in their discharge requirements.

9.3.3.1 Types of Oily Contaminants

Contaminants in this category are oil & grease and TPH, as well as the oily fraction of BOD, COD, and TOC. In terms of removal, the discussion covers the *insoluble* fraction of these parameters; removal of the soluble fraction is covered under organic contaminants, above.

9.3.3.2 Source Reduction Potential for Oily Contaminants

The main potential for source reduction of oil lies in reducing formation of emulsions (non-separable oil, see 7.5), with the most promising approach being segregation of surfactants from oily wastewater.

9.3.3.3 Treatments for Oily Contaminants

The prime treatment for oily contaminants, already practiced in some fashion by most facilities, is oil/water gravity separation (9.5), which is the only technique applicable for removal of separable (non-emulsified) oils. For removal of the residual emulsified oil, biological treatment (9.6) and activated carbon treatment (9.10) are effective, with the former being much more cost-effective for this purpose. In some cases, advanced oil/water separation using air flotation (9.9.5.8) may be justified, particularly when levels of emulsified oil are very high.

9.3.4 SOLID CONTAMINANTS

Solid contaminants are those which are insoluble in water, and are distinguished from oily contaminants by settling (rather than floating) and by being solid (rather than liquid), characteristics which control the means for removal.

9.3.4.1 Types of Solid Contaminants

Solid contaminants include TSS, as well as the solid components of BOD, COD, TOC, and metals, and the settleable, solid (non-fluid) fraction of oil & grease (usually, oil trapped on solid particles). For storm water, the main solids source is usually eroded soil and dust which settles on the ground. For tank bottoms water, a major solids source is iron sulfide corrosion product (caused by anaerobic biological generation of hydrogen sulfide). Other streams (e.g., truck wash water) will contain solids as an inherent aspect of the operation.

9.3.4.2 Source Reduction Potential for Solid Contaminants

In order to assess the source reduction potential for solids, it is necessary to determine the solids source. If runoff water is the source, and contains high levels of silt, then source reduction by erosion control (e.g., with plant covers or other means) may be cost-effective. If process water is the source, then source reduction is probably not promising.

It should be noted that controlling solids by source control will also help in reducing the amount of oil in the wastewater (by removing a source of emulsion stabilizers) and will also reduce the formation of oily sludges.

9.3.4.3 Treatments for Solids

Some solids (those readily settleable) will be removed in the oil/water separation device (9.5). Those remaining (suspended) can be removed by biological treatment (which traps fine solids in the biological sludge, see 9.6) or, if high TSS levels are present, by air flotation (9.5.8) or filtration (9.8).

Biological treatment itself generates suspended solids, as soluble organic matter is converted into insoluble bacterial mass, and can be the major source of effluent TSS in those facilities employing this type of treatment. This biological TSS can also contain appreciable quantities of BOD, COD, TOC, metals, and oil (the latter two because biotreatment removes metals and oil by trapping them in the biofloc). To remove excess TSS from biotreatment effluent, coagulation (9.7) can be used in connection with clarification and/or filtration.

9.3.5 METALS

Although toxic metals are usually not major contaminants at petroleum products terminals, extremely strict restrictions on metals in some locations may make metals removal a concern. In addition, some facilities may have toxic levels of some metals.

9.3.5.1 Source Reduction Potential for Metals

Unless the metal in question is a component of purchased materials (e.g., boiler chemicals or laboratory chemicals), there is little potential for source reduction. Arsenic, copper, and zinc all appear to be mostly derived from petroleum products water (tank bottoms).

9.3.5.2 Treatments for Metals

Heavy metals (such as copper and zinc) are mostly insoluble, and so can be removed by techniques which remove suspended solids: biological treatment (9.6), filtration (9.8), and flotation (9.5.8). In addition, activated carbon can be effective for removing the soluble component of many heavy metals. Since all of these treatments are designed for removal of other components, which treatment is selected may depend mostly on the overall treatment scheme.

Soluble metals (mostly arsenic) are more difficult to treat. None of the standard treatments will remove arsenic, and no commercial process is available for this purpose. Arsenic has been successfully removed in a laboratory procedure (9.14.3), which may adaptable in the future for full-scale treatment.

In cases where metals limits are very strict (mg/L range), even the low soluble levels of heavy metals may be excessive. In these cases, specialty treatment techniques are commercially available, as well as laboratory techniques which may be usable in the future for full-scale treatment (9.14).

9.3.6 AMMONIA

Ammonia appears to be present in most tank bottoms water, and may be present in final effluent water at levels exceeding permit limits for ammonia or toxicity.

9.3.6.1 Types of Ammonia

Strictly speaking, there is only one type of ammonia, the material itself. However, *amines* (organic derivatives of ammonia) can be converted to ammonia, in biological treatment, for instance.

9.3.6.2 Source Reduction Potential for Ammonia

Ammonia appears to be mostly delivered to terminals along with products. Unless this source can be controlled, there appears to be little potential for source reduction. Although amines are not likely to be a significant source of ammonia in terminals, this may be a controllable source in some cases, particularly if amines are used as steam system corrosion inhibitors, and steam condensate is sent to wastewater collection instead of being returned to the boiler.

9.3.6.3 Treatments for Ammonia

Where biological treatment is practiced, ammonia removal by nitrification (oxidation by nitrifying bacteria to nitrate and nitrite) is usually possible; however, the degree of nitrification is usually incomplete, and may be unreliable (nitrifying bacteria are slow to reproduce and are susceptible to chemical inhibition). The use of other ammonia removal techniques is currently rare, although new regulations of effluent toxicity may change this. Alkaline air stripping can be used for removing ammonia, as well as breakpoint chlorination (9.13), although these techniques may be expensive and difficult to operate.

9.3.7 pH OUT OF RANGE

In wastewater, pH is influenced by the balance of acidic and alkaline materials of various types. For most petroleum products terminals, pH will naturally fall within the regulated limits.

9.3.7.1 Source Reduction Potential for pH Extremes.

Unless significant quantities of strong acids or bases are used as purchased chemicals in a terminal, there is little potential for source reduction as a solution to pH extremes.

9.3.7.2 Treatment for pH Extremes

Treatment systems often can influence pH inadvertently. Biological treatment, for example, can remove organic acids (and thus make pH more alkaline), or can convert alkaline ammonia to strongly acidic nitric acid (and thus make pH more acidic). When pH control is needed, the solution is usually addition of strong acids or bases as regulated by a pH control system, although manual control using other materials such as lime can also be effective in some cases (9.11).

9.4 General Wastewater Treatment Factors

Although the types and degrees of wastewater treatment vary considerably, the following factors are applicable to all types of treatment in petroleum products terminals.

9.4.1 WINTERIZING AND TEMPERATURE MAINTENANCE

Most treatment processes operate best within a certain temperature range since the rate of chemical and biochemical reactions is directly influenced by temperature (typically, reaction rate doubles for every 18 F rise in temperature). Maintaining such temperatures is not a problem for large treatment systems such as in municipalities and refineries which receive warm water, and process it in large systems with relatively low heat losses. For most terminals, however, particularly those located away from the southern US, temperature maintenance in cold weather can be a problem. Contaminated terminal wastewater generally has very low flow (0.1 gpm is not uncommon), and so heat losses to atmosphere while it passes through pipes and the small treatment system (with relatively large surface area) can be very significant. In addition, most terminals do not have any source of hot or warm water in their contaminated water system, so the wastewater (which is held for long times in product tanks) is cool when it enters the treatment system. In most terminals, therefore, it will be necessary to warm the cold season feed water prior to treatment, and to keep it warm in the treatment reactor, either with heaters or with good insulation. If a terminal normally generates steam, then it may be the best and safest source of heat. About the only other option is electrical heat with immersion resistance heaters. While these are economical and easy to use, ample precautions must be taken to prevent explosion hazards if the wastewater is contaminated with gasoline. Such precautions include low-level liquid shutoffs on the heater circuit to prevent the heater from operating dry, and internal high-temperature shutoffs in the heater body.

Rather than insulate and heat trace a reactor and all its associated equipment, it will be preferable in many cases to house the entire treatment system in a heated building. Any vents from the process, particularly from aerated biotreatment systems, should be routed outside of the building to prevent generation of an explosive atmosphere inside the building (see below). Note that this procedure only ensures temperature maintenance; it will still usually be necessary to also heat the incoming feed water.

Another option is to store low-flow wastewaters during cold months, and to perform treatment after ambient temperatures have reached the acceptable range (this may be a necessity in very cold climates, since the tank bottoms water in the product tanks will be frozen in the winter).

9.4.2 EXPLOSION PROOFING

Although wastewater is not ignitable, much of the contaminated water in a petroleum products terminal is drawn directly from gasoline tanks, and occasional malfunctions in equipment or operations could cause pure gasoline to enter the wastewater treatment system. For this reason, the *wastewater treatment equipment should be subjected to the same explosion proofing precautions which are used for handling gasoline*. Some of these precautions are as follows:

- All electrical equipment such as mixers, aerators, pumps, and lighting which may contact vapors from the wastewater treatment unit should be explosion proof. It should be kept in mind that gasoline vapors are heavier than air, and so will flow downwards when emitted.

- If treatment is conducted inside a building, then vapors from the treatment system should be vented outside the building. The building itself should be well-ventilated with a constantly-operating fan.

- The treatment system (particularly package treatment systems not designed for petroleum products terminal use) design and construction should be carefully examined to make sure that explosion proofing is employed, and to ensure that there is essentially no possibility of vapors and ignition sources coming together. Some processes appear to be inherently difficult to explosion proof. UV light systems, for example (9.12.4), use high voltage lamps in quartz tubes immersed in the wastewater, with no means for preventing ignition if a quartz tube were to break.

9.4.3 BATCH PROCESSING

Most treatment systems (except sequencing batch biological reactors) are designed to operate in a continuous mode, and are most economically operated that way (since operations are full-time instead of sporadic). For facilities such as petroleum products terminals, with small amounts of wastewater, and little available manpower for wastewater operations (the common situation), it may be advantageous to do *batch processing* of wastewater through continuous treatment. Batch processing, shown on Figure 9-1, involves (a) collecting a batch of wastewater in a tank, (b) processing the batch continuously through treatment until it is exhausted, and (c) collecting the treated effluent in another tank; the process is then repeated with another feed batch and effluent batch. Compared to simple continuous processing, the batch processing technique requires at least two extra tanks (sometimes four extra tanks, if the tanks are used alternately). The advantages which justify the cost of these (usually small) tanks are brought about by improvement in operational reliability:

- The batch of feed water can be inspected and analyzed to make sure that it has the right pH and is water, not product, and to determine the contaminant level (for those treatment processes which must be adjusted to accommodate different contaminant levels).

- The batch of effluent water can be analyzed to make sure it meets quality specifications before it is discharged.

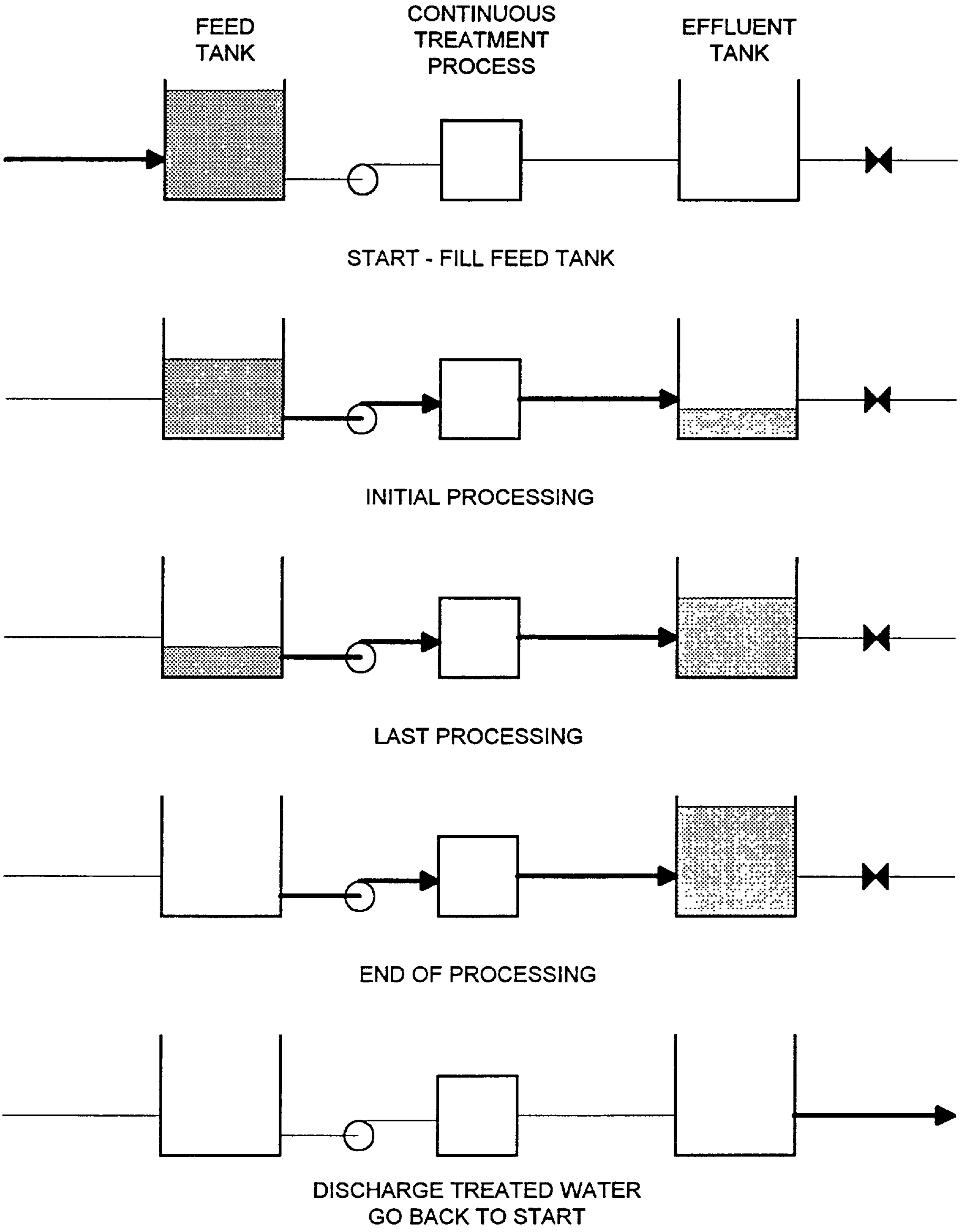
- By discharging in batches, and only analyzing effluent when batches are discharged, it may be possible to achieve significant savings in analytical costs.

By contrast, continuous operation either runs the risks of (a) feeding off-spec wastewater, (b) feeding excess contaminant load, and (c) discharging off-spec effluent, or requiring expensive continuous monitoring to reduce these risks. For facilities which are not necessarily even manned full-time, batch processing provides assurance of treatment reliability at relatively low cost.

Batch processing offers another advantage, in that the feed tank can be used as a final oil separation device, as shown in Figure 9-2. By allowing more feed water into the tank, the oil layer can be forced over the oil weir, and skimming mechanisms are not needed. Also, if the feed water requires any pretreatment such as pH control or nutrient addition, this can conveniently be done in the batch feed tank if it is equipped with a mixer.

FIGURE 9-1

BATCH PROCESSING



9.4.4 CONTINUOUS VS. PERIODIC TREATMENT

Since most terminals do not generate high flows of contaminated wastewater, they have the option of either treating a low flow of wastewater continuously or storing the water and periodically treating a higher flow. Each option has advantages and disadvantages.

9.4.4.1 Advantages of Continuous Low-Flow Treatment

The advantages of continuously treating a low flow of wastewater are as follows:

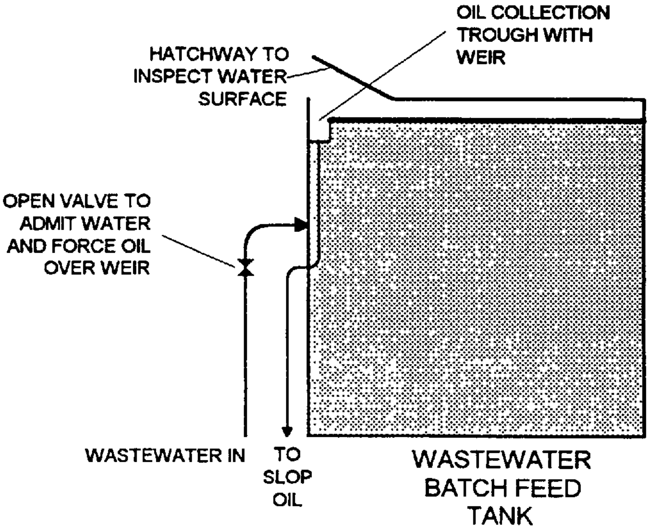
- The treatment equipment can be smaller. The factor by which it is smaller is directly related to the frequency of periodic treatment: continuous equipment will be seven times smaller than equipment sized to treat a week's wastewater in a day.

- It is not necessary to turn the equipment on and off. Frequently, when treatment equipment is turned on or off, it takes a significant amount of time to do the startup (lining out treatment conditions, making sure everything is operational) and shutdown (purging lines, cleaning vessels).

- Biological treatment must be operated continuously. Biological treatment is probably the most cost-effective type of treatment, and it can only be operated in the continuous mode since living bacterial populations cannot be turned on and off (see 9.6.2).

FIGURE 9-2

BATCH FEED TANK OIL SKIMMING



9.4.4.2 Advantages of Periodic Treatment

The advantages of collecting batches of wastewater for periodic (weekly, monthly, etc.) treatment are as follows:

- Less time is used for treatment, which means that less operator time will be required and/or that the operation can be continuously monitored by operators while it is being performed.

- Periodic treatment has the batching advantages of tailoring the treatment to the feed batch, of allowing the effluent batch to be tested before discharge, and of possibly saving analytical costs (however, continuous batch processing can achieve the same benefits; see 9.4.3 above).

- Mobile treatment units can be used in place of permanent units (see below).

9.4.5 PERMANENT VS. MOBILE TREATMENT

For facilities which generate large quantities of wastewater, it is generally assumed that any treatment equipment will be permanently located on-site, and owned by the facility. For most terminals, this assumption is not necessarily valid, since the option exists of doing periodic treatment of collected wastewater (see above), and this need not be done with equipment permanently kept at the facility, but could be done with mobile truck-mounted equipment periodically brought on-site. The equipment could either be owned and operated by the terminal company, and moved about from terminal to terminal, or could be a contracted service. The advantages and disadvantages of continuous and periodic treatment are compared above. If periodic treatment is used, a comparison can be made between doing it with permanent or with mobile equipment.

9.4.5.1 Advantages of Permanent Equipment:

- Equipment availability when needed is assured.

- If mobile contract services are used to treat water which is discharged under the facility's permit, then compliance with the permit is dependent on the contractor's performance.

- The cost and time of transporting mobile equipment, and of making equipment rugged enough to withstand frequent road travel, is avoided.

- Treatment equipment is not limited to that which can placed on a mobile platform.

9.4.5.2 Advantages of Mobile Equipment:

- The cost of expensive equipment can be spread over all the users, and more sophisticated treatment can be employed at lower cost.

- Full time operator/drivers can be thoroughly trained and kept current. In a terminal, operation of permanent equipment is likely to be a part-time job for operators, whether the equipment is operated continuously or periodically.

- If contract mobile services are used, there may be financial advantages to hiring a service as compared with amortizing capital equipment.

9.4.6 TREATMENT SEQUENCE

Many treatment schemes utilize more than one type of treatment, and so the question of treatment sequence (which comes first, which comes next, etc.) must be determined. Some guidelines on this are as follows:

- **Oil separation should always come first**. Removability of oil is better in raw wastewater than in water which has been sent through other forms of treatment. Equally important, almost all wastewater treatment processes are harmed by the presence of oil. Because of these constraints, oil removal is commonly known as *primary treatment.*

- **Removal of dissolved organics (if needed) should probably come second.** Since many methods for removing dissolved organics also remove some inorganic contaminants, and since the presence of high levels of dissolved organics can interfere with other types of treatment, it is generally preferred to remove organics immediately after oil removal. For this reason, removal of dissolved organics (particularly by biotreatment) is commonly known as *secondary treatment.*

- **The sequence for any additional treatment depends on the treatment(s) used.** Treatment downstream of organics removal is commonly called *tertiary treatment.* In most cases, tertiary treatment is not needed to meet discharge standards (although this is becoming less true as regulations become broader and stricter). The treatment sequence, and the possibility of combining treatments, depend on which technologies are used. As an example, if biological treatment is used, and the effluent must meet limits on suspended solids, then the biotreatment may have to be followed by filtration. As another example, some contaminants are removed by chemical precipitation, followed by clarification (and possibly filtration). If several contaminants are to be so removed, it may be possible to combine the precipitation reactions so that only one mix tank, clarifier, and filter are needed.

9.4.7 REQUIREMENTS FOR LABORATORY OR PILOT TESTING OF WASTEWATER TREATMENT

If petroleum products terminals wastewaters were uniform in the nature of their contaminants, then there would be little need for experimental testing of various treatment methods: each method would have its well-characterized capabilities and costs for various degrees of treatment, which could be used to directly calculate the optimum treatment system once the wastewater quality and desired effluent quality were known. Unfortunately, this is far from true, as seen for various contaminants:

- Dissolved organic matter can be composed of a very large number of different compounds, few of which have been directly identified in terminal wastewater, and all of which have widely varying susceptibility to wastewater treatment. Testing on actual terminal wastewaters (Hall, 1994) has shown considerable variability between terminals with regard to biological treatment, activated carbon treatment, and oxidative treatment. More extensive experience with related petroleum refinery wastewater has shown that it is impossible to predict which type of biological treatment will be effective (or even operable) for a given plant, and what degree of each type of treatment will be required.

- Removal of suspended (free) oil by gravity separation is influenced very strongly by oil droplet size (degree of emulsification). While simple testing can show the amount of emulsified oil to be expected in gravity separation effluent, it is not possible to predict the success of various techniques at removing the residual emulsified oil, since this depends on the (widely varying) oil droplet sizes, and the unmeasurable degree of emulsion stabilization by surfactants and solids.

- Suspended solids removal is strongly influenced by the size and characteristics of the solids (which vary considerably), and success of various types of removal cannot be predicted from knowledge of TSS levels.
- Removal of insoluble metals is subject to the same limitations as found for suspended solids. Soluble metals can be easy to remove (if simple ions), but can also be nearly impossible to remove (if solubilized by strong chelating agents), and there is no means for readily determining which form is present in a wastewater.
- Toxicity can be caused by a wide variety of materials, only some of which are known, and measurable. From chemical and toxicity analysis of a raw wastewater, it is quite impossible to predict the degree of toxicity removal to be expected from various types of treatment.

The above factors lead directly to a general rule: *In any specific application, laboratory or pilot testing of treatment technology should be done before selecting and sizing the treatment technology, whether it is permanently installed on-site or brought in as mobile treatment.* Depending on the type of treatment, the testing can be done in small test units (generally for suspended growth biological treatment processes and many physical/chemical treatments), or in pilot-size units (generally for attached growth biotreatment processes, and some physical/chemical treatments, whose performance is affected by system geometry). For biological treatment, test time for each system and loading is about 2 months to allow for acclimation (development of a bacterial culture) and collection of performance data. For physical/chemical treatments, test time can usually be much less since a living culture does not have to be developed and stabilized. The above recommendation is not made lightly, since it is recognized that it can add significantly to the cost and time of developing a system design. However, to re-emphasize its necessity, *design of treatment for petroleum industry wastewater should not be done solely from a textbook, nor solely from vendor's recommendations, nor from previous experience alone, nor from consultants who rely on those in place of test data. To do so is to run a significant risk of installing a system which is undersized, oversized, not capable of meeting treatment standards, or not operational at all.*

9.5 Oil/Water Separation

9.5.1 BASIC PRINCIPLES

The basic principles which govern gravity separation of oil are as follows.

9.5.1.1 Gravity Separation

By far the most common type of oil/water separation is gravity separation, in which the oil and water separate into layers based on their different densities (specific gravities). Gravity separation of oil is controlled by four factors: oil density, oil droplet size, water velocity through the separator, and presence of emulsions. By their nature as separation devices, separators made for oil removal also accomplish solids removal.

9.5.1.2 Product Density

The density of oil fractions ranges from slightly heavier than water (e.g., asphalt) to somewhat lighter than water (e.g., naphtha). Oil/water separators are universally designed to remove oil as the upper layer, so it is generally easier to separate lighter oils than heavier oils. Fortunately, most petroleum products (gasoline, diesel fuel, and fuel oil) are sufficiently lighter than water that gravity separation is achievable. Table 9-3 shows the specific gravities (density relative to water) for several petroleum products.

Table 9-3

Typical Specific Gravities of Petroleum Products

Product	Specific Gravity
Gasoline	0.707
JP3	0.760
JP4	0.773
Kerosine	0.792
Kerosine	0.816
No. 2 Fuel Oil	0.860
Lube Oil	0.880
No. 6 Fuel Oil	0.963
No. 6 Fuel Oil	0.982

The specific gravity is the density relative to water (specific gravity of water = 1.000) at standard temperature.

9.5.1.3 Stoke's Law and Droplet Size

Oil/water separation is a branch of general gravity separation (the other main branch is *settling*), which is controlled by Stoke's Law. Stoke's Law states that particle separation is enhanced by larger density differences between the two phases, and by larger particle sizes. In the case of oil separation, this means that large oil droplets are easier to separate than small droplets. In 7.5.2.1, means for enhancing wastewater oil droplet size are described. Some oil/water separators (including parallel plate separators covered below) use the principle of *coalescence*, in which small oil droplets are made to fuse together as large easy-to-separate droplets.

9.5.1.4 Hydraulic Loading

A gravity oil/water separator is essentially a vessel through which water flows. For oil to be successfully separated, it must rise to the top of the water before the water reaches the outlet end of the separator. This is controlled by the relative travel times of the main water flow and the oil droplet upward movement. The oil droplet travel time is the vertical distance from the bottom of the separator to the top of the water (depth) divided by the Stoke's Law oil droplet velocity. The water travel time is the separator volume divided by the water volumetric flow rate. Any oil droplet whose travel time is less than the water travel time will be separated. There are two main implications of these relationships: a larger separator will provide better separation than a smaller one, and lower water flow through a separator of a given size will give better separation than higher water flow. Separator design sizing is covered below, and control of water flow to a separator is covered in 8.3.

9.5.1.5 Laminar Flow

An issue related to hydraulic loading is *laminar flow*. Laminar flow (literally, flow in layers) is smooth, non-turbulent flow. Oil separation requires laminar flow conditions, since turbulence will cause oil droplets to be carried from the water surface back down into the bulk water volume. To promote laminar flow, high velocities must be avoided, temperature gradients (e.g., hot water in a cold-walled tank) which cause thermal convection must be avoided, and mixing must be avoided.

9.5.1.6 Emulsion Effects

One of the main problem areas in oil/water separations is emulsions. As described in 7.5, emulsions are stable suspensions of oil in water or water in oil. Generally, oil/water separators cannot remove emulsified oil from water, so the control technique must involve prevention of emulsion formation, or elimination of emulsion discharges to oily water sewers, which are covered in 7.5.

9.5.1.7 Solids Separation

Although not necessarily desired, oil/water separators will also function as solids/water separators since conditions are established to achieve good separation in either direction (floating or sinking). For this reason, provision must be made for removing settled sludge from separator bottoms.

9.5.2 SETTLING TANK OIL SEPARATION

For low-flow wastewater such as tank bottoms water from covered tanks, probably the optimum procedure for separating oil is to place the water in a long-retention-time collection tank. The long retention time, and the normal absence of turbulence, lead to very good removal of separable oil. Although basically simple, there are a few design features to be considered:

9.5.2.1 Retention Time

To be most effective, the minimum retention time (tank volume divided by maximum daily water throughput) should be about a week.

9.5.2.2 Turbulence

Turbulence, particularly vertical movement of water, directly counteracts separation of oil. To minimize the effects of turbulence, water should be placed in the tank from the bottom (to avoid disturbing the oil layer), and withdrawal of bottoms water should not be done until several days after the last addition of significant amounts of water. Water draw from the tank should be done with the same control measures for oil entrainment described for product tank water draws in 7.4.1.

9.5.2.3 Removal of Oil Layer

The presence of an oil layer on the top of the water does not harm oil separation performance until it becomes thick enough to significantly reduce tank water volume, or until removal of tank water must be done near the oil/water interface. In all of the oil draw procedures, it is necessary, or at least desirable, to be able to determine the thickness of the water layer and the oil layer; means for doing this are similar to those described for product tanks in 7.4.1.1. Means for removing the oil, shown on Figure 8-7, include:

- Use of multiple draw nozzles at various elevations
- Use of a swing line to place the withdrawal elevation at any point desired
- Drawing the water completely from the bottom, and then drawing the oil

9.5.2.4 Removal of Sludge Layer

With time, any oil/water separator will accumulate settled solids; in a tank, these will accumulate in the bottom of the tank. When the height of the solids layer approaches the elevation of the water placement/draw nozzle, the solids should be removed. If the settled sludge is fluid, or can be fluidized with gentle agitation, then the solids can be removed by draining out of a low-level sump as shown on Figure 8-7. If the solids cannot be fluidized, then the tank will have to be emptied, and the solids removed by manual cleaning. More frequent removal of the solids will usually help to keep them in a fluid state.

9.5.2.5 Tank Mixing vs. Separation

As described in 8.3.3.2, the tank bottoms collection tank plays a primary role in equalizing the concentrations of various wastewater streams placed in it as a means for leveling out the quality of water sent to downstream treatment. To accomplish this equalization, the waters must be mixed, and mixing is not compatible with good oil separation. The following procedure provides a means for reconciling these two requirements: after each batch placement of water in the tank, mix the tank contents gently for enough time to blend the water, and then shut off the mixer until the next batch of water is accepted. "Gentle mixing" means about 1 HP/10,000 gallons of tank water, which should enable water blending in about 30 minutes. Depending on tank design, and designer preference, mixing can be done with top-mounted or side-mounted mixers, or can be done with pump-around mixing.

9.5.3 API SEPARATORS

Separators designed to API standards, commonly known as API separators, are considered to be the optimum means for simple gravity oil/water separation. The design principles involved (avoidance of short-circuiting, avoidance of turbulence, provision of adequate separation time, and optimized skimming) are applicable to all gravity separators, but the term is usually reserved for large in-ground or above-ground field-constructed units, which are used in terminals, but are more common in facilities such as refineries which have high wastewater flow rates. Terminals more commonly employ much smaller package separators (9.5.6) which are suited for their low oily water flows. Features of the standard API design are illustrated in Figure 9-3.

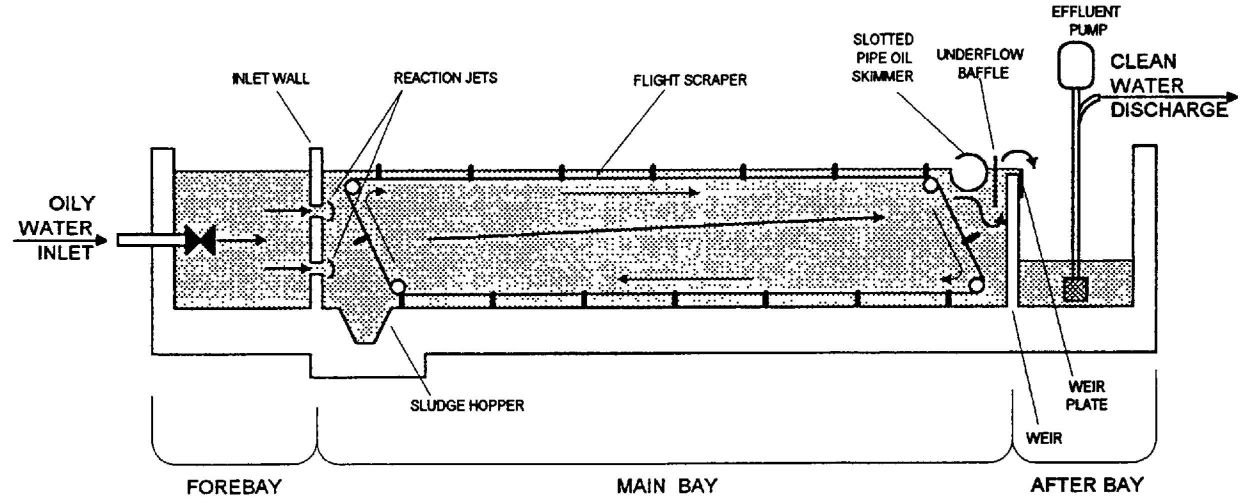
9.5.3.1 Design

Gravity oil/water separator design has been thoroughly covered by a document published by the American Petroleum Institute (API, 1990). The following summarizes the design principles in that document, along with some supplemental recommendations.

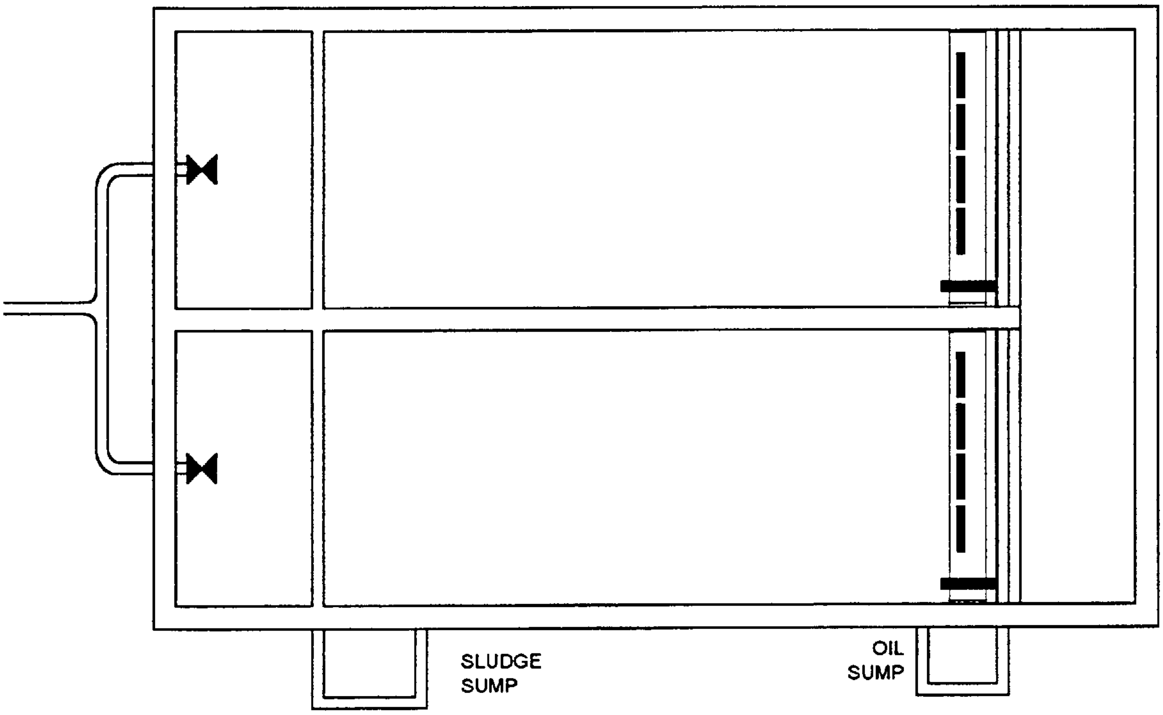
A gravity oil/water separator has three basic parts: an inlet section, a main separation section, and an outfall section.

FIGURE 9-3

API OIL/WATER SEPARATOR



CROSS SECTION VIEW



PLAN VIEW

9.5.3.2 Inlet Section

Several functions are served by the inlet section, sometimes known as the *forebay*: collection point, trash separation, and flow distribution. It commonly serves as a collection point for several oily water sewers. It can be equipped with a trash rack to keep large materials out of the main separator. The trash rack generally is a bar screen or mesh with 2-5 cm openings, which is manually cleaned as needed. More elaborate systems use a traveling trash rack, a motorized mechanical system which continuously separates and deposits the trash.

Two types of flow distribution are done by the inlet section. The first type involves even distribution of the flow across the width and height of the separation section to prevent turbulence and short-circuiting of the water flow in that section. Two recommended means for doing this are use of *reaction jets* or *vertical-slot baffles*. At the very least, the flow distribution should be controlled by an impingement plate mounted on an inlet pipe.

The second type of inlet flow distribution is control of flow to each of several main separation bays, if multiple bays are used. This is a shutoff function, and enables stopping the flow to any bay to enable doing maintenance work in the bay. It is commonly accomplished by providing an inlet pipe to each bay, with a shutoff valve, as illustrated in Figure 9-3.

In most inlet system configurations, oil will be trapped in the forebay since water leaves the bay below the water surface; in some cases more oil will separate at this point than in the downstream separation section. For this reason, skimmers are usually placed in those inlet sections where oil can be trapped; skimmer design is covered below.

9.5.3.3 Separation Section

The separation section, commonly known as the *main bay(s)*, is usually a rectangular chamber with an inlet wall on one end, an outfall weir at the other, and a skimmer.

Selection of the number of bays requires consideration of several factors. Generally, fewer bays (with the same overall separator dimensions) will result in lower costs, but the minimum number of bays should be two to enable temporary shutdown of a bay for maintenance and cleaning. Another factor is the availability of various sizes of standard hardware such as skimmers and flight scrapers.

Sizing of the main bays requires a detailed analysis summarized as follows. The analysis is based on sizing one bay based on the design flow through that bay. Typical oil droplet size and density are assumed (if the oil specific gravity is significantly greater than 0.92 and/or the oil droplet size is significantly less than 0.15 mm, then detailed API design procedures should be used).

> The horizontal velocity (volumetric flow divided by vertical cross-sectional area [height times width]) should be less than 3 feet per minute. Thus, the vertical cross-sectional area (in square feet) should be greater than the volumetric flow (in cubic feet per minute) divided by 3. As an example, if the design flow is 300 cubic feet per minute, the product

of the height and width of the bay (vertical cross-sectional area) should be greater than 100 square feet: $A_v=HxW=Q/3=300/3=100$.

The bay depth should be at least 3 feet, and at most 8 feet. To continue the example, if the bay width is 20 feet, the depth should be at least 5 feet: $D=A_v/W=100/20=5$.

The bay length is determined by the horizontal cross-sectional area (width times length). The guideline is that this area should be at least 6 times the volumetric flow in cubic feet per minute, but no less than 5 times the width. The length is then determined by dividing the horizontal cross-sectional area by the width. To finish the example, the minimum length should be 90 feet: $L=6xQ/W=6x300/20=90$. Since 5 times the width is 100 feet (more than 90 feet), 100 feet should be used as the length.

The *outlet weir* is the downstream wall of the main bay. It can be either a flat or V-notch type weir, but in any case must be absolutely horizontal to ensure even distribution of water flow across the width of the separator. Generally, the weir comprises a concrete wall with an adjustable steel plate mounted on it as shown on Figure 9-3. Immediately upstream of the outlet weir is the *underflow baffle*. This baffle prevents separated oil from overflowing the outlet weir. The baffle should be about 1-2 feet upstream of the outlet weir, and should be immersed in the water to a depth of at least one foot, but no more than 55 percent of the total water depth. It should extend above the water surface at least one foot.

Mechanical movement of oil towards the skimmer, and sludge towards the sludge hopper, is accomplished by *flight scrapers*, shown on Figure 9-3. Flight scrapers, which are commonly (but not universally) used in refinery service, comprise horizontal baffles (*flights*) mounted on two endless chains which move slowly on the water surface towards the downstream (skimming) end of the separator and then submerge to scrape along the bottom of the separator towards the upstream (sludge hopper) end of the separator. By forcing oil towards the skimmer, they improve the skimming operation (the oil layer near the skimmer is thicker); the main function, however, is continuous removal of settled sludge, which otherwise must be done by periodic manual cleaning (shutting down and draining the separator bay, and scooping out the sludge). The convenience of automatic sludge removal must be balanced against the maintenance required for mechanical equipment in this corrosive and fouling service. Since flight scrapers are generally purchased (not fabricated), design specifications are not given. An even more elaborate mechanical device for moving oil and sludge is the *traveling bridge*, a track mounted device with a surface baffle and a sludge scraper blade which travels back and forth along the length of the separator; the baffle and blade are brought into service as the bridge moves downstream and upstream, respectively.

Oil skimmers come in a variety of types; for all types, the intent is to achieve adequate oil removal while minimizing the amount of water which is skimmed.

Probably the most common type of separator skimmer is the slotted pipe skimmer, shown in Figure 9-3. As the name indicates, this skimmer is a section of pipe with a slot cut along the length. The pipe can be rotated around its axis (usually with a worm gear arrangement) to adjust the skimming depth. The pipe diameter is 8-12 inches, and the slot width is 7 cm. The pipe must be mounted perfectly horizontally to enable uniform skimming across the separator width and avoidance of excess water skimming.

Less convenient, but sometimes used, is the *adjustable height skim trough*. The elevation (and thus the skimming depth) of the trough is adjusted with screws at each end. The difficulty in achieving equal elevation of the two ends is one of the main disadvantages of this type of skimmer.

There are several types of *mechanical skimmers*. These function on the principle that oil will stick to a surface more strongly than will water. This type includes the *rotary drum skimmer*, in which a rotating drum immersed in the water picks up oil, with a scraper blade to remove the oil, and the *moving belt* or *rope skimmer*, in which a plastic belt or rope floats on the water surface and is continuously moved by a pair of rollers which squeeze the surface oil from the belt or rope.

Floating skimmers are buoyed to float at such an elevation that oil will overflow their weir, but water will not.

Oil skimmed by any of the above skimmers is routed to a *skimmed oil sump* located adjacent to the separator as shown on Figure 9-3. Since the skimmings flow by gravity, the sump must be at such an elevation to permit this. Generally, the sump is equipped with a submerged pump operated by a sump level control. It is strongly recommended that this pump be of the positive displacement type, since centrifugal pumps will emulsify the skimmed oil/water mixture. The pumped skimmings are generally routed to a *skimmed oil tank*, located above grade, to enable separation of skimmed oil from skimmed water. The separated water is sent back to the separator inlet section, and the oil is routed to a recovery system for reprocessing.

Another common means for removing oil from the oil sump and transporting it is with a vacuum truck. In this case, the truck should discharge its oil/water cargo to a slop oil collection tank. To minimize emulsion generation, agitation should be minimized in the transfer operations by avoiding high water velocities (e.g., avoid small diameter pipes and nozzles), and by discharging the truck contents either by gravity or with a positive displacement pump.

As noted above, oil/water separators are also effective as solids separators, although the quantity of solids removed is generally much less than the quantity of oil. To maintain separator effectiveness, the depth of settled sludge should not be allowed to become excessive (no more than one third of the water depth). As described above, the sludge can be removed by periodic shutdown and manual cleanout, or can be removed continuously with a flight scraper or traveling bridge system. If the latter are used, then provision needs to be made for removal of sludge from the sludge hopper. If the sludge is sufficiently fluid, it can be removed by pumping or siphoning it with a hose inserted into the hopper. If the sludge is not fluid, a screw conveyor in the hopper can be used to move the sludge outside the separator.

Separators are generally open on top, although covers are sometimes used as a means for controlling regulated air emissions or odors. There are several disadvantages to covering separators. First, separator operations (skimming and checking on flight scraper operation) are usually done by visual inspection; a cover greatly hinders this. Second, a tight cover on a separator makes the vapor space confined, and it is likely that an explosive atmosphere will develop as hydrocarbon vapors mix with the air. To reduce hazards, either the vapor space needs to be filled with an inert gas, or sources of ignition such as vehicles need to be kept well away from the separator. Overall, unless mandated by regulation, it is preferred not to cover an oil/water separator.

9.5.3.4 Outfall Section

The outfall section, shown on Figure 9-3, is a channel to collect the water from the separation bays. If the water needs further pumping, vertical centrifugal pumps are usually placed in this section, with level controls.

9.5.3.5 Operation

Separators are basically simple devices, and operate unattended most of the time. The only routine operations, essential for good performance, are oil skimming, sludge removal (in separators equipped with mechanical sludge conveyors), and checking on mechanical parts such as skim pumps and flight scrapers. By far the major operation is skimming.

Oil skimming is an operation which it is easy to overdo. The disadvantage of overskimming is excess water skimming, which leads to mixing of oil and water as the skimmed fluid is pumped, and thus frequently to generation of oil emulsions which the separator cannot remove. The key point is that *a reasonably thick layer of oil on the top of the separator does not hinder separator function, and overskimming usually does hinder separator function*. Separation occurs in the water phase, and several centimeters of oil on top of the water do not significantly affect the separation. Excess oil only becomes a problem when the layer is so thick that it can pass under the underflow baffle at the downstream end of the separator. As a general guideline, the skimming should be done to maintain the oil layer thickness in the range of 2-4 cm. A separator in which the water surface is easily visible may look better than one with a heavy oil layer, but the oil content of the effluent will probably be higher than if the skimming were done less thoroughly. A convenient means for maintaining the proper oil thickness is careful adjustment of the skim height (for slotted pipe or adjustable height trough skimmers). Since oil is less dense than water, the liquid surface height will rise as the oil layer accumulates; this enables setting the skimmer elevation such that only oil will be skimmed.

9.5.4 LAMINAR FLOW SEPARATORS

Laminar flow separator is a general term for several types of commonly-used separators which use mechanical means to divide the water flow amongst a multitude of narrow channels. This technique is based on three principles. First, the water is induced to achieve *laminar flow* (smooth, non-turbulent flow), thus suppressing the turbulence which counteracts oil/water separation. Second, the height of the flow channel is greatly reduced compared to the separator depth, which allows the oil droplets to rise to the top of the channel in a shorter time. Third, the top of the flow channel acts as a coalescing surface (see below) to promote the joining of small oil droplets into large, easily separable droplets. The two main types of laminar flow separators are corrugated plate interceptors and tube separators.

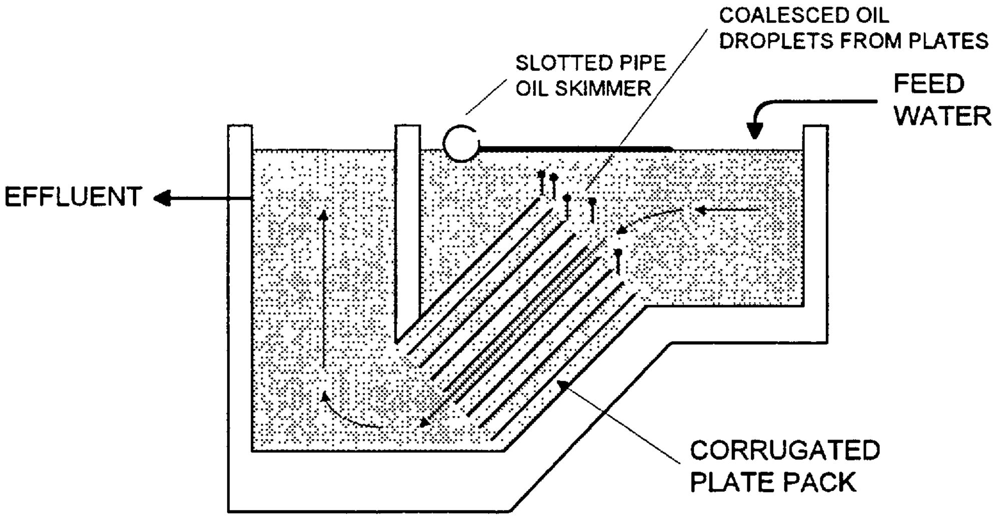
The main potential problem with laminar flow separators is fouling, since they contain narrow passages which can be difficult to clean. However, for facilities which only handle light products (e.g., gasoline and diesel fuel), fouling should not be a severe problem.

9.5.4.1 Parallel Plate Separators

Parallel plate separators, or corrugated plate interceptors (commonly known as *CPIs)*, are made of inclined stacks of corrugated metal or plastic sheets as shown on Figure 9-4. In addition to providing stiffening, the corrugations are claimed to promote oil coalescence and channeling in the upwardly convex sections of the plates.

FIGURE 9-4

DOWNFLOW PARALLEL PLATE SEPARATOR



9.5.4.2 Tube Separators

Tube separators are made of bundles of metal or plastic (plastic is claimed to enhance oil coalescence) inclined tubes, and work similarly to parallel plate separators.

9.5.5 COALESCERS

Coalescence is the process of fusion of oil droplets, which makes larger, more easily separated, droplets from small droplets. Generally, coalescence is done on a surface to which oil adheres better than water; a multitude of small droplets adhere and join to make an oil film, which other droplets join. When the oil film becomes thick enough, large oil drops separate and rise to the surface of the water. Many materials can be used for coalescing surfaces, but plastic is common because of its pronounced oleophilic nature (i.e., it is wetted much better by oil than by water). Coalescence is usually done in beds of material constructed in such a manner as to provide high surface area; one such design uses intermeshed plastic threads. The beds are placed so that all of the wastewater passes through them, followed by gravity separation of the water and coalesced oil.

Because they have high surface area and narrow passages, coalescing beds are prone to fouling, and may be difficult to clean. For this reason, coalescers should not be used in fouling service. If a wastewater contains high levels of suspended solids and/or heavy oils, then it should probably be subjected to gravity oil/water separation upstream of the coalescer. For water which contains only light products, fouling should not be a severe problem.

9.5.6 PACKAGE SEPARATORS

Package separators are simply oil/water separators of various types which are shop-constructed and shipped in one piece; the only field construction required is connection of the water inlet and outlet lines, the slop oil line, and (in some cases) electrical supply. Because they are shipped by truck, dimensions are usually limited to about 8 feet wide by 80 feet long; most units are much smaller than this. Since they are convenient to install, and are made for relatively low flows, package separators are very common in petroleum products terminals.

Package separators generally employ any or all of the means for achieving oil/water separation described above: gravity separation, laminar flow separation, and coalescence. Frequently they will employ some means for "automating" oil removal, based on oil's lower specific gravity and various weir arrangements.

9.5.7 LOCATION OF SEPARATORS

As described in 7.5.2.1, it is not recommended to pump oil/water mixtures prior to separation, particularly not in turbulent centrifugal pumps, so as to avoid generation of unseparable emulsions. For this reason, oily water sewers are generally made to flow by gravity all the way to the separator; the separator effluent is then pumped to the next destination. To enable gravity flow, separators are commonly located below grade, and are sometimes (particularly package units) completely buried except for access ports. Buried installation has the disadvantage of making the unit non-observable, hard to check for leaks, and hard to maintain (of course, simple separators do not require much maintenance). To overcome these disadvantages, some facilities install separators completely above ground, and use low-turbulence Archimedes screw pumps to elevate the water into the separator.

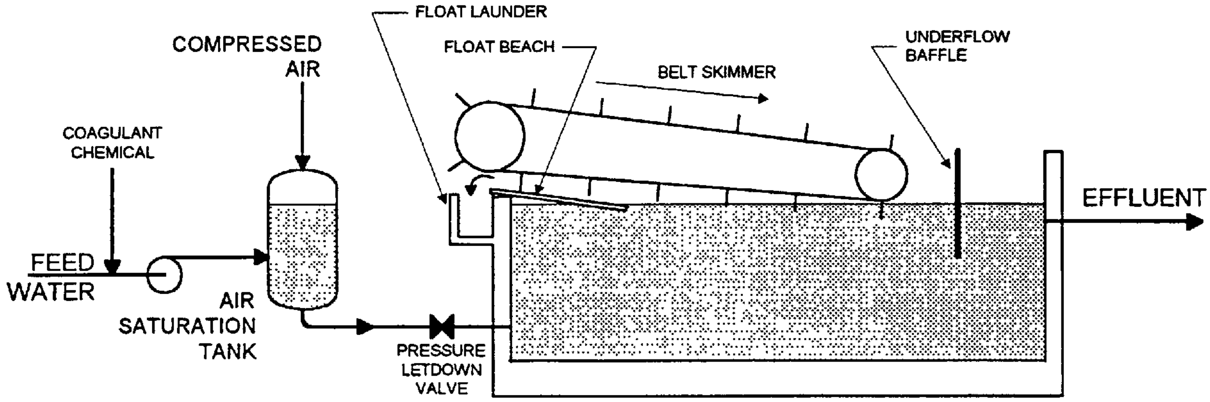
9.5.8 AIR FLOTATION

Air flotation is a means, usually quite effective, for enhancing oil separation. It employs chemicals to flocculate small oil particles, and microscopic air bubbles which become attached to the floc particles and lower their specific gravity enough to cause them to readily float. In addition to removing oil, air flotation units are quite effective at removing fine solid particles, and have been used for dewatering sludges.

The floating material, called the *float*, is removed from the air flotation unit surface by some skimming means, usually a blade which moves over the surface and onto the *beach*, as shown on Figure 9-5. When used, air flotation units are normally placed downstream of the primary oil separation devices described above. There are two basic types of air flotation units: induced air flotation units, and dissolved air flotation units.

FIGURE 9-5

DISSOLVED AIR FLOTATION



9.5.8.1 Induced Air Flotation

Induced air flotation (also called dispersed air flotation) uses mechanical devices to aspirate an air stream, and break it down into small bubbles inside the water chamber. Although simpler and less expensive than dissolved air flotation (described below), induced air flotation has the disadvantage of making more float to be managed. It has the significant advantage, however, of being able to recycle its air stream from above the water surface back into the water; this enables the unit to be sealed, and air emissions to be eliminated.

9.5.8.2 Dissolved Air Flotation

Dissolved air flotation, commonly called *DAF*, is based on the principle that gases dissolved in a liquid at high pressure will come out of solution as microscopic gas bubbles when the pressure is released; the principle can be seen when carbonated beverages are opened. In a DAF, water is saturated with compressed air at about 40 - 50 psi in a saturation chamber, and then sent through a letdown valve into the separation chamber, as shown on Figure 9-5. There are two types of DAF; in the first type, the entire water stream is saturated with air and passed through the unit (Figure 9-5). In the second type, a portion (15-120 percent) of the deoiled effluent water is recycled back through the air saturation chamber, and mixed with the main water stream after the pressure release. The recycle type is thought to provide better oil removal since the oil floc in the feed water is not disturbed by the air saturation process, but it is generally more expensive since the system is more complex, and the separation chamber must be larger since it has higher water throughput.

Although dissolved air flotation makes a lower-volume float stream, it has the disadvantages of being more expensive, and requiring more maintenance. In addition, it generates an offgas stream from the flotation air which will be saturated with all of the hydrocarbons (particularly volatile hydrocarbons such as gasoline components) in the feed water. Although a dissolved air flotation unit could be operated in a recycle gas mode (by routing the offgas back into the compressor), this is not normally done, perhaps because of the explosion hazard represented by compressed air and light hydrocarbons.

9.5.9 PERFORMANCE OF OIL/WATER SEPARATORS

Although it is usually very desirable to be able to predict the effluent quality to be expected from various type of oil/water separator at various loadings, this cannot be done. The reason for this is the unknown nature of the feed oil, particularly the oil droplet size which directly controls oil separation. Wastewater oil contamination can range from a layer of oil floating on clear water, which needs no separation, to very stable emulsions, which cannot be separated in any device.

Probably the best approach to determining susceptibility of a given wastewater to oil separation is to run separation tests. These can range from simple jar tests in which a wastewater sample is allowed to stand, and the degree of separation with time visually noted, to pilot testing of the separation device in question. In the case of advanced oil removal in coalescers or air flotation units, pilot testing is probably a necessity to establish treatment effectiveness and treatment size.

9.6 Biological Wastewater Treatment

9.6.1 INTRODUCTION

Biological wastewater treatment is the use of naturally-occurring living micro-organisms, mostly bacteria, for the removal of dissolved contaminants from wastewater. The bacteria utilize the contaminants as a food source, along with oxygen and trace nutrients, and produce as byproducts carbon dioxide gas and biological sludge (excess bacteria). Biological treatment processes are extensively used worldwide for treatment of wastewaters from municipalities and various industries, including the petroleum industry. Product streams from biological treatment are generally of high quality, and are usually discharged to receiving waters without further treatment.

9.6.1.1 Requirements for Wastewater

The only essential requirement for a wastewater to be suitable for biological treatment is that it contain biodegradable material, generally indicated by the presence of biochemical oxygen demand (BOD); downstream petroleum industry operations generally make wastewater that is suited for biological treatment.

9.6.1.2 Requirements for Treatment

Other requirements for biological treatment are that the temperature be maintained in the range which will allow the bacteria to be active, but not killed, which is generally a temperature range of 60-95 F, while pH levels must be in the range of 6-9. In addition, for the type of treatment covered below, oxygen is needed for *aerobic* biotreatment. *Anaerobic* (oxygen-free) biotreatment can also be employed, but it is generally not very effective for petroleum industry wastewaters, although specialty applications may exist.

9.6.1.3 Natural Selection

Biological treatment operates by developing a population of bacteria suited to treating a given waste stream. This is automatically achieved by a process of natural selection, in which those bacteria which can utilize the contaminants as food are those that rapidly multiply, while those not so adapted die off. Because the population is governed by the food supply, it is necessary to supply a biological treatment system with a fairly steady supply of contaminants. If the contaminant load falls off significantly, then some of the bacteria will starve. If the contaminant load rises quickly, or a new contaminant is introduced, then it will take time to develop a population adapted to the new conditions. The means generally used to achieve this steady supply is flow and concentration equalization of the wastewater (8.3).

9.6.2 ADVANTAGES AND DISADVANTAGES OF BIOLOGICAL TREATMENT

For good reasons, biological treatment is by far the most popular wastewater treatment technique used by municipalities and industrial dischargers. It also has disadvantages, however, as described below.

9.6.2.1 Advantages of Biological Treatment

The advantages of biological treatment over other methods for removing soluble organic matter are as follows:

- Biological treatment provides very broad spectrum removal of an array of contaminants. In addition to removing almost any type of organic matter (some types better than others), it also, to varying degrees, removes oil, ammonia, and metals.

- Biological treatment usually has low operating cost. Aside from operating manpower (the need for which varies amongst different types of biotreatment), about the only operating cost is for the electric power used in mixing and aerating the bacteria; compared to other types of treatment, this power consumption can be quite low.

9.6.2.2 Disadvantages of Biological Treatment

The disadvantages of biological treatment compared with physical/chemical techniques for removing soluble organic matter are as follows:

- Biological treatment does not respond rapidly to changes in contaminant load. Unlike physical/chemical methods, many of which are adjustable in their degree of treatment, biotreatment requires time for bacterial populations to respond to changes.

- Biological treatment cannot be turned on and off. As a living system, biotreatment must be kept alive by providing a fairly steady contaminant (food) load. Most physical/chemical techniques are not subject to this limitation.

- Biological treatment is susceptible to killoff. Although any treatment device can be fed material which it is incapable of removing, only biological treatment is subject to destruction of its main "reagent", the bacteria, and requires significant time for recovering a viable bacterial population.

- As aerated processes, biological treatments have more potential for air emissions than some other types of treatment. Although these emissions can be minimized or eliminated (9.6.9.10), this can be costly.

9.6.3 FUNDAMENTAL CONCEPTS

The fundamental concepts which apply to all aerobic biological treatment systems are *bacterial population, food-to-micro-organism ratio* (*F/M ratio*), *sludge age, sludge wastage, mixing, nutrients*, and *dissolved oxygen* (*DO*).

9.6.3.1 Bacterial Population

Bacterial population is the total amount (mass) of active bacterial cells contained in the bioreactor; in a mixed system, it is the bacterial population density (expressed as Mixed Liquor Volatile Suspended Solids) multiplied by the bioreactor volume. (In an attached growth system, the bacterial population is more difficult to measure, but still exists as the active outer layers of bacteria on the media surfaces.) Since each bacterium is capable of eating a certain amount of contaminant per day, the higher the bacterial population, the more contaminant can be consumed.

9.6.3.2 Food-to-Micro-organism Ratio

The F/M ratio is a basic concept which relates the amount of food for the bacteria (in terms of mass/day) to the amount of bacteria contained in the bioreactor (in terms of mass of bacterial sludge, the bacterial population). Like any living organism, each bacterium is capable of eating a certain amount of food per day. Biological systems with a steady food source will come to an equilibrium in which the amount of bacteria will be just enough to eat the food supplied; this establishes the F/M ratio. If the amount of food declines (F/M ratio declines), then some bacteria will be starved, and either cease functioning and reproducing, or die, until the reduced M value causes the F/M ratio to be restored. If the amount of food increases (F/M ratio increases), some of it will pass through the system untreated, and the bacteria will start reproducing more rapidly until the increased M value causes the F/M ratio to be restored. The F/M ratio is a control parameter in some (mostly activated sludge) biotreatment systems, in which the amount of bacteria can be controlled by the amount of biosludge wastage.

The formula for F/M ratio is lb of food/day per lb of biomass (VSS) in the reactor. The term "food" is commonly taken to mean BOD, but for marketing terminal wastewater, it has been found (Vuong, 1993) that ΔCOD, which is defined as the reduction in COD in biotreatment, is a better parameter to represent consumption of organic matter (ΔCOD is somewhat larger than BOD).

9.6.3.3 Sludge Age

Sludge age is the average amount of time a bacterial cell remains in a bioreactor from the time it is produced until the time it dies or is washed out of the system, and is controlled by the size of the bioreactor and the rate of sludge wastage. It is important because different bacteria reproduce at different rates, and a system with a low sludge age will not allow the slow-reproducing bacteria to establish a significant population, even though ample food (contaminant) supply is available. This is notably true with nitrifying bacteria, which convert ammonia into the more innocuous nitrate form; nitrifying bacteria are slow to reproduce, and thus not found in systems with low sludge age.

9.6.3.4 Sludge Wastage

As a rule of thumb, about half of the biodegradable organic matter fed to a bioreactor becomes carbon dioxide, and about half becomes new bacteria. Clearly, for a system to be stable, the new bacteria must be continuously removed as they are generated. This is done by the process known as sludge wastage. Sludge wastage is a combination of deliberate removal of a sludge stream, generally in a concentrated form (settler bottoms sludge), and carryover of suspended solids in the biotreatment effluent water. An exception to the general rule of sludge production is found in systems with very long sludge ages; in these systems, the bacteria start to consume themselves, with a result of producing less net sludge to be wasted.

9.6.3.5 Mixing

To be effective, bacterial particles must be brought into contact with contaminants in the water; as with any chemical reaction, this means that mixing is required, either by moving the water, the biomass, or both. In suspended growth systems, as described below, there is an additional mixing requirement simply to keep the bacteria from settling out from the water.

9.6.3.6 Nutrients

About half of the activity of biotreatment bacteria is involved with making new bacteria, an essential feature of biological treatment. Since bacteria are made of more than carbon (from the organic matter being metabolized) and oxygen, they also need minimum levels of nitrogen and phosphorus nutrients, generally regarded as about 12 percent of the feed TOC as nitrogen (ammonia or nitrate), and about 2 percent of the feed TOC as phosphorus. Some wastewaters will contain this much (and more) of the nitrogen and phosphorus, but those which are deficient should have supplemental nutrients (lawn or garden fertilizer will suffice) added. (NOTE: excess nutrients should not be added, since this can cause the effluent to contain excess levels of ammonia and phosphorus).

9.6.3.7 Dissolved Oxygen

Dissolved oxygen, or DO, is the concentration (mg/L) of oxygen in the bioreactor. It is a critical parameter, since aerobic bacteria require oxygen to function. At normal atmospheric pressure and water temperatures, the amount of oxygen in water saturated with air is about 8 mg/L (oxygen solubility is proportional to air pressure, and inversely related to temperature). As a rule of thumb, biotreatment reactors should maintain a minimum DO level of 2 mg/L to ensure adequate oxygen for bacterial respiration.

9.6.4 TYPES OF BIOTREATMENT

There are two general types of biological treatment system, both of which are used in the petroleum industry. The first, and most common, type is *suspended growth biotreatment*, in which clumps of bacteria (biofloc particles) are kept suspended by mixing action in the water being treated. The second type is *attached growth biotreatment*, in which the bacteria are provided with surfaces on which to grow as a bacterial film.

9.6.5 SUSPENDED GROWTH BIOTREATMENT

Suspended growth biotreatment uses bacteria suspended in the water being treated, and includes the very popular aerated lagoon and activated sludge processes, and also sequencing batch reactor and other specialty treatment processes. By their nature, these processes require positive means for oxygen transfer by *aeration* (the reaction chamber is generally known as the *aeration basin*), mixing energy to keep the bacteria in suspension, and generally employ some means for settling and retaining the bacteria to keep suspended solids out of the effluent water and to enable building up a high biological population.

9.6.5.1 Aeration

Aeration can be done in a number of ways. Compressed air can be supplied from a compressor or high pressure blower and released under the surface of the water as bubbles through a number of different types of devices. Mechanical surface aerators are quite common in large treatment systems, and involve both spraying the water through air and entrainment of air bubbles in the descending water as means for oxygen transfer into the water. Jet aerators use the venturi principle to aspirate and entrain air into a rapidly moving pumped water stream. All of these types of aerators are effective, and selection depends on the specific application (size of system, depth of water, oxygen demand, turndown requirements) and favorable operating history of specific units.

9.6.5.2 Mixing

There are also various means for mixing a wastewater treatment aeration basin, many of which combine the aeration and mixing function. Mixing can be done with compressed air (the air bubbles create upwards water movement at the release zone), with surface aerators (whose design is usually made to ensure that water is pulled from the bottom of the basin below the aerator and dispersed across the surface of the basin), and with pumped mixing (commonly combined with jet aeration). Mixing can also be done with ordinary mixers, particularly as a supplement when the mixing achieved by the aeration requirements alone is inadequate (a common situation). It should be noted that suspended growth biotreatment systems are usually based on having a completely mixed and completely aerated aeration basin; for this reason, it is critical that the mixing be designed to avoid "dead zones", and that aeration be evenly distributed to avoid zones with low dissolved oxygen. As a rule of thumb, in order to achieve adequate suspension of bacterial particles, about 1 horsepower of mixing per thousand cubic feet of aeration basin water is needed.

9.6.5.3 Settling and Clarification

Water leaving the well-mixed aeration basin will contain bacteria at the same concentration as in the basin, and these generally must be settled from the water before it is discharged in order to meet effluent quality requirements. In addition, many suspended growth processes require that the settled bacteria be returned to the aeration basin as a means for building up a high population of bacteria in the basin. As with oil removal (9.5.1), solids settling requires either still or slowly moving water. The settling function is done in a variety of ways, and is a major distinction between the different types of suspended growth biotreatments.

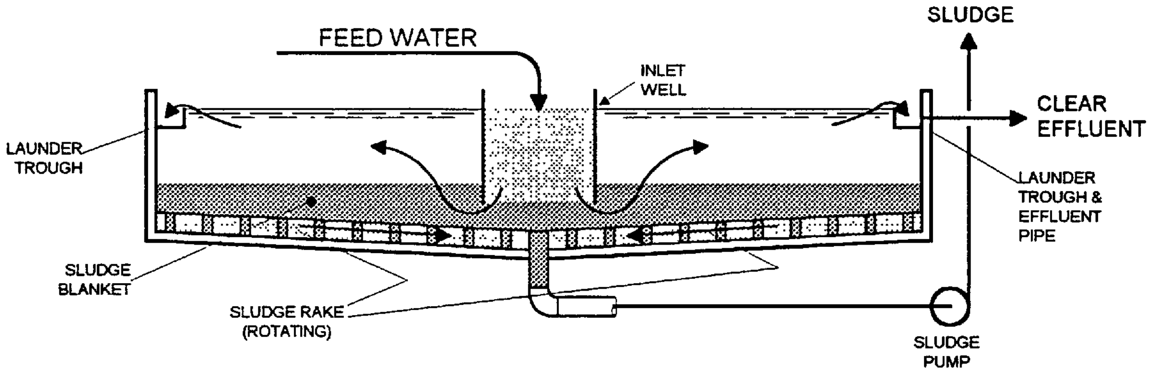
In aerated lagoon treatment, a section of the treatment lagoon is used for settling. The settled sludge is periodically removed by dredging.

In sequencing batch reactor treatment, the aeration basin itself is used as the settler as part of the sequencing process, as described below.

In activated sludge treatment, settling is done in a *clarifier* (see Figure 9-6) or *settler*, which is usually a cylindrical basin with water entering at the bottom of the center well, and leaving at the top of the periphery. Water leaves by passing over an *outfall weir* into a *launder*, which is a collection trough for the treated water. Sludge settled on the bottom is commonly removed by a continuously slowly rotating sludge rake which moves the sludge to the center of the clarifier where it enters the sludge pump suction. There are also other means for removing the sludge which work just as well, including a steep cone bottom shape (Figure 9-7) which is usually only practical for small clarifiers because its geometry would require a very tall unit for a large clarifier. As a rule of thumb, a clarifier is sized such that the upwards water velocity (volumetric water feed rate divided by clarifier cross-sectional area) is about 0.023-0.070 feet/minute, or 250-750 gallons/day/square foot. In addition, for activated sludge use, the settling zone in the bottom of the unit must be sized such that the sludge is *thickened* (dewatered) enough to enable control of aeration basin bacterial population by return of the sludge to aeration.

FIGURE 9-6

BIOLOGICAL TREATMENT CLARIFIER



9.6.6 SUSPENDED GROWTH BIOPROCESSES

9.6.6.1 Aerated Lagoon Treatment

An aerated lagoon, shown on Figure 9-8, is essentially a pond with aerators at one end and a quiet settling section on the other end. Generally, an aerated lagoon has a low bacterial population, since there is no means to keep the bacteria which grow from being carried out of the aeration zone with the water (i.e., there is no return of bacteria settled in the settling zone). Aerated lagoons are simple to build, require relatively high amounts of land area, are simple to operate, provide a moderate degree of biotreatment, are moderately tolerant of wastewater variability, and are moderately tolerant of oil. The main design parameters are the volumes of the aeration zone and settling zone, and the amount of aeration.

FIGURE 9-7

CONE-BOTTOM CLARIFIER

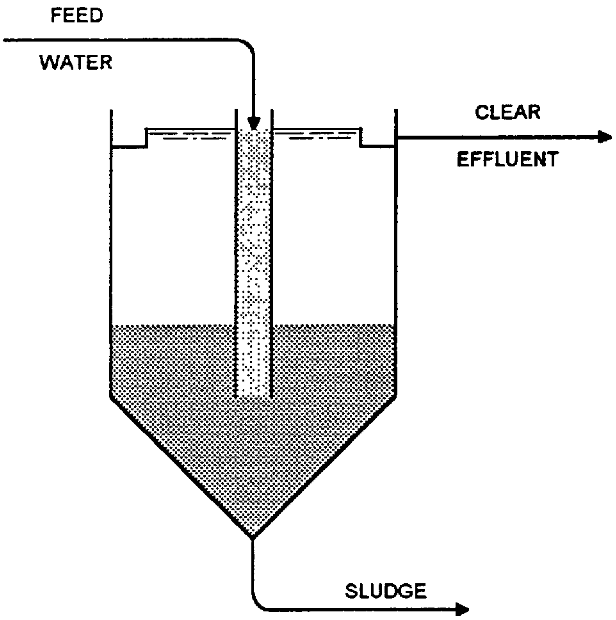


FIGURE 9-8

AERATED LAGOON

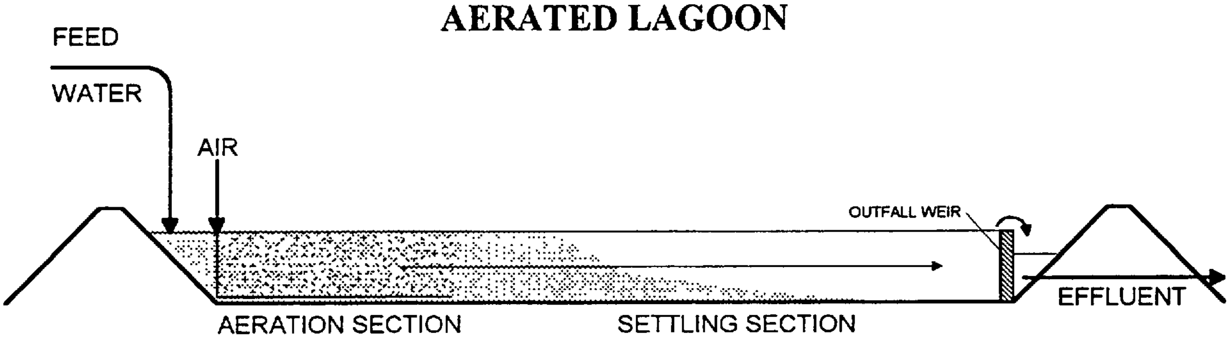
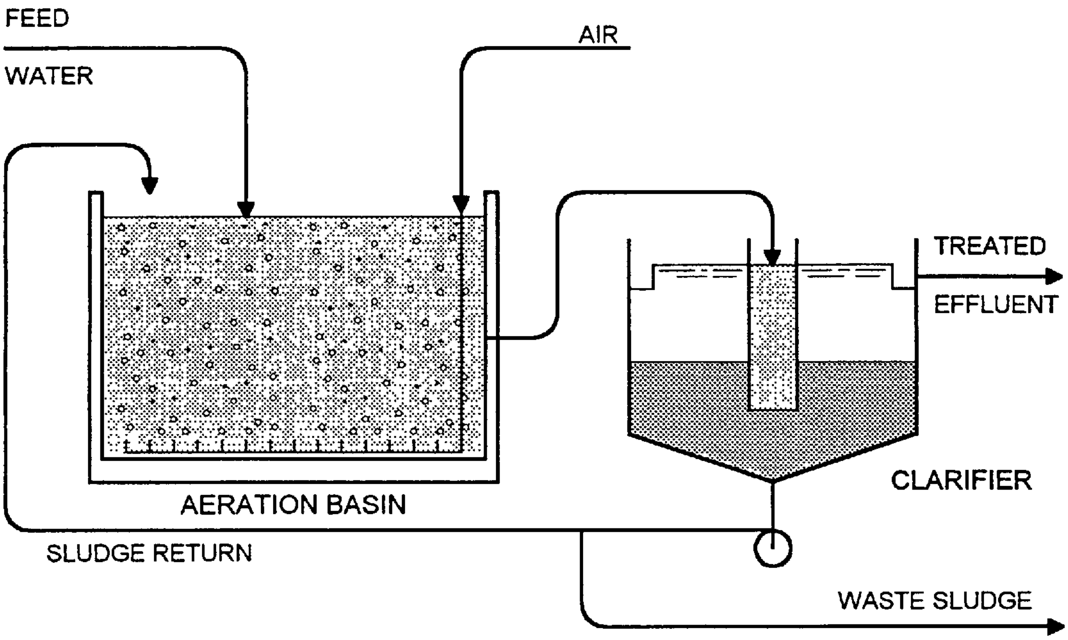


FIGURE 9-9

ACTIVATED SLUDGE PROCESS



9.6.6.2 Activated Sludge Treatment

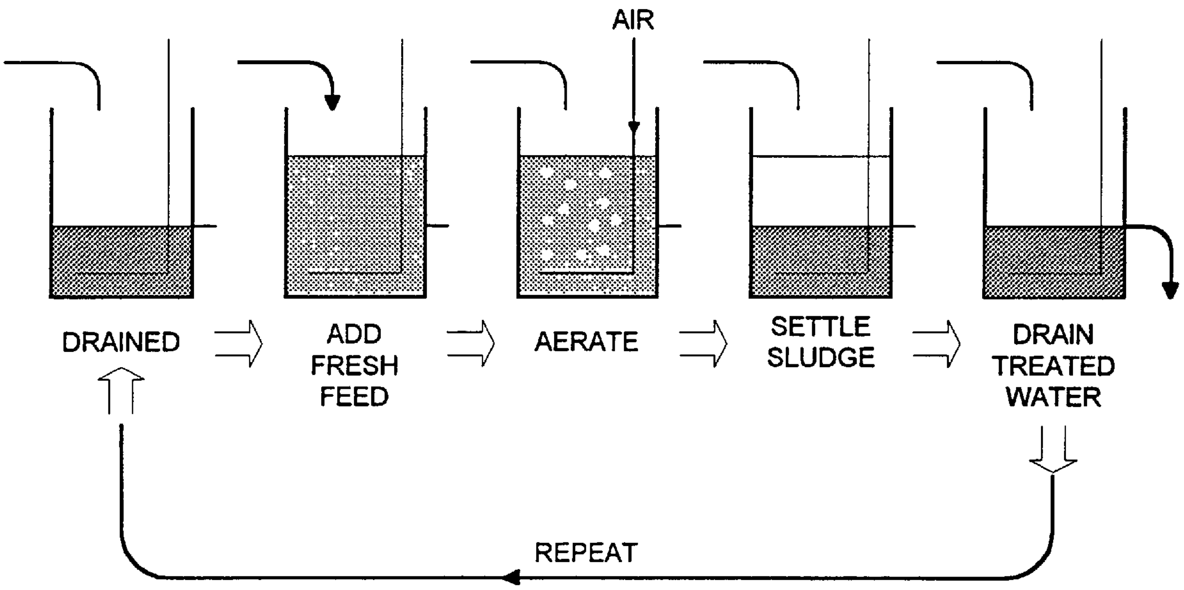
As shown on Figure 9-9, an activated sludge process is an aeration basin followed by a clarifier, with return of most of the settled sludge to the aeration basin (the excess is waste sludge). Bacterial population in an activated sludge unit is usually maintained in the range of 2000-4000 mg/L MLVSS by control of the sludge return rate, and sludge wastage. Activated sludge units are the standard by which all other biotreatments are judged, and generally provide excellent treatment so long as the basic requirements are met. They are relatively difficult to operate (mostly due to maintenance of clarification and sludge wastage), and are not very tolerant of oil (oil causes the sludge to float, and thus not be settled, and thus not be returned to aeration). The main design parameters are the aeration basin volume, the clarification square footage and depth, the amount of aeration, and the sludge return pump capacity. Results from use of full-scale activated sludge treatment in a terminal (following trickling filter treatment) are given in Appendix B.

9.6.6.3 Sequencing Batch Reactor Treatment

A sequencing batch reactor (commonly known as an *SBR*), shown on Figure 9-10, is a fill-and-draw version of the activated sludge process. The equipment is quite simple, being a single basin used for both aeration and settling. As shown, the treatment process comprises sequential aeration, settling, drawing of clear treated effluent from the top of the reactor (with settled bacteria retained in the lower portion of the reactor), and refill with new untreated wastewater. As a version of the activated sludge process, SBR treatment produces high quality effluent, but is not very tolerant of oil. Sequencing batch reactors are somewhat easier to operate than activated sludge reactors since little attention is required except on the days of sequencing. The main design parameters are basin volume, sequencing frequency, draw percentage of total volume, and amount of aeration. Appendix B gives detailed treatment results and design criteria based on a pilot study of SBR treatment of wastewaters from four marketing terminals.

FIGURE 9-10

SEQUENCING BATCH REACTOR TIME SEQUENCE



9.6.7 ATTACHED GROWTH BIOTREATMENT

Attached growth biotreatment depends on the formation of bacterial films on surfaces within the bioreactor, with thicknesses ranging from microscopic up to about a centimeter. Water is passed over the surfaces, and oxygen is supplied in various ways. Because the bacteria are attached to surfaces, much less mixing energy is required than in suspended-growth processes. Another advantage is that a high biological population can be maintained without return of solids settled from the effluent, which means that suspended growth processes do not depend on settling, and are thus tolerant of oil. Also, since the bacteria are fixed on the surfaces, it is easier to maintain a population when feeding a low-strength waste (in suspended growth processes, low-strength feed tends to produce washout of the bacteria). Counteracting these advantages is the fact that effluent from attached growth processes is usually not quite as good (in terms of removal of soluble organic matter) as effluent from the better suspended growth processes, perhaps because contact between the bacteria and the water is not as intimate, and perhaps because the range of bacterial species capable of attaching to a surface with a slime layer is not as great as those capable of growing in suspension.

9.6.7.1 Aeration

Each type of attached growth treatment has a different means for oxygen transfer to the bacterial layer, as described below.

9.6.7.2 Mixing

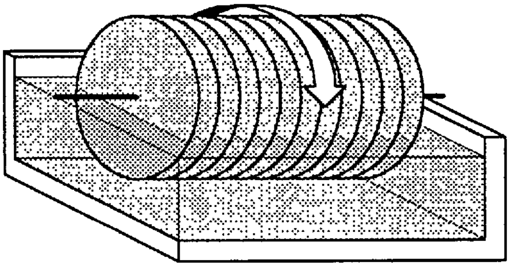
Mixing is not required in these processes to keep bacteria suspended, and so all mixing energy involves that required to contact the bacteria film with the water. This is done in different ways for the different processes, as described below.

9.6.7.3 Settling and Clarification

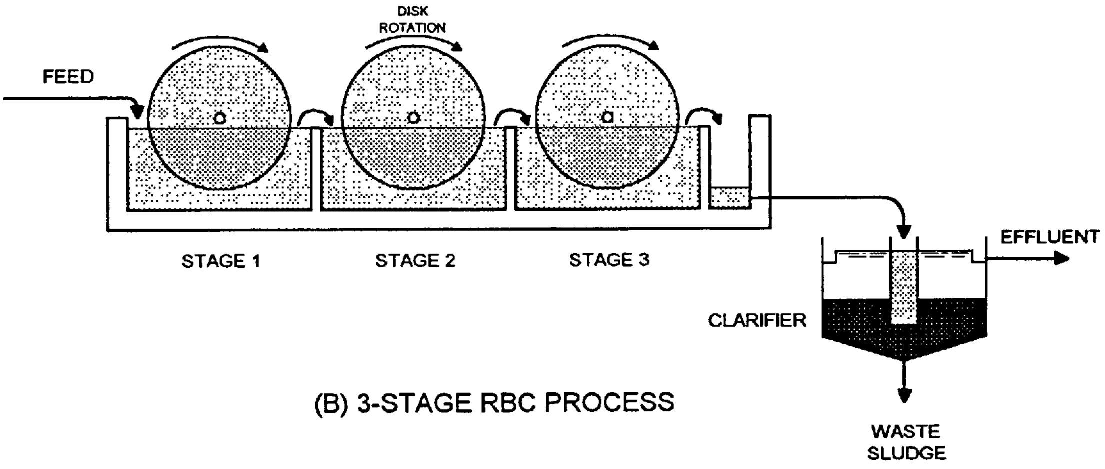
As with any biotreatment, all the attached growth processes produce excess biosludge which is contained in the effluent from most processes, and in the backwash water from the submerged biofilter. Clarification is not necessary for return of biomass to aeration, but usually is required for obtaining adequate effluent quality (low TSS). For this reason, the effluent must usually be routed through a clarifier (or backwash sent to a settling tank in the case of the submerged biofilter).

FIGURE 9-11

ROTATING BIOLOGICAL CONTACTOR



(A) ARRANGEMENT OF DISKS ON SHAFT



(B) 3-STAGE RBC PROCESS

9. 6.8 ATTACHED GROWTH BIOPROCESSES

9.6.8.1 Rotating Biological Contactor Treatment

Rotating Biological Contactors, or *RBC*s, are made of corrugated plastic disks (diameter range 3 ft - 12 ft) mounted on a horizontal shaft as shown on Figure 9-11. The disks are about 40% submerged in the water basin, and the shaft is rotated at slow speed to alternately move each section of a disk into the water and then into the air above. Bacterial growth occurs as a film on the disk surfaces. Bacteria/water contact is achieved by the motion of the disks through the water, and oxygen transfer by motion of the disks through the air space. RBCs are characterized by periodic sloughing of the biofilm from the disk surface when its thickness becomes great enough; the sloughed solids are carried out in the effluent water to a clarifier. The disks are usually covered to protect against weather; with a tight cover, and controlled air throughput, air emissions from the units can be readily minimized and controlled. RBC treatment has been successfully applied to refinery wastewater treatment and marketing terminal treatment, in which it has demonstrated its claimed advantages of oil tolerance, resistance to foaming, low operating manpower, low energy consumption, and low air emissions. The main design parameters for an RBC unit are the total disk area, the number of stages (usually one to four), and the clarifier sizing. Appendix B gives detailed treatment results and design criteria based on a pilot study of RBC treatment of wastewaters from four marketing terminals.

9.6.8.2 Trickling Filter Treatment

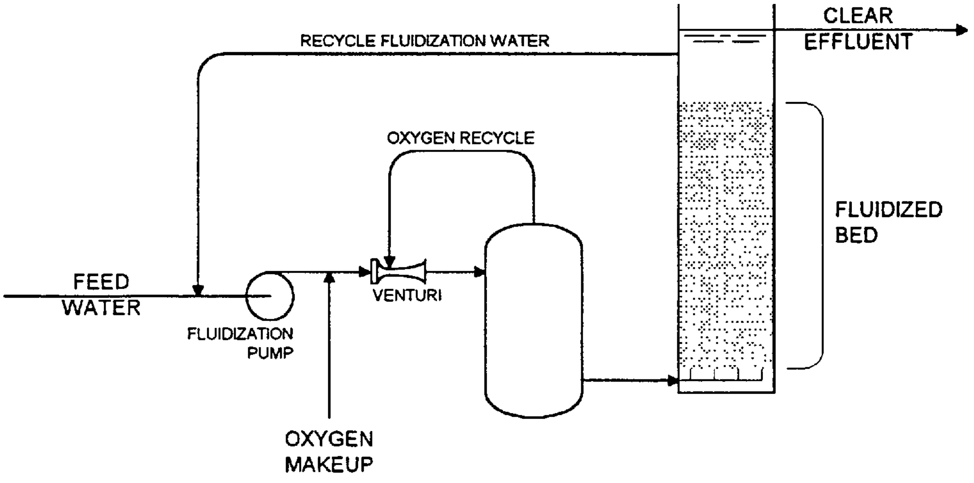
Trickling filters are above-ground beds of rocks or plastic media in a cylindrical containment which are sprayed with wastewater. The water trickles down through the bed and contacts the bacteria growing on the media surface. Oxygen is supplied by natural convection of air through the bed. The water is usually supplied by a slowly rotating spray arm, and water/bacteria contact is normally enhanced by recirculating most of the effluent water back to the top of the bed. As with RBCs, bacterial growth usually accumulates until it becomes thick enough to slough off and be carried out in the effluent water to a clarifier. Trickling filters are simple to operate, but have a major disadvantage of not providing very good treatment, perhaps because of mass transfer limitations: water can easily short-circuit (*channel*) through the bed if portions of the bed become blocked with biogrowth, and uniform oxygen transfer, particularly to the center of the bed, is hard to maintain. Air emissions tend to be high, since untreated wastewater is sprayed on the top of the bed, and since air throughput is uncontrolled. Trickling filters are sometimes used as *roughing devices*, to remove excessive organic matter upstream of a more sophisticated treatment system. This must be done with caution, however, since it can result in starvation of the downstream biotreatment. The main design parameters for trickling filters are bed volume and depth, media type and surface area, recirculation rate, and clarifier sizing. Full scale treatment conditions and results for trickling filter treatment of a terminal wastewater are given in Appendix B.

9.6.8.3 Submerged Biofilter Treatment

Submerged biofilters are essentially trickling filters filled with water in which air is bubbled into the bottom of the reactor. The reactor comprises a vertical tank filled with packing on whose surface the bacteria grow. Compressed air is injected into the bottom of the bed, and bubbles up through the bed to exit at the top. Wastewater flows through the bed in either the upflow or downflow direction. Downflow operation is claimed to produce an effluent with lower suspended solids levels (the bed acts as filter), but air emissions of volatile components are higher since the exiting air is in direct contact with the incoming wastewater. To remove excess biogrowth, the submerged biofilter must be backwashed with high water flow periodically, usually daily. The spent backwash water can be settled in a tank to enable disposal of somewhat dewatered sludge. At this time, few submerged biofilters are in operation, so information on their performance is scanty. Their claimed advantage over suspended growth biotreatment is higher density of bacteria in the water, thus allowing equal treatment in a smaller reactor. Potential operating problems are bed plugging with biosolids and consequent water and air channeling, and determination of proper backwash conditions (how much flow for how long). Design parameters include air supply volume and pressure, bed depth and volume, packing type (shape, density, size, and surface area), backwash supply flow and volume, and spent backwash volume.

FIGURE 9-12

FLUIDIZED BED BIOREACTOR



9.6.8.4 Fluidized Bed Bioreactor Treatment

A fluidized bed is a bed of particles which is kept suspended by upwards movement of gas or liquid; a fluidized bed bioreactor contains media particles on which bacteria grow which are fluidized by upwards flow of wastewater. As shown on Figure 9-12, the reactor bed is kept fluidized by a recirculated flow of clear water (taken from above the bed). Feed water is added to this recirculated flow, and effluent water is overflowed from the top of the reactor. Oxygen is added to the recirculated water in such a manner as to saturate the water entering the bottom of the bed with oxygen (about 40 mg/L dissolved oxygen), but not to allow bubbles in the reactor feed. This keeps bubbles from disturbing the bed fluidization, and also eliminates air emissions (at the cost of supplying oxygen instead of air). Perhaps because of the limited amount of oxygen available in the reactor, the system has mostly been used on dilute groundwater, with the main objective of BTEX removal. However, at a low enough feed rate, the system should be capable of treating even very high strength wastewater (such as tank bottoms water), although no results are available on this application. Based on groundwater treatment, general design values are hydraulic residence time in the bed of 2-5 minutes (at fluidization flows), COD loading of 0.2 - 0.5 lb COD/day per cubic foot of reactor (for a terminal with 1000 gal/week of 4000 mg/L COD wastewater, a 10 - 24 cubic foot reactor would be required), and a fluidization flow of 8-15 gpm/ft^2.

Potential operating problems with fluidized bed systems could be maintenance of fluidization when the media particles are irregularly coated with biogrowth: if some particles become too buoyant, they will be washed out of the system, and if some particles lose too much buoyancy, they will settle to the bottom of the reactor. Also, free oil would probably cause problems by coating the particles, and making them float. Design parameters include reactor volume, depth, and shape, media shape, size, density, and surface area, oxygen supply volume and pressure, water recycle flow, and means for removing and handling waste biosludge. Commercial units with proprietary design features are available.

9.6.9 COMPARISON OF BIOTREATMENT TECHNOLOGIES

Table 9-4 summarizes the characteristics of various types of biological wastewater treatment for comparison. Generally, more than one technology could be used in a given application; selection depends on the significance of the various characteristics in that application (for instance, in some cases land area may be critical, and in others, ease of operation may be essential). One important factor which is omitted from the table, and the discussion below, is the capital cost of the system. This is not listed because it is impossible to provide a general comparison which will apply to all sizes and constraints of specific applications.

Table 9-4

COMPARISON OF BIOLOGICAL TREATMENT PROCESSES

Treatment Process	Land Area	Operating Manpower	Energy Usage	Effluent Quality	Response to Feed Variability	Oil Tolerance	Foaming Tolerance	Suitability for High-Strength Waste	Low-Strength Waste Tolerance	Number of Units
Aerated Lagoon	High	Low	High	High	Moderate	Moderate	Poor	Good	Moderate	High, declining
Activated Sludge	Moderate	High	High	High	Good	Poor	Poor	Good	Low	Very High
Sequencing Batch Reactor	Moderate	Moderate	High	High	Good	Poor	Poor	Good	Moderate	Few
Rotating Biological Contactor	Moderate	Low	Low	High	Good	Good	Good	Good	Good	Moderate
Trickling Filter	Moderate	Low	Low	Moderate	Good	Good	Good	Good	Good	Moderate, declining
Submerged Biofilter	Low	Moderate	Moderate	Unknown	Good	Unknown	Unknown	Good	Good	Few
Fluidized Bed Bioreactor	Low	Low	Moderate	Unknown	Good	Poor	Unknown, probably good	Poor	Good	Few

9.6.9.1 Land Area

Because of the need for a large settling section, aerated lagoon treatment requires much more land than other biotreatment processes. The land requirements for the other processes is somewhat under the control of the designer, since most can be built tall, rather than wide, if needed. Supporters of the submerged biofilter process claim that its reactors are smaller because the biomass density in the reactor is greater than in a suspended growth process. Clarifiers, which are needed for all non-lagoon processes, can use significant land area. RBC clarifiers (and possibly those for trickling filters) can be somewhat smaller, since the sloughed sludge particles are larger, and thus easier to settle, than suspended growth particles.

9.6.9.2 Operating Manpower

Especially for small facilities, operating manpower can be a significant constraint for new systems. Because they involve no controls, the aerated lagoon, RBC, and trickling filter processes have very low manpower requirements. Activated sludge treatment requires significant manpower (full 7-day shift coverage in some plants) to keep the settling/sludge return in balance, and it is estimated that fluidized bed bioreactors may require extensive coverage to keep the bed properly fluidized. The SBR and submerged biofilter processes require moderate manpower to conduct the periodic operations (sequencing of the SBR and backwash of the submerged biofilter).

9.6.9.3 Energy Usage

All systems which use mechanical mixing to suspend biosolids (the suspended growth processes) have relatively high energy consumption, as may the fluidized bed bioreactor process (it is more difficult to keep media suspended than biofloc particles, but the total reactor volume may be less). Those which provide compressed air for oxygen demand only (the submerged biofilter and fluidized bed bioreactor processes) have moderate energy consumption, while those with "passive" aeration (the RBC and trickling filter processes) use the least energy.

9.6.9.4 Effluent Quality

Although side-by-side comparison of all processes has not been done, enough experience has accumulated to say that *usually* the effluent quality sequence for the processes is

activated sludge = SBR > RBC > aerated lagoon > trickling filter

Effluent quality from the less-used submerged biofilter process and fluidized bed bioreactor process is not known for petroleum industry wastewaters.

Appendix B summarizes the results of biotreatment (and other treatment) done in full-scale and pilot-scale treatment systems. The results, in terms of percent removal of various contaminants, is shown on Table 9-5. For purposes of comparison, secondary treatment by activated carbon columns is also shown. Since the treatments were being applied to different wastewaters, and with different degrees of treatment (unit sizing with respect to feed loading), the results should be used with caution. As noted elsewhere, it is strongly recommended that no biological treatment system be installed at a terminal until its performance and sizing parameters are established in pilot testing of treating that terminal's wastewater.

9.6.9.5 Response to Feed Variability

As noted above, any biological system requires some time to respond to changes in food loading, particularly to an increase. All the biotreatment systems are capable of handling feed variability if rapid changes in the loading are avoided by feed equalization or flow control.

9.6.9.6 Oil Tolerance

The major adverse effect of oil (note: only suspended oil is meant in this context) on a biological treatment system is the physical effect of reducing the specific gravity of biological floc particles; as far as is known, oil does not actually harm the biotreatment process by chemical or biological means. For this reason, the systems which have poor response to oily feed water are those suspended growth processes which rely on the biofloc having a minimum specific gravity: activated sludge units and SBRs. Aerated lagoons are somewhat affected, since oil will tend to float the biofloc to the top of the aerated section, and thus reduce mixing between the wastewater and the biofloc. The effects of oil on the submerged biofilter and fluidized bed bioreactor are unknown, although the latter, with its suspended media particles, may be somewhat more sensitive. Since fluidized bed bioreactors employ feed oxygen saturation under pressure, there is potential explosion hazard if the feed water contains suspended oil. RBCs and trickling filters have demonstrated good tolerance for moderately high oil levels.

Table 9-5

Comparison of Secondary Treatments of Petroleum Products Terminals Wastewaters

All values are long-term average Percent Removals

Treatment	SBR	RBC	SBR	TF	TF/AS	AC
Location	a	a	b	c	c	d
BOD	98	97	95	93	95	36
COD	84	82		61	68	59
TOC	83	80	97	77	76	43
Oil & Grease	82	82	92	31	59	96
TPH	99	99	94			92
Phenols	99	98	100			99
MBAS	53	53				
CTAS	79	87				
Methanol	99	99				
Ethanol	75	75				
Benzene	100	100	100			
Ethylbenzene	100	100	100			
Toluene	100	100	100			
Xylenes	100	100	100			
MTBE	100	100				
Copper	34	90				
Zinc	36	93				

TREATMENTS

SBR = Sequencing Batch Reactor (Biological)
RBC = Rotating Biological Contactor
TF = Trickling Filter (Biological)
TF/AS = Trickling Filter + Activated Sludge (Biological)
AC = Activated Carbon Columns

LOCATIONS

a = Semi-full-scale treatment of wastewaters from 4 petroleum products terminals
b = Full-scale treatment of tank bottoms water from a marketing terminal
c = Full-scale treatment of tank bottoms water from a petroleum products terminal
d = Pilot-scale treatment of wastewater from a marketing terminal

Note: the above discussion does not address *removal* of oil from wastewater, but only the effects of oil on biotreatment. Suspended oil is not very biodegradable at the retention times encountered in most treatment systems, since it is very insoluble, and thus not available as biological food. Despite this, biotreatment systems can be effective at oil removal, mostly as a result of its being trapped on the waste biosludge. It is usually true that increasing the oil in the feed to the biotreatment will result in more oil in the effluent from biotreatment.

9.6.9.7 Resistance To And Tolerance Of Foaming

Many tank bottoms water samples when subjected to biotreatment display considerable amounts of foaming, even though not thought to contain detergents. Either the water contains “natural” surfactants, or surfactants are made as part of the biodegradation process. Foam can harm biotreatment by floating bacteria in suspended growth aeration basins, by causing clarifier sludge to float (foam traps air bubbles), and by being a general operational and aesthetic nuisance. Foam is most likely to be generated in those processes which use “positive” aeration: suspended growth processes and those attached growth processes which employ air sparging (submerged biofilters). The two non-aerated attached growth processes (RBC and trickling filter) have demonstrated lack of foam generation when treating water which foams with other treatments, probably because agitation and formation of air bubbles are minimized in these processes.

The processes which are most susceptible to being rendered non-operable by foaming are those in which the foam will cause the bacteria to leave the water, namely, the suspended growth processes. Although probably not susceptible to foaming, the submerged biofilter and fluidized bed processes have not been tested in this regard.

Foam can be controlled by two means: use of antifoam agents, and water sprays. Antifoam agents change the surface properties of the water, and thus destabilize the foam, and water sprays physically destroy the foam. Both have disadvantages: neither is entirely certain to be effective, antifoam agents are expensive and add foreign material to the water, and sprays add extra flow to the effluent.

9.6.9.8 Low-Strength Waste Tolerance

In some applications, it is desired to remove low levels of organic contaminants from a dilute wastewater. This can be difficult for some types of biotreatment, since not enough food is supplied to maintain a biological population (the bacteria are washed out as fast as they can grow). In this regard, the best processes are expected to be the attached growth processes, since attached bacteria are not susceptible to washout. The fluidized bed process, in particular, is claimed to work well on dilute wastewater. Activated sludge treatment is not suited for this type of water, since an adequate MLVSS level cannot be sustained. Aerated lagoon treatment and SBR treatment are moderately suitable for dilute feed, since the former does not rely on population buildup, and the latter employs a flexible settling time, which can be extended if needed to retain low concentrations of biosolids.

9.6.9.9 Number of Existing Units

The number of installations of a particular type of treatment is not a direct indication of its value. It is somewhat desirable, however, to employ popular treatments, since more information will be available on designing and operating them, and since they will have a large body of performance data. The number of trickling filter and aerated lagoon systems is quite large, but those numbers are declining because those systems are known to produce inferior quality effluent. Both activated sludge and RBC treatment have amply demonstrated their utility for treating petroleum industry wastewaters. In the case of the more "exotic" treatment processes (SBR, submerged biofilters, and fluidized bed bioreactors), the lack of much real-world experience must be balanced against the claims for superior treatment and performance. For the latter technologies, the need for pilot testing is even more critical than for better-demonstrated technologies.

9.6.9.10 Air Emissions

Petroleum products terminals are minor emitters of wastewater (4.10), and thus minor emitters of volatile contaminants from their wastewater. For example, a typical terminal with 1000 gallons/week of contaminated water containing 200 ppm of volatile organic compounds would emit less than 100 lb/year of those compounds even if they were (as is unlikely) totally volatilized. This fact, combined with the fact that most (89-99%) volatile compounds are biodegraded rather than vaporized in biotreatment (Vuong, 1993), means that biotreatment of terminal wastewater is very unlikely to be a significant or regulated source of air emissions. The following discussion will thus be relevant only in exceptional circumstances (areas with extremely strict emission controls, terminals with very high water flows, and facilities with odor problems).

Air emissions of volatile contaminants result when gases leave the wastewater being treated, usually carried by the spent aeration air. The only process which inherently has low air emissions is the RBC process, since it is normally covered, and has no positive ventilation (sufficient air diffuses in to maintain biological activity). It should be noted that low air emissions can be achieved from *any* of the processes, if they are covered, if the air is recycled, and if the air from the offgas vent is treated. The main question, then, is how amenable the processes are to being covered and to employing air recycle.

The practicality of using covers is a function mostly of the horizontal reactor area: the smaller the area, the more easily it can be covered. By their nature, it is probably not practical to cover aerated lagoons or trickling filters. Activated sludge units, SBRs, submerged biofilters, and fluidized bed bioreactors can reduce their reactor area by increasing their height. Also, it is claimed that the latter two processes are inherently smaller devices, and thus more amenable to covering.

Air recycle design is perhaps more challenging than cover design. In systems which use compressed air (submerged biofilters, fluidized bed bioreactors, and those SBRs and activated sludge units which utilize compressed air aeration), a recycle blower can be used to take suction off the air space above the water. Even activated sludge systems with floating aerators could employ air recycle, so long as sufficient air space is provided between the cover and the water surface for the aerators to function. As part of air recycle design, it will be necessary to provide a means to control the input of fresh air, based probably on the dissolved oxygen levels in the reactor.

Air emissions can be reduced, but not eliminated, by improving the efficiency of oxygen transfer from air. In a typical aeration system, offgases from the aeration basin contain a substantial amount of residual oxygen, indicating inefficient usage. Some of the techniques for improving oxygen transfer include making finer bubbles in a dispersed air system (finer bubbles will have greater surface area, and thus mass transfer rates, and will also rise to the top of the reactor more slowly, thus enhancing oxygen transfer) and use of deeper aeration basins (the higher hydraulic pressure at the bottom of a deeper basin will act to compress and pressurize the air bubbles, thus enhancing mass transfer by size reduction and pressure increase, and it will take bubbles longer to rise to the top of a deeper basin).

Another approach to reducing air emissions, usable with all closed bioreactors, is use of oxygen instead of air. When air is used as an oxygen source, it is inherently necessary (no matter how efficiently the air is used) to discard as offgas the residual nitrogen (about 80% of the air). With pure oxygen fed to the system, there is no inherent need for any offgas to be disposed of, so long as the byproduct carbon dioxide from the biodegradation is soluble in the effluent water. Even if the carbon dioxide is not soluble, the quantity will be much less than the quantity of nitrogen left over from air aeration. The main disadvantage of using oxygen is the cost. Depending on the usage rates, oxygen can be purchased in compressed gas cylinders (commonly available from welding supply vendors) or as liquified oxygen. If usage rates are great enough, oxygen can be made on-site with pressure-swing-absorption units, or (for very large usage rates) with cryogenic air separation plants.

In any closed biotreatment system, there is a question of explosion hazard, since the confined vapor space may develop an explosive mixture of oxygen and hydrocarbons.

9.6.10 BIOLOGICAL TREATMENT OPERATIONS

Each of the various types of biological treatment has its own operating procedures, which will not be discussed here. Certain features, however, common to all systems, and which influence system design to some extent, are discussed below.

9.6.10.1 Protection Against Upsets

Since biotreatments are living systems with somewhat slow recovery times, it is important to ensure that nothing is fed to them which will kill the bacteria. In a petroleum products terminal, the most likely upsets are offtest pH (below 6 or above 9), which might result from acid or caustic spills in the facility, or from delivery of contaminated water with product, and feeding of pure product. Use of the batch feeding system (9.4.3), with checking of the batch for pH and the presence of product, is one simple way to accomplish this. In a continuously-operated system, pH and conductivity probes should be placed in the feed water line, and connected to alarms in the control room.

9.6.10.2 Biotreatment Startup

Biotreatment units are bacterial cultures, and so need *seed cultures* to initiate growth. Bacteria are found ubiquitously in the natural environment (air, water, and soil), and will, in time, naturally seed any bioreactor which is receiving feed, nutrients, and oxygen. To accelerate this process, it is usually desirable to obtain a concentrated seed culture, and place it in the bioreactor before adding feed water. Sources of the seed culture, in order of likelihood of containing appropriate organisms, are waste sludge from other petroleum products terminal biotreatment, waste sludge from refinery biotreatment, waste sludge from municipal biotreatment (probably the easiest to obtain), and purchased bacterial cultures.

Probably the best startup technique is to place the seed sludge into the reactor, along with enough clean water to fill the reactor volume, and to gradually begin to feed the wastewater. As a rule of thumb, the wastewater flow should be raised from an initial zero up to full flow over at least a two-week period. If the process is a fixed film process such as a trickling filter, a submerged biofilter, or a fluidized bed bioreactor, then the sludge mixture should be recirculated through the bed until bacteria begin to grow on the media surfaces (sludge recycle is not necessary in the RBC fixed film process, since the sludge can be left in the disk basins while the disks rotate). Initially, a large fraction of the bacteria will die off (since they are not suited for the terminal wastewater contaminants) and be washed out of the reactor. This is normal, and not a cause for concern.

9.6.10.3 Use of Bacterial Cultures

Bacterial cultures for wastewater treatment are available commercially, sometimes in dry form, and marketing of these can be vigorous. As a rule, such cultures are no better than, and usually inferior to, bacteria obtained from the natural environment or from other biotreatment systems (tests to demonstrate their effectiveness are usually run without controls, i.e., without side-by-side comparison with natural bacterial sources). Despite this, it will sometimes be desirable to purchase bacteria to accelerate system startup, after an upset, for instance, particularly if no sources of biosludge are available in the vicinity of the terminal.

9.7 Coagulation

Coagulants, also known as flocculants, are chemicals which cause small particles to clump together and make large particles, by neutralizing the electric charges which keep particles separated, and by physically linking the small particles. Coagulants are used for several purposes: enhancement of settling (as in a clarifier), enhancement of filtration (particularly granular media filtration), and enhancement of air flotation. In all of these processes, it is easier to separate large particles than small particles.

9.7.1 TYPES OF COAGULANTS

Coagulants can be either inorganic or organic. Inorganic coagulants are typically alum (aluminum sulfate, $Al_2(SO_4)_3$), ferric chloride ($FeCl_3$), or ferrous sulfate ($FeSO_4$). In use, these materials become the corresponding hydroxides: $Al(OH)_3$, $Fe(OH)_3$, and $Fe(OH)_2$. The inorganic coagulants work by neutralizing negative charges on the particles with positive aluminum or iron ions, and by making a coherent metal hydroxide floc which traps the particles. Organic coagulants are commonly known as polyelectrolytes, due to their nature of being large molecules (polymers) with numerous electrically charged (electrolytic) groups attached along the polymer chain. Organic coagulants can be obtained as cationic (with positively charged groups), anionic (with negatively charged groups), and nonionic (groups which are polar [attracted to water] but not charged). Organic coagulants work by charge neutralization, and also by providing a means for chemically linking small particles together. Although more expensive than inorganic coagulants, organic coagulants have the advantage of generally producing less sludge. In addition, the large variety of organic coagulants increases the chances of finding an effective treatment for a given wastewater.

9.7.2 COAGULANT USAGE

In practice, coagulants are usually added to water in a two-stage process. In the first stage, known as *rapid mix*, the injected coagulant is mixed at high speed with the water; typical mix chamber retention times are 0.5-3 minutes. The rapid mix ensures that the coagulant is evenly dispersed throughout the water. In the second stage, known as *slow mix*, the rapid mix effluent is gently mixed for about 10-20 minutes. In the slow mix process, the small particles are allowed to grow into large particles.

9.7.3 JAR TESTING

The phenomenon of coagulation depends on the surface properties of the solids, and the chemical nature of the water. Because these properties cannot be readily determined, selection of coagulants is always done by a trial and error procedure known as *jar testing*. In jar testing, samples of the water are given a known dosage of coagulant, rapidly stirred for a specified time, slowly stirred for a specified time, and then allowed to settle; the appearance of the resulting floc (large or small particles, water clear or cloudy) is noted. This testing is usually done for a wide variety of coagulants, over wide dosage ranges, until an effective and economical coagulant type and dosage are found.

9.8 Filtration

Filtration of wastewater means generally the removal of insoluble material from the water. In practice, this means mostly the removal of suspended solids, although some oil removal can also be accomplished, partly because oil can be a component of the solids, but also by direct removal (particularly for heavy viscous oil). The two basic types of filters used for petroleum industry wastewater service are *granular media filters* and *surface filters.*

9.8.1 GRANULAR MEDIA FILTERS

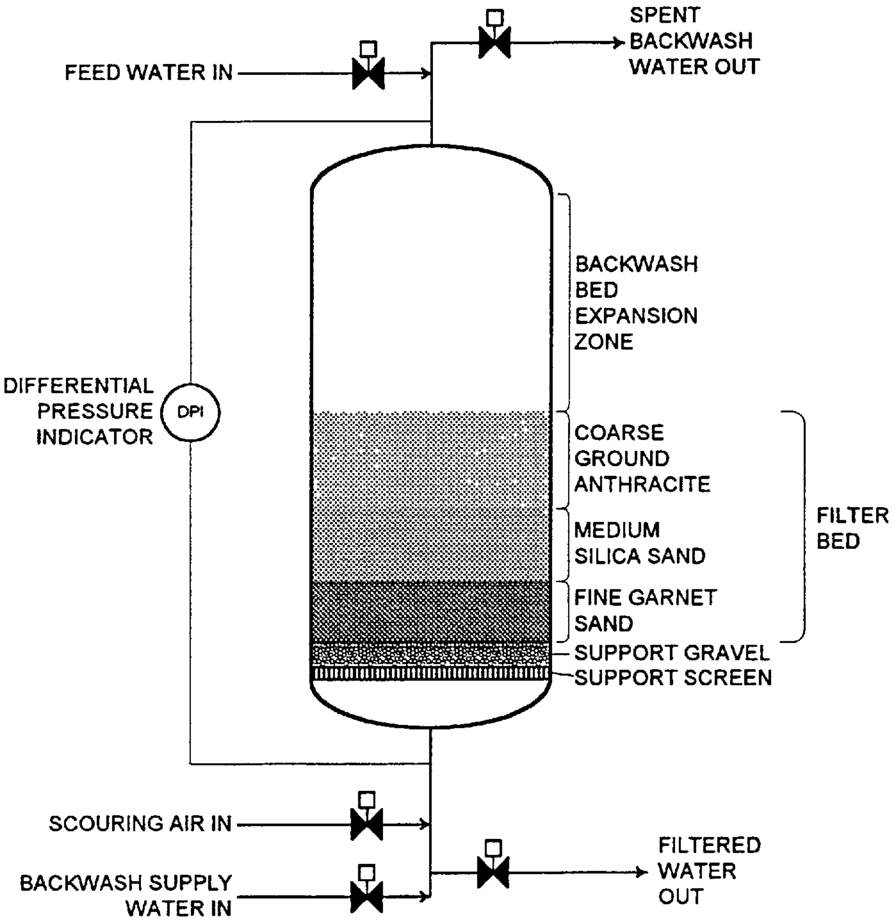
As shown on Figure 9-13, granular media filters, commonly known by the generic term of *sand filters*, are beds of granulated media through which the wastewater is passed. Common materials for filter media are ordinary silica sand, ground anthracite coal, and garnet sand; other ground and graded materials are also available. This type of filter is commonly used in filtering swimming pool water.

9.8.1.1 Mode of Action

Contrary to common impression, granular media filters do not work mostly by *sieving* action; i.e., the particles which are removed are not necessarily larger than the pore spaces between the media grains. Instead, the particles are essentially removed by adherence to the media grains, brought about by various fluid dynamic actions such as impingement. It remains true, however, that generally media with finer grain sizes (smaller *mesh*, a measure of grain diameter) will remove particles more thoroughly, and that larger particles are easier to filter than smaller particles. For this reason, coagulants are commonly employed to improve the filterability of water. For filtration, unlike settling, it is essential that a *tough floc* be developed by the coagulant to prevent breakup of the floc by the water shearing action in the filter bed. Floc toughness can be estimated by mechanically agitating the floc developed in coagulant jar testing (rapidly mixing the settled floc) and observing its re-settling behavior.

FIGURE 9-13

PRESSURE SAND FILTER



9.8.1.2 Operating Cycle

Granular media filtration is a semi-continuous process in which water is passed through the filter bed until the solids accumulated on the bed either cause pressure drop through the filter to become excessive, or until solids start coming through the filter (know as *breakthrough* of solids). Filtration can also be terminated on a time cycle, based on a known filtration time which will avoid high pressure drop or breakthrough. Once filtration is stopped, the filter is *backwashed* with water (water is pumped upwards through the filter bed) at a rate sufficient to expand the bed (usually about 50% expansion) and dislodge filtered solids from the media grains; this is done until the backwash water is mostly free of solids. The bed is then allowed to settle, and normal filtration is resumed. The backwash water leaving the top of the filter (known as *spent backwash*) is usually accumulated in a tank. From the tank, the spent backwash can be sent back upstream to a clarifier, or the solids can be allowed to settle and removed as a solid waste.

Enhancements to the backwash procedure include *air scour*, in which air is bubbled up through the filter bed prior to backwash water as a means for shaking loose the filtered solids without generation of spent backwash. When a backwashed filter is returned to service, it is usually advisable to send the first water which comes through back to the filter feed, since it can contain excessive levels of solids. In many filter systems, the backwash cycle is automated with automatic valves and either mechanical or electronic controls; this can result in significant manpower savings and improved backwash effectiveness.

9.8.1.3 Media Gradation

The most efficient use of a granular media filter is achieved when the media grain sizes vary from large at the filter entrance to small at the filter exit. The reason for this is that large particles can be removed in the top of the bed, and smaller particles in the bottom, thus achieving a significantly increased filter capacity compared to a filter bed made of uniformly-sized particles. Unfortunately, backwashing a granular media filter tends to produce just the opposite gradation: a backwashed bed has the largest grains on the bottom, and the smallest on the top. To overcome this, multi-media filters have been developed. In a multi-media filter bed, the bed comprises low-density large grains (usually ground anthracite), medium-density medium size grains (usually silica sand), and high-density small grains (usually garnet sand). When a multi-media bed is backwashed, the large light particles are moved to the top, and the small dense particles stay on the bottom, the desired result. Typical size ranges for the media are 1 mm for anthracite, 0.5 mm for silica sand, and 0.27 mm for garnet sand. In one example, bed depths of these media are 20 inches of anthracite, 10 inches of silica sand, and 6 inches of garnet sand.

Typical design values for multimedia filters are shown in Table 9-6.

In another means for achieving proper size gradation, upflow filters with beds of single media are used. In an upflow filter, the water being filtered passes upwards, but at a velocity insufficient to expand the bed. Since a backwashed bed has the largest grains on the bottom, this type of filter meets the criterion for media size gradation. As with a normal downflow filter, backwashing is done from the bottom, but at a higher flow than the filtering flow.

Table 9-6

Typical Sand Filter Operating Conditions

Parameter	Units	Range	Typical
Hydraulic loading	gpm/sq.ft.	2.5 - 10	7
Filtration time	hours	4 - 24	8
Backwash flow	gpm/sq.ft.	20 - 30	25
Backwash duration	minutes	15 - 30	20

9.8.1.4 Other Granular Media Filters

Other types of granular media filters include moving-bed, continuously backwashed, filters and slow sand filters. In slow sand filters, water is passed by gravity head through a sand bed at low rate (low gpm/ft^2).

9.8.2 SURFACE FILTERS

Surface filters utilize relatively thin porous sheets of material, made of paper, string, cloth, or metal, to remove solids from water with essentially a sieving action (i.e., only particles larger than the specified pore size are removed). Once solids start to accumulate on the filter surface, some of the smaller particles can also be removed by the bed thus developed. Generally, surface filters have specified pore sizes, e.g., 1 micron. The two types of surface filters are cartridge filters and bag filters.

9.8.2.1 Cartridge and Bag Filters

Cartridge filters can be obtained with either disposable cartridges (by far the most common type) or reusable cartridges. Disposable cartridges can be made of pleated paper (similar to automobile oil filters) or wound string. Reusable cartridges are generally made of porous metal (felted metal strands or sintered metal powder), which can be backwashed to remove the collected solids.

Bag filters utilize filter cloth, made of various woven or felted materials, with specified pore size, as the filter medium. Solids can be removed from the cloth by backwashing.

9.8.3 CHOICE OF GRANULAR OR SURFACE FILTERS

By far the most common type of surface filter for wastewater service is the disposable cartridge filter. Compared with sand filters, cartridge filters have the advantage of low capital cost and simplicity of operation. On the other hand, operating costs for disposable cartridges can be significant if cartridges must be changed frequently, since this involves the cost of the cartridge, the disposal cost for the spent cartridge, and the manpower for handling the cartridges. Because of this factor, disposable cartridges are suited for low-load applications (low lb/day of filterable solids), and sand filters are suited for high-load applications. In some cases, sand filters are used to remove most of the solids, and cartridges are used downstream to remove the residual solids from the sand filter effluent.

9.9 Wastewater Gas Strippers

9.9.1 STRIPPING

9.9.1.1 Vaporization and Henry's Law

Wastewater strippers are devices in which vapor is passed upwards through water to remove (strip out) volatile contaminants from the water by transferring them to the gas stream. The process of vaporization from the water into the vapor, and moving the vapor carrying the contaminants away from the water, is called *stripping*. Stripping is a function of three basic factors: vaporization of contaminants, gas/liquid volumetric ratio, and gas/liquid contact.

Vaporization of contaminants from water is described by the Henry's Law constant, a term which relates the equilibrium concentration of a contaminant in water to the corresponding concentration in gas in contact with the water, according to the equation: $P = HC$, where P = partial pressure of the contaminant, H = the Henry's Law Constant, and C = the concentration of the contaminant in the water. Table 9-7 gives Henry's Law constants for several common volatile contaminants at 20 C. The constants (and thus the volatilities and strippabilities) rise with temperature.

As an example of a Henry's Law calculation, water with 25 ppm benzene dissolved in it would have an equilibrium vapor pressure of benzene in the air space above the water of

$$25 \times 0.00102 = 0.0255 \text{ psia } (\times 1{,}000{,}000/14.7 \text{ psia } = 1735 \text{ ppm in air}).$$

9.9.1.2 Gas/Liquid Volume Ratio

The gas/liquid volume ratio affects stripping because passing more gas through the water will enable carrying more volatiles out of the water (by a combination of greater carrying capacity and lower partial pressure of the contaminant in the gas stream). Note that only the volume of the gas, not its mass flow, is significant, since partial pressure of a contaminant in the gas is independent of the gas density or mass flow.

Table 9-7

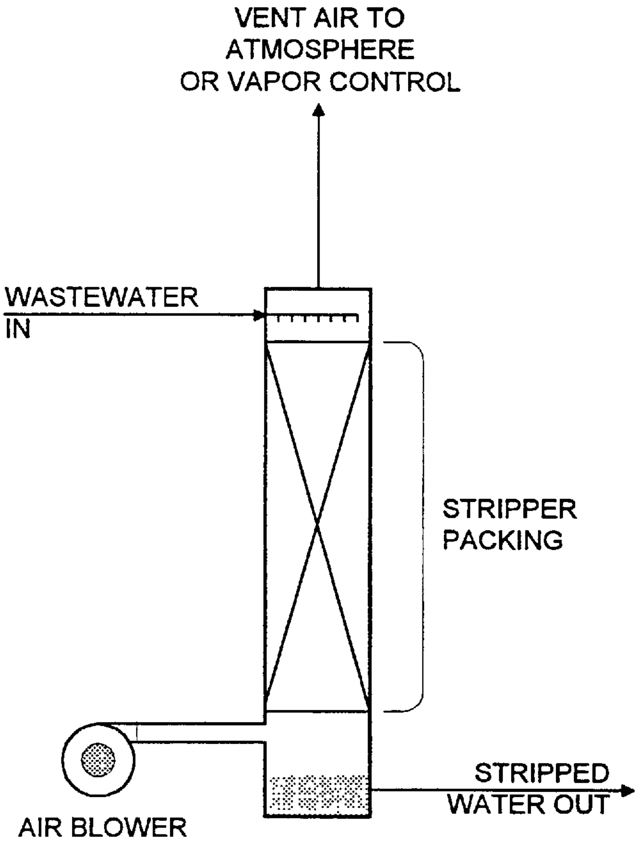
Henry's Law Constants at 20C

Contaminant	Henry's Law Constant, psia/ppm
Benzene	1.02E-03
Toluene	9.48E-04
o-Xylene	7.07E-04
m-Xylene	1.06E-03
p-Xylene	1.06E-03
Ethylbenzene	1.17E-03
Naphthalene	3.99E-05
Cyclohexane	3.37E-02
Phenol	6.20E-08
2-Cresol	2.18E-07
3-Cresol	1.18E-07
4-Cresol	1.31E-07
2,4-Dimethyl Phenol	7.58E-08
Methanol	6.20E-05
Ethanol	2.01E-06

Reference: Howard, Philip H, "Handbook of Environmental Fate and Exposure Data for Organic Chemicals", Volumes I and II, Lewis Publishers, Chelsea, Michigan, 1989

FIGURE 9-14

AIR STRIPPER



9.9.1.3 Interfacial Area

Since vaporization involves moving a contaminant from a liquid stream to a vapor stream, the contact area (*interfacial* area) between these two phases is critical to obtaining adequate rates of vaporization. Stripper packings are designed to maximize the interfacial area while still accommodating high liquid and vapor flow rates, as described below.

9.9.2 AIR STRIPPERS

Gas strippers can use any gas without significant changes in the stripping performance: air, nitrogen, and natural gas have all been used. In the following discussion, it will be assumed that air is the stripping gas (since it is the most commonly-used gas), but it should be recognized that any other gas could be used. The reasons for using other gases are discussed below.

9.9.2.1 Design

The basic elements of an air stripper are simple, as shown on Figure 9-14. A cylindrical vertical stripping tower is provided, and filled with packing (distillation trays can also be used). Water is pumped to the top of the tower, and passed downwards through the packing. Air, usually from a blower, is passed upwards through the packing and out the top of the stripper. In many applications, these are the only basic elements used in an air stripper.

The most important stripper design factors are the packing depth, the liquid loading, the air flow, and the type of packing. These factors, and the relationships between them, are described below.

- The packing depth determines the number of stages of stripping; a stage is conceptually a zone in which the air and water are equilibrated. With all other factors being equal, greater packing depth (more stages) provides more effective stripping. As an example of this, if 10 foot of packing provides 80% removal of volatile material, then 20 feet would provide 96% (= 80% + 80% of the remaining 20%) removal. Note that the packing depth is somewhat shorter than the column length, since space must be provided for gas and liquid distribution and disengagement at the top and bottom of the column.

- Liquid loading is the volumetric flow of the water sent to the stripper divided by the horizontal cross-sectional area of the stripper. Thus, the liquid loading is the basic sizing parameter for the stripper diameter. To minimize column size, it is desirable to maximize the liquid loading. However, as noted below, the maximum liquid loading is controlled by other design parameters.

- Since air is the medium used to remove contaminants, their extent of removal is directly related to the flow of air, usually expressed as the air/water volumetric ratio. As a rule of thumb, the ratio will fall in the range of 3-15 cfm air/gpm water. As described below, the flow of air is limited by other design factors.

- There are a multitude of available packing materials, which vary in their material of construction (generally plastic or metal or ceramic), their size (expressed as diameter), and their shape. The material of construction affects the packing weight, the corrosion resistance, the shape, and the cost. For wastewater treatment service, plastic media are usually preferred. The size of the packing affects the total surface area (along with the shape), with more area being available from smaller packing, albeit at higher total cost, and more pressure drop. As a rule, packing diameter should not exceed one tenth the column diameter in order to achieve good liquid distribution. Packing shape is the factor which varies most amongst suppliers, and a wide variety of proprietary shapes, each with its claimed advantages, is available. Factors affected by shape are total surface area (controls the amount of water surface exposed to the air flow, and thus the stripping efficiency), liquid distribution (even distribution is preferred to maximize water surface area and avoid short-circuiting), pressure drop for the air flow, flooding (formation of zones of bulk liquid within the packing instead of the desired thin liquid films), and resistance to fouling by accumulated solids or heavy oils.

- The various design factors strongly interact, and this must be taken into account when designing a stripper. Water passes downwards countercurrent to the upward moving air, and the flows interact: higher liquid loading causes more air pressure drop, and higher air flow increases the chances of liquid flooding. Different sizes and shapes of packing also strongly affect the pressure drop and flooding. The factors are sufficiently complex that computer program packages are generally used to design strippers in a new type of service.

In addition to the major design factors of packing height and diameter, water flow, and air flow and pressure, there are also design details which can significantly affect the effectiveness and reliability of strippers. Some of the detail design factors are as follows:

- A liquid distributor is required to provide even distribution of the water over the top of the packing.

- Particularly in tall narrow columns, liquid redistributors along the length of the column may be required to move water off the column wall back into the packing.

- Other column internals are packing support plates and holddowns.

- In many cases, it will be desirable to place a mist eliminator (e.g., mesh) at the top of the column to prevent carryover of liquid water. This may be particularly important for some types of offgas treatment (see below).

- Liquid level must be maintained in the bottom of the stripper column to prevent air from blowing out the liquid exit line. This can be done with a level control valve, or with an overflow arrangement.

9.9.2.2 Offgas Handling

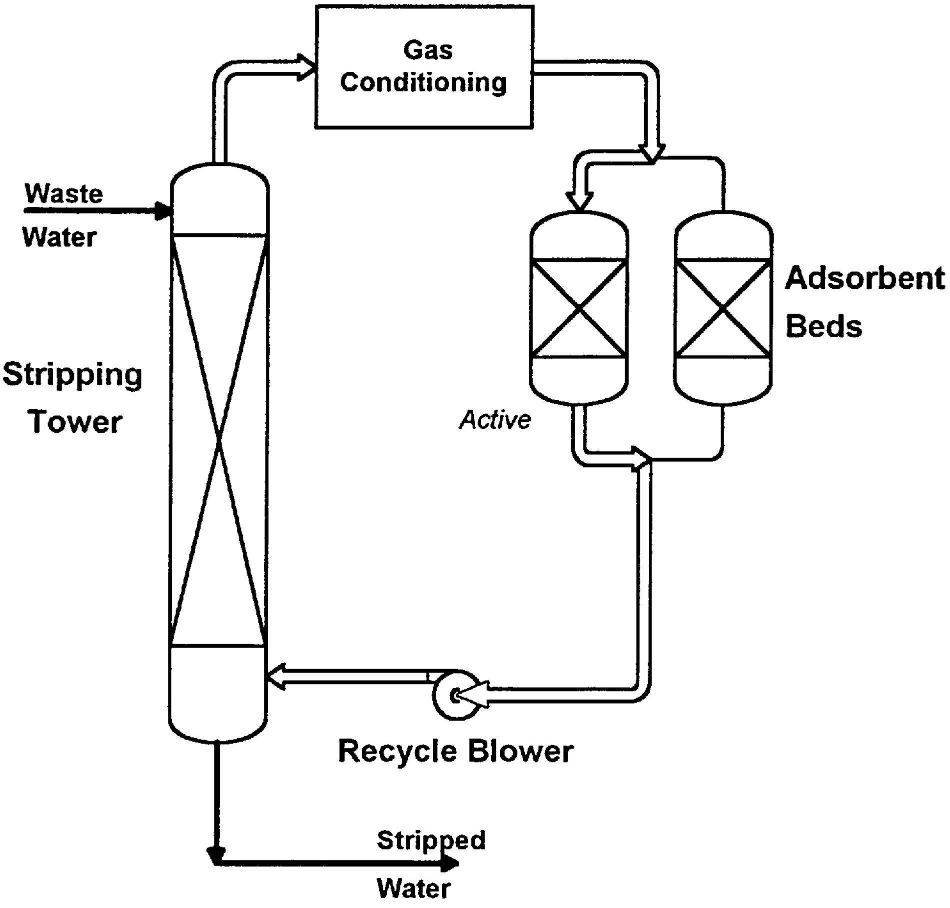
In situations where air contamination or odors are a problem, the offgas from the stripper can be treated, usually after bringing it back down to ground level in ductwork. The most common types of treatment technology are activated carbon adsorption beds (using carbon designed for this service to have low pressure drop) and gas incinerators, which usually require auxiliary fuel (normally, natural gas) to maintain a combustible mixture. If activated carbon is used, it must be periodically tested for exhaustion. Once exhausted, it must be regenerated, either on-site (usually with low pressure steam), or off-site (taken to a regeneration plant).

9.9.2.3 Air Stripping of Wastewater

Air strippers are very commonly used for removing contaminants from groundwater which has become contaminated with hydrocarbons or other volatile solvents as a result of leaks or spills. Contaminated groundwater is usually characterized by containing low concentrations of hydrocarbons or solvents, and is easily treated in an air stripper. *Air strippers must be used with*

Figure 9-15

Closed Loop Stripper



Note: Diagram courtesy of Westates Carbon, Los Angeles. Reprinted with permission.

caution, however, for water with higher levels of contamination, particularly non-volatile contamination of the type normally found in water bottoms from petroleum products storage tanks. The problem with stripping this type of water is that it commonly contains high levels of biodegradable organic matter, and an air stripper is an ideal environment for aerobic biological activity: temperatures are in the correct range, and more than enough oxygen is available for biological growth. This would not be a problem (contaminants are still removed) except for the fact that the biological growth will rapidly plug the stripper packing, hinder the stripping action, and eventually prevent passage of water and air through the stripper.

A related issue is the presence of dissolved iron in the wastewater. The solubility of iron is strongly affected by its oxidation state. The more reduced form, ferrous (+2) iron, is much more soluble that the oxidized ferric (+3) form. Soluble ferrous iron tends to be formed in anaerobic environments such as groundwater and tank bottoms. When exposed to oxygen, as in an air stripper, the iron rapidly oxidizes and deposits as gelatinous ferric hydroxide sludge. This may happen at such a rate as to make air stripping impractical, or may require periodic cleaning by acid washing.

As a means for handling these problems, oxygen-free gas, such as natural gas, could be used. To make this alternative economically feasible, it would be essential to use a natural gas stream already being used for combustion at the flow rates required for stripping. In this case, the gas could be routed through the stripper on its way to the combustion device (this would also have the advantage of providing a cost-free method for destroying the offgas contaminants).

Another option for oxygen-free stripping is available as a proprietary commercial process, used successfully in refinery wastewater service, and shown on Figure 9-15. In this process, known as recycle gas stripping or closed loop stripping, nitrogen is used as the stripping medium, and activated carbon is used to remove the stripped contaminants from the nitrogen offgas. The unique aspect of the process is that the contaminant-free nitrogen from the carbon is returned to the blower suction, thus creating a closed-loop system for the stripping gas, and making it economically practical to use a stripping gas other than air. The carbon is manufactured to be periodically regenerable with low-pressure steam, with the steam condensate usually sent back to product tankage or other system for recovery of the product. Since the stripping gas is free of oxygen, biological growth does not occur in the tower. An additional benefit of the process is that it produces no air emissions, since no air or other offgas leaves the unit.

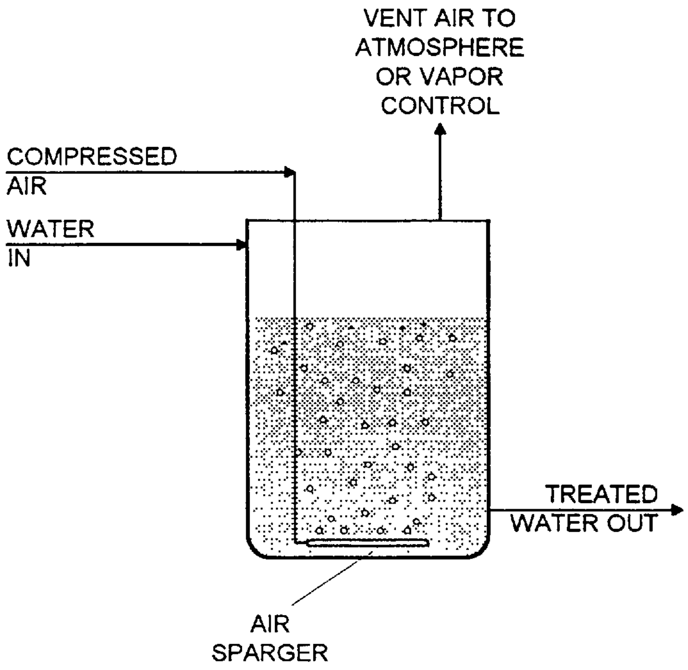
Another potential problem with wastewater strippers is foaming, since stripping conditions (intimate mixing of air and water with agitation) tend to make foam. If severe foaming occurs (as has been found in petroleum product tank bottoms waters), and cannot be suppressed with anti-foam agents, it may make stripping of the wastewater impossible.

9.9.3 SPARGER STRIPPERS

Sparger strippers is a term used for simple single-stage strippers which are essentially aerated tanks, as shown on Figure 9-16. Although not very efficient in their usage of air because of the single-stage design, they are simple and inexpensive to construct, and relatively simple to operate.

FIGURE 9-16

SPARGER STRIPPER



9.9.3.1 Design Features

Some of the design features for sparger strippers are as follows:

- The required air/water flow ratio can be estimated directly from the Henry's law constant for the material being removed (usually benzene), with an efficiency factor added in. As a rule, air usage efficiency will be greater if smaller air bubbles are generated, and if the tank is deeper, although these must be balanced against the higher equipment and operating costs for a higher-pressure compressor.

- A sparger stripper can be operated in either a continuous flow or batch mode. The latter may be preferred as being easier to operate if small quantities of water are being treated (e.g., low-flow tank bottoms water).

- A sparger stripper will very likely contain biological growth, since its operating conditions are ideal for this. This is probably more of a benefit than a problem (since benzene can be removed by biotreatment as well as by stripping), but the presence of high levels of biological solids in the effluent water should be taken into account in the system design.

9.9.3.2 Comparison With Packed Column Strippers

The relative advantages and disadvantages of sparger strippers in comparison with the more common packed column strippers are as follows:

- Sparger strippers are not affected by biological growth, unlike packed column air strippers, since they do not employ packing which can foul. Since biological growth makes packed column air strippers unusable on tank bottoms water, this is a significant advantage (however, other types of column strippers also avoid this problem, as noted above).

- Sparger strippers require higher-pressure air than packed column strippers, since there are significant pressure drops in the air sparger and in the water head to be overcome. This means that unlike air strippers which use low-head blowers, sparger strippers must use high-head blowers, or compressors, which are significantly more expensive to buy and operate.

- Sparger strippers have much higher air flow than packed column strippers, and thus higher air emissions. The main disadvantage of sparger strippers is their single-stage operation, which means that much more air is required to remove a given level of contaminant than is required by a multi-stage packed column stripper. In addition to raising operating costs, this also makes control of air emissions (if such is required) more difficult and expensive.

9.9.4 STEAM STRIPPERS

Steam strippers are commonly used in refineries for removing ammonia and hydrogen sulfide from process sour condensate water. Since their high temperature and reflux operation promotes fouling and scale formation on the packing or trays, they are not much used for "dirty" wastewater (wastewater which contains oil or solids or salts). This factor, along with their very high construction and operating cost, and the general unavailability of steam in petroleum products terminals, means that steam strippers are not used in terminals for removing volatile contaminants.

9.10 Activated Carbon Adsorption

Adsorption of contaminants onto activated carbon is an old and established technique for removing primarily low concentrations of organic contaminants from water. Activated carbon, usually made from coal and other natural materials, obtains much of its adsorptive capacity from its very high porosity and surface area, which can be over 1000 square meters/gram. The main barrier to more widespread use of activated carbon is its high cost, which normally limits its use to treating water without high concentrations of contaminants, such as drinking water, slightly contaminated ground water, or (rarely) treated wastewater.

9.10.1 ADSORPTION ISOTHERMS

As with any adsorptive system, the capacity of activated carbon to hold contaminants is a function of the concentration of the contaminants in the water, generally expressed as an *adsorption isotherm*, so named because it is obtained at constant temperature. As shown on the example of an isotherm on Figure 9-17, it is generally true that the concentration of contaminant on the carbon rises as the concentration in the water rises. For an ideal system, the logarithmic isotherm plot as shown will have a straight line isotherm. Before designing any activated carbon treatment system for a wastewater, it is essential to develop an isotherm for the water and the carbon in laboratory tests to establish the carbon effectiveness for removing various contaminants and the carbon usage rate.

9.10.2 MODE OF CARBON USAGE

There are two basic ways of using activated carbon: column operation with granular carbon, and stirred tank operation with powdered carbon. These are quite different in their effectiveness, complexity, and performance.

9.10.2.1 Granular Carbon in Columns

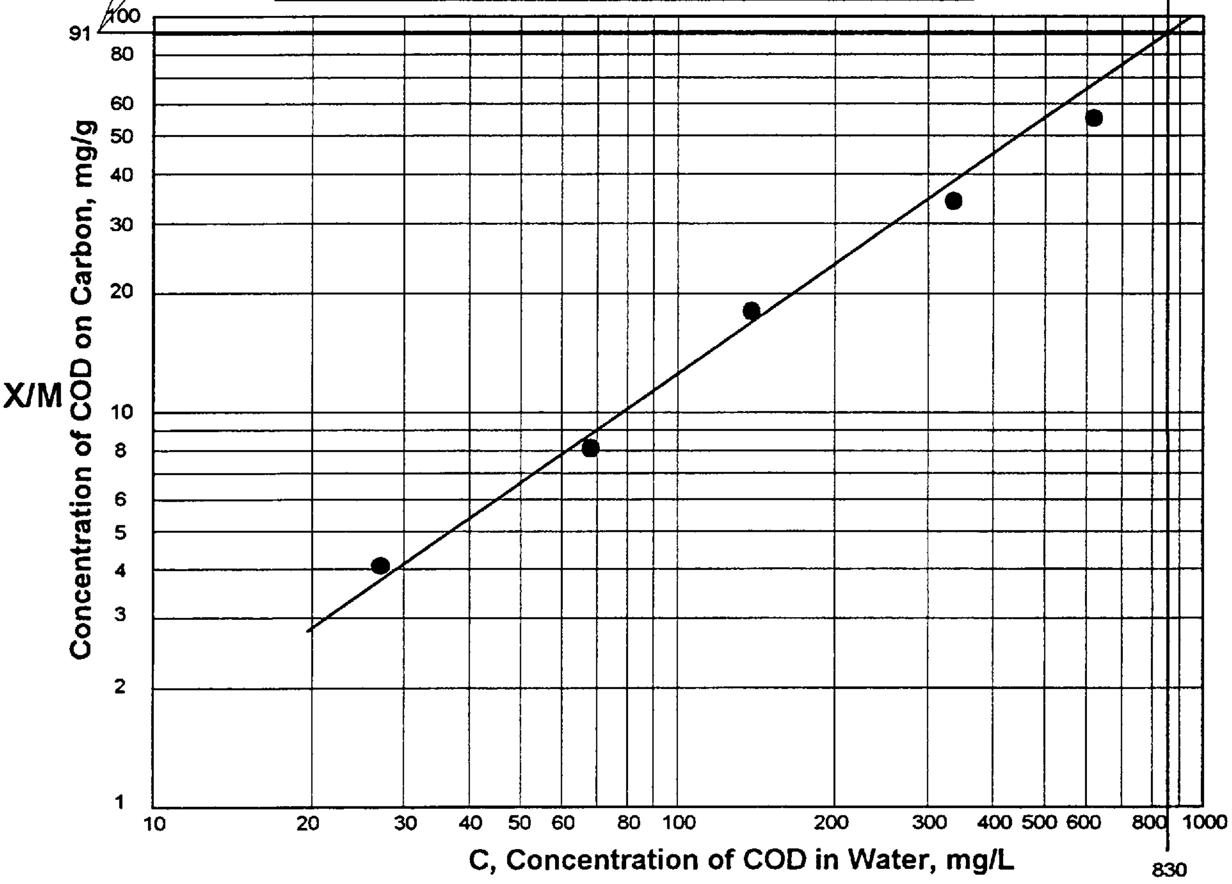
The classical means for using activated carbon is as a columnar bed of granular carbon, with the water passed down through the bed. In this type of treatment, as shown on Figure 9-18, various zones of depletion are set up, and move with time as the carbon bed is progressively exhausted. At the top of the bed is the exhausted zone. In this zone, which is equilibrated with the feed water, the absorptive capacity of the carbon towards the contaminants in the water is used up, and no more activity occurs. At the bottom of the bed is the unexhausted zone, which is equilibrated with the effluent water, and in which little of the carbon capacity has been used. In between these is the transition zone, which is the active zone for removing contaminants. When the transition zone moves down to the bottom of the column, contaminant levels in the effluent water rise, which is known as *breakthrough*. Once breakthrough occurs, the bed is considered to be exhausted, and the carbon is removed and replaced with fresh carbon.

Figure 9-17

ACTIVATED CARBON ISOTHERM EXAMPLE

Experimental Data: Weighed portions of dried ground carbon added to 100 mL samples of 830 mg/L COD wastewater, stirred for 24 hours, filtered, and analyzed for COD.

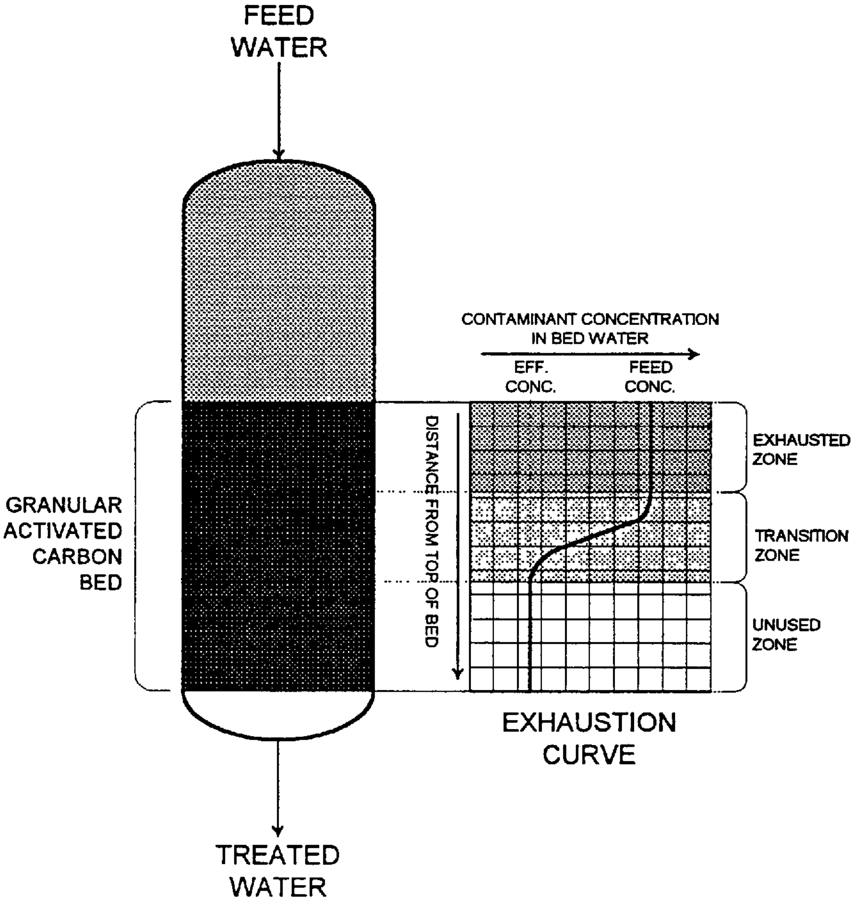
	C		X/M
Carbon Dosage, mg	COD in Water, mg/L	COD Removed, mg	COD on Carbon, mg/g
0	830	0	0
407.4	610	22	54
1500.0	320	51	34
3605.3	145	68.5	19
9395.1	69	76.1	8.1
19561.0	28	80.2	4.1



Carbon Dosage Calculation: To treat water with 830 mg/L COD with carbon which can hold 91 mg of COD per gram of carbon, the dosage = 830 mg/L / 91 mg/g = 9.12 g carbon/L of water. Treating 1000 gallons/week of water will use up (1000 x 3.785 L/gal x 9.12 =) 34,519 g carbon = 76 lb/week of carbon.

FIGURE 9-18

GRANULAR ACTIVATED CARBON COLUMN OPERATION



Column operation with granular carbon is usually a very efficient means for utilizing carbon, since most of the discarded exhausted carbon contains high loading of contaminants, being equilibrated with the high-concentration feed water as shown on the isotherm. In addition, the effluent is of good quality, since it has left the column in contact with unexhausted carbon. Counteracting these advantages are the significant disadvantages of high carbon cost and high handling cost. Granular activated carbon is significantly more expensive than powdered activated carbon (although similar in its adsorption behavior). Costs of handling carbon can be very high, since the carbon column must be periodically emptied, refilled with fresh carbon, refilled with water and purged of air (carbon tends to hold air in its pores, which blocks its activity). The spent carbon must be collected and shipped offsite for regeneration (only very large carbon consumers can afford to regenerate carbon on-site using the traditional multihearth furnace technique). To avoid some of this cost for small treatment systems, pre-packaged carbon columns with the carbon and distribution piping contained in a standard plastic drum are commercially available; these drums can be connected in series as shown on Figure 9-19. When the carbon in a drum is exhausted, it can be removed and sent back to the vendor, and a replacement drum can be placed at the end of the system. While this type of application is convenient and saves considerable manpower, the replacement cost of the carbon is still high.

The use of granular activated carbon beds, whether in columns or drums, is unique amongst treatment processes in that the reagent (carbon) is used up over time. For this reason, when using

FIGURE 9-19

USE OF GRANULAR ACTIVATED CARBON DRUMS

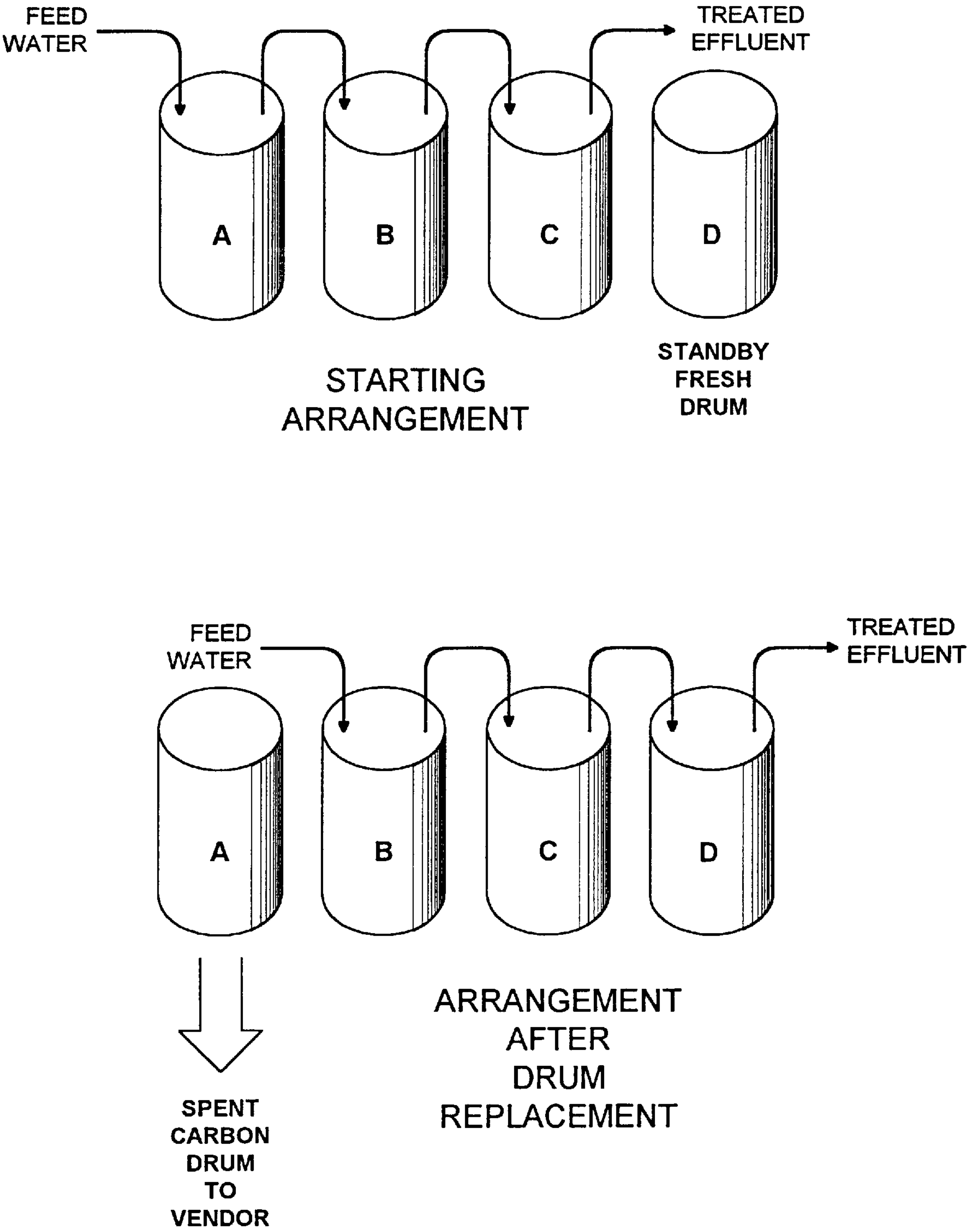
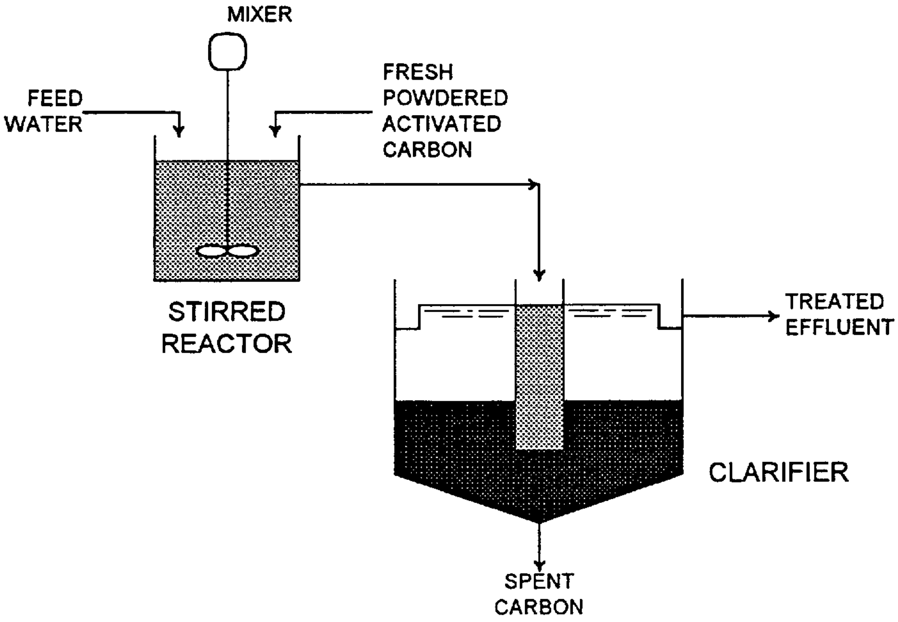
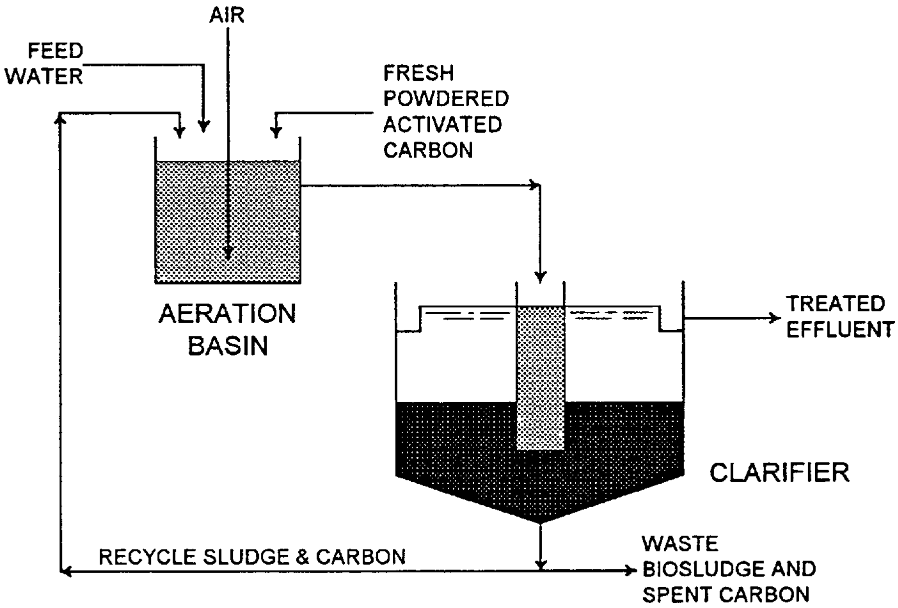


FIGURE 9-20

POWDERED ACTIVATED CARBON USAGE



POWDERED CARBON TREATMENT

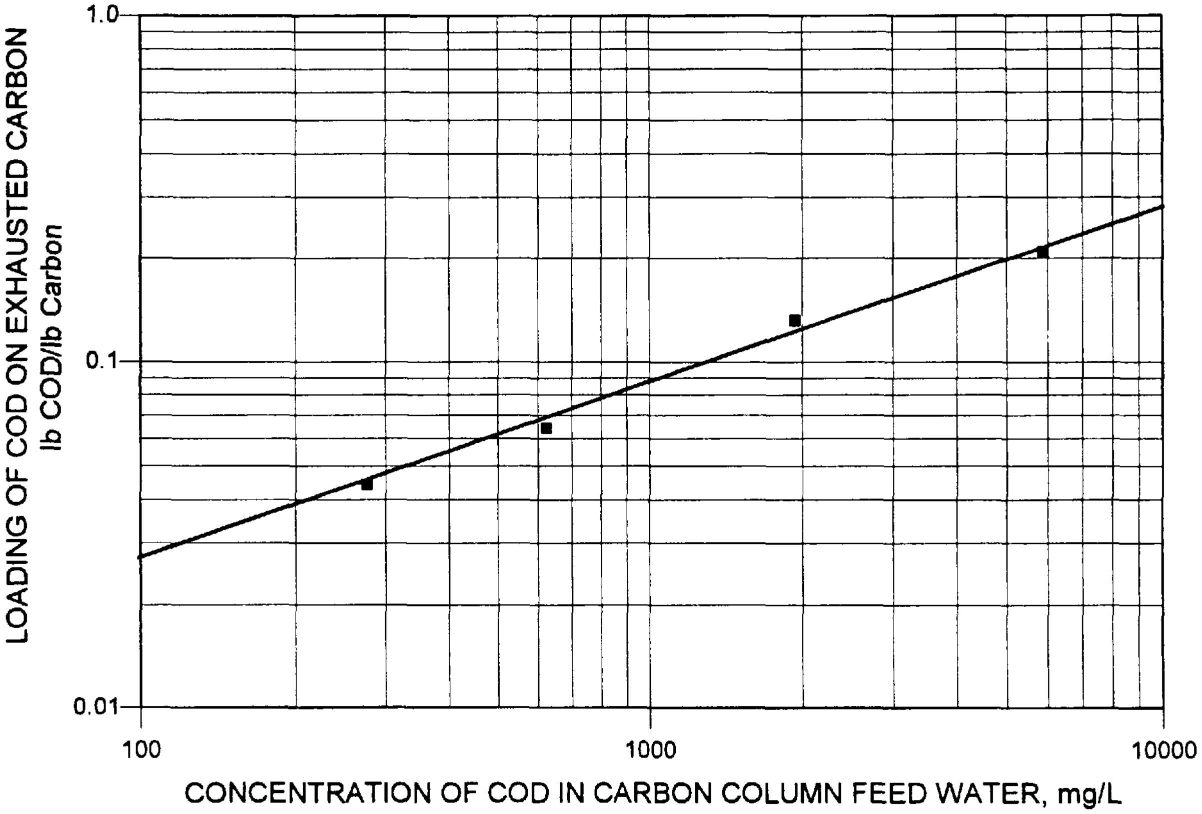


COMBINED POWDERED CARBON / BIOTREATMENT

FIGURE 9-21

Granular Activated Carbon Column Capacity for COD Based on Exhaustion of Full-Scale and Pilot Scale Activated Carbon Columns

The data and graph on this figure were obtained from actual usage rates for granular activated carbon in columns or drums as determined in full-scale usage or pilot tests on marketing terminal wastewaters in the studies described in Appendix B. "Usage rate" is defined as the amount of carbon used before breakthrough of contaminants required changeout of the carbon. The table at the bottom shows the percent of feed COD in the effuent at the time of breakthrough. COD loading was calculated based on the average amount of COD removed from the feed water multiplied by the total volume of water passed through the carbon bed. Figure 9-22 shows similar data for TOC loading. Although the data are based on actual experience, they should be used with caution, since different wastewaters have different adsorption characteristics, and different modes of carbon usage can influence usage efficiency.



Linear regression equation for best-fit line shown is LW = 2.0060xLC + 5.1353, where LW is log10 of COD concentration in water (mg/L) and LC is log10 of COD loading on exhausted carbon (lb COD/lb carbon).

Water Being Treated	COD		% Effluent COD/Feed COD	
	Conc. in Water	Loading on Carbon, g/g	Initial	At Breakthrough
Trickling Filter / Activated Sludge Effluent	5962	0.206	31	71
RBC Effluent	616	0.06497	17	62
Untreated Wastewater	1931	0.125	21	51
RBC & SBR Effluents	263	0.04509	13	21

activated carbon beds, it is essential to frequently monitor the carbon effluent quality to ensure that adequate treatment is still being achieved Since a bed of activated carbon acts as a filter, since carbon activity is blocked by solids, and since carbon columns are not made to be backwashed, it is important to keep solids out of feed to a granular carbon bed by filtering the feed in a sand or surface filter (9.8).

9.10.2.2 Powdered Carbon in Stirred Reactors

Powdered activated carbon is generally used by mixing it with water in a stirred tank (Figure 9-20), similar to using any chemical reagent. Following the mixing, the mixture of carbon and water must be settled, and the spent carbon removed from the bottom of the settler and disposed of as a sludge. Powdered activated carbon has the advantage of being less expensive than granular carbon, and somewhat simpler to use. Its main comparative disadvantage is that its effective capacity is significantly lower, since the spent carbon is equilibrated with *effluent* water (see Figure 9-17), not feed water. For the same reason, the effluent quality is not as good as can be obtained with granular carbon treatment, since the effluent is equilibrated with *spent* carbon. For treatment systems which use the activated sludge or SBR suspended growth biotreatment processes, a convenient proprietary commercial process is available in which the powdered activated carbon is mixed with the aerated biosolids, and the spent carbon is removed along with the waste biosludge. Although the performance is not necessarily any better than expected from biological treatment followed by powdered carbon treatment, the ease of use (since only one mixer and settler are needed, and only one sludge needs to be disposed of) is significantly improved. As another consideration in the use of powdered carbon, it should be noted that it is electrically conductive and electrochemically active, which makes the water containing it more corrosive, particularly to carbon steel.

9.10.3 EFFICIENCY AND EFFECTIVENESS OF GRANULAR CARBON USE IN COLUMNS

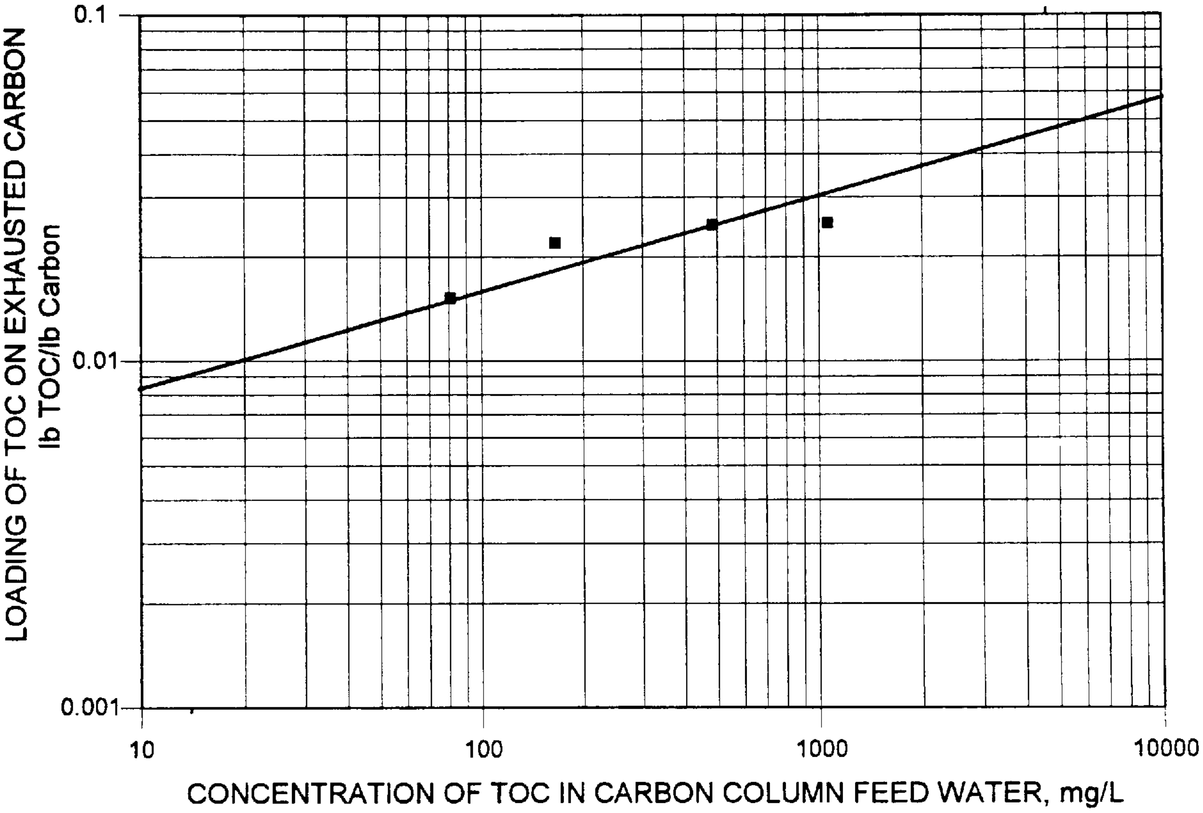
As noted in 9.10.1, adsorption isotherms can be used as an experimental technique to predict the loading on carbon exhausted at feed water concentrations, and thus the theoretical usage rate for activated carbon used in columns (or drums). However, as noted in 9.10.2.1, carbon in columns is not totally used, since the carbon must be changed out when the transition zone (not the exhausted zone) reaches the bottom of the carbon column. Depending on the relative depths of the carbon column and the transition zone, this can potentially reduce the effective capacity of carbon significantly.

Appendix B summarizes the results from full-scale and pilot scale treatment of petroleum products terminals wastewaters by various means, including carbon column treatment of both untreated wastewater and various types of biologically treated wastewater. From the data in these studies, the total loading of COD and TOC on the carbon columns at exhaustion (breakthrough) was calculated and plotted against feed contaminant concentration in Figures 9-21 and 9-22. These graphs can be used as an initial guide for estimating carbon usage, with the usual caveat that different wastewaters have different adsorbabilities, and that efficiency of use is influenced by mode of use.

FIGURE 9-22

Granular Activated Carbon Column Capacity for TOC Based on Exhaustion of Full-Scale and Pilot Scale Activated Carbon Columns

The data and graph on this figure were obtained from actual usage rates for granular activated carbon in columns or drums as determined in full-scale usage or pilot tests on marketing terminal wastewaters in the studies described in Appendix B. "Usage rate" is defined as the amount of carbon used before breakthrough of contaminants required changeout of the carbon. The table at the bottom shows the percent of feed TOC in the effuent at the time of breakthrough. TOC loading was calculated based on the average amount of TOC removed from the feed water multiplied by the total volume of water passed through the carbon bed. Figure 9-21 shows similar data for COD loading. Although the data are based on actual experience, they should be used with caution, since different wastewaters have different adsorption characteristics, and different modes of carbon usage can influence usage efficiency.



Linear regression equation for best-fit line shown is LW = 3.6238xLC + 8.5479, where LW is log10 of TOC concentration in water (mg/L) and LC is log10 of TOC loading on exhausted carbon (lb TOC/lb carbon).

Water Being Treated	TOC		% Effluent TOC/Feed TOC	
	Conc. in Water	Loading on Carbon, g/g	Initial	At Breakthrough
Trickling Filter / Activated Sludge Effluent	1087	0.0252	22	57
RBC Effluent	163	0.02197	9	75
Untreated Wastewater	484	0.0246	24	59
RBC & SBR Effluents	80.8	0.0140	15	14

9.10.3.1 Carbon Column Usage Technique and Efficiency

The two main usage technique factors which affect carbon efficiency are column length and uniformity of flow distribution.

As described above, a carbon column is effectively exhausted when excessive levels of contaminants break through the bottom of the column as the transition zone reaches this point. For this reason, longer carbon columns (or more carbon drums in series) will generally lead to more efficient carbon usage, since a greater fraction of the carbon column is totally exhausted when the carbon must be changed. In the worst extreme, when the column depth is less than the depth of the transition zone, breakthrough will be immediate, and the effective capacity of the carbon column will be zero.

Theoretical analyses of carbon column performance assume that the carbon is uniformly loaded, i.e., that at any elevation in the carbon column, the carbon granules across the bed will have the same degree of exhaustion, and the water in the bed will be at the same contaminant concentration. This assumption is the best case for carbon use efficiency, since it implies that none of the carbon is being "bypassed" by the adsorption. In actual operations, however, this theoretical efficiency may not be obtained, since parts of the carbon bed may be blinded, and some of the water may *channel*, and reach the bottom of the column without having been exposed to the full quantity of carbon. This behavior leads to broadening of the transition zone, and thus to early breakthrough (as a worst-case example, water may pass through an open channel in the carbon directly to the bottom of the bed, and break through immediately). Some of the steps to minimize channeling are as follows:

- Particularly in wide carbon columns, provide good flow distribution of the feed water across the cross-section of the bed.
- Rigorously exclude suspended solids from the carbon column feed water (this water should always be filtered). Since a carbon bed is an effective filter, solids will accumulate in the bed, and cause the water to bypass the sections thus blinded.
- If the column is packed by the user, care should be taken to ensure uniform bed packing. This is commonly done by backwashing and gently fluidizing the fresh carbon bed, and allowing it to settle into a compact, uniform, bed.

9.10.3.2 Effectiveness of Carbon Treatment

As noted in section 4.11, petroleum products wastewater contains a wide variety of organic contaminants, most of which have not been identified or characterized. Applying treatment to the water can make the mixture even more complex as some compounds are converted to new compounds by biological treatment or oxidation. This complexity means that general wastewater parameters such as COD and TOC are in fact very diverse, and that the carbon absorbability of components of COD and TOC can be expected to vary widely, with some components being hardly adsorbed at all. Some indication of this can be seen in the tables at the bottom of Figures 9-21 and 9-22, in which the initial (fresh carbon) concentrations of COD and TOC in the carbon column effluents is shown as a percentage of the feed concentration. For example, the table shows that when treating untreated terminal wastewater, the initial carbon effluent COD level was 21 percent of the feed level; for a typical terminal with 4000 mg/L COD, the best effluent which could be obtained with carbon (in this case) would be 840 mg/L COD. This factor must be taken into account when considering the use of carbon for treatment, and re-emphasizes the desirability of performing field tests before adopting this type (or any other type) of treatment.

9.10.3.3 Example of Carbon Usage Calculation

The following example is provided for purposes of estimating the success and cost of using carbon columns or drums for a given application. Before installing permanent equipment, it is strongly recommended to conduct field tests to confirm such estimations (one advantage of carbon drums is that they can be tried in the field without significant capital investment).

In the first example, it is assumed that a typical marketing terminal with 1000 gallons per week of wastewater with 4000 mg/L COD wishes to treat this water directly with granular activated carbon. The weekly quantity of COD is

$$1000 \text{ gal/week} \times 8.34 \text{ lb/gal} \times (4000 - 840) \times 10^{-6} = 26.35 \text{ lb COD/week}$$

From Figure 9-21, the effective capacity of carbon at a feed concentration of 4000 mg/L is

$$\log10(\text{capacity}) = (\log10(4000) - 5.1353)/2.0060 = -0.7643$$

$$\text{capacity} = 10^{x} = 0.1721 \text{ lb COD/lb carbon}$$

The weekly carbon usage will thus be

$$26.35 \text{ lb COD/week} / 0.1721 \text{ lb COD/lb carbon} = 153 \text{ lb carbon/week.}$$

At an assumed cost of $1/lb for carbon, the annual carbon cost would be $7956.

In the next example, it is assumed that the terminal wishes to produce an effluent with no more than 200 mg/L COD, and that activated carbon alone can only achieve a COD level of 840 mg/L (see above). It is also assumed that biological treatment will achieve 80 percent COD removal, to produce a bioeffluent with 800 mg/L COD, and that carbon treatment of the bioeffluent can reduce this to 21 percent of the feed value (breakthrough value at the bottom of the table on Figure 9-21), for an effluent with 176 mg/L COD. The weekly quantity of COD in the carbon column feed water is

$$1000 \text{ gal/week} \times 8.34 \text{ lb/gal} \times (800 - 176) \times 10^{-6} = 5.204 \text{ lb COD/week}$$

From Figure 9-21, the effective capacity of carbon at a feed concentration of 800 mg/L is

$$\log10(\text{capacity}) = (\log10(800) - 5.1353/2.006 = -1.1128$$

$$\text{capacity} = 10^{x} = 0.07713 \text{ lb COD/lb carbon}$$

The weekly carbon usage will thus be

$$5.204 \text{ lb COD/week} / 0.07713 \text{ lb COD/lb carbon} = 67.5 \text{ lb carbon/week.}$$

At an assumed cost of $1/lb for carbon, the annual carbon cost would be $3510. Note that carbon usage for treating the bioeffluent is not much less than the cost of treating the raw wastewater. This is a consequence of the fact that carbon has lower capacity when exposed to lower contaminant concentrations (also, bioeffluent COD may be less adsorbable, e.g., more polar, than raw wastewater COD). The main reason for using biotreatment in this case is that effluent concentration will be reduced from 840 mg/L to 176 mg/L. Of course, this may be a very good reason in some cases.

9.11 pH Control

pH control will normally not be needed for terminal wastewater, since the water is normally in the range suitable for treatment or discharge. If pH adjustment is needed, possibly because of spills of acidic or caustic material into the wastewater system, or because contaminated water has been received with product, then the optimum method for adjustment will be to add acid or caustic (or lime) to the water in a batch system (see 9.4.3). On-line, continuous pH adjustment, particularly in a system which is not monitored at all times, is quite risky, because various parts of the pH control system can fail, and cause excessive amounts of acid or caustic to be placed in the discharged water, causing downstream havoc by corrosive destruction of equipment, killing of biotreatment systems, and destruction of aquatic life in the receiving water.

9.12 Oxidation

Organic materials, the main contaminants in petroleum products terminal wastewater, are removable by chemical as well as biochemical oxidation, with the final product potentially being harmless carbon dioxide. The optimum oxidants are those which themselves do not produce a byproduct stream, namely hydrogen peroxide and ozone.

9.12.1 COMPARISON OF CHEMICAL OXIDATION WITH BIOTREATMENT

Since both biotreatment and oxidation are used for oxidative removal of organic matter, a comparison between these is of interest. As noted in 9.4.7, before *any* treatment is chosen, laboratory or pilot testing should be done to demonstrate its capability at removing the contaminants of concern, and to establish the degree of treatment (equipment size and dosages) required. This is particularly true of chemical oxidation treatment, for which few performance data are available.

9.12.1.1 Advantages of Biotreatment Over Chemical Oxidation

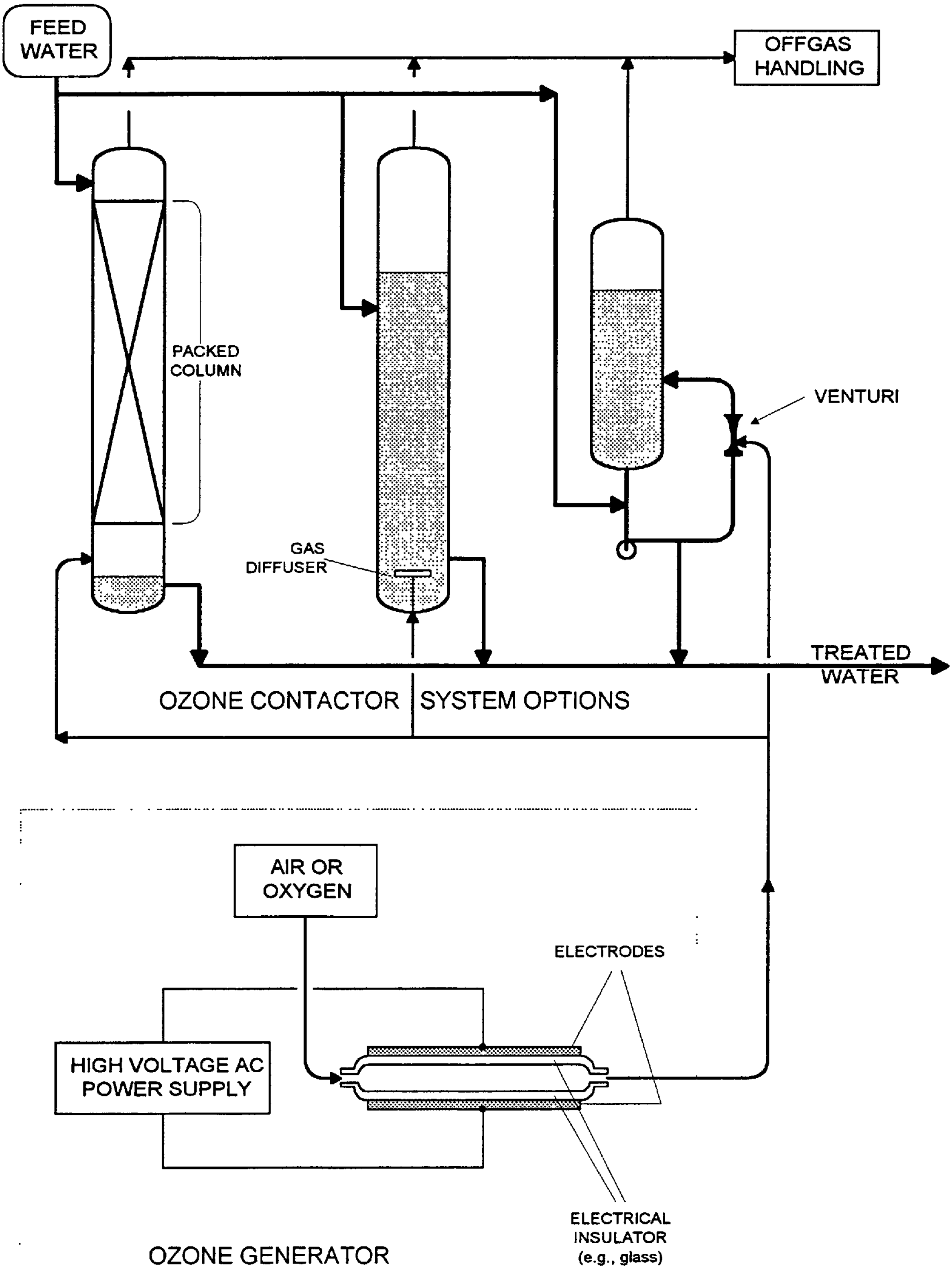
- Biotreatment has demonstrated its capability for removal of a wide array of contaminants much more thoroughly than have chemical oxidative treatments.
- Biotreatment generally has lower operating cost, particularly for chemicals.
- Biotreatment will usually have lower investment costs.
- Biotreatment does not leave any excess reagents in its effluent, unlike some oxidative treatments.
- Biotreatment does not involve the use of dangerous oxidizing chemicals.

9.12.1.2 Advantages of Chemical Oxidation Over Biotreatment

- Unlike biotreatment, the intensity of chemical oxidation can quickly be adjusted for different strengths of wastewater by changing the oxidant dosage.

FIGURE 9-23

OZONE GENERATION AND USE



- Chemical oxidation can be turned on and off, unlike biotreatment.
- Chemical oxidation does not make a byproduct sludge to be disposed of.

9.12.2 HYDROGEN PEROXIDE TREATMENT

Hydrogen peroxide, H_2O_2, is a mild oxidizing agent which can be thought of as oxygen-enriched water, which is the normal byproduct of its use: $H_2O_2 \rightarrow H_2O + (O)$. Hydrogen peroxide is completely soluble in water, which facilitates its use, and it is easily pumped at controlled dosage and mixed into a wastewater stream. By itself, hydrogen peroxide is almost inactive, and so requires a catalyst, generally iron, to enable it to become active. Since most iron compounds are insoluble in water at normal pH levels, it is common to use chelated iron as a catalyst.

Even catalyzed hydrogen peroxide is not a strong oxidizing agent, and so will not usually be capable of removing most of the organic matter from petroleum products terminal wastewater. However, it can remove some specific contaminants such as phenols, and so may be of use when only those contaminants need to be removed. Also, as described below, it becomes a much stronger and more effective oxidant when used with ultraviolet light.

Since iron catalyzes the decomposition of hydrogen peroxide to make water and oxygen, the concentrated reagent (normally a 30% solution in water) must not be stored in steel vessels, or handled in steel equipment. Hydrogen peroxide vendors must be consulted to determine proper methods for storing and delivering the reagent.

9.12.3 OZONE TREATMENT

Ozone, O_3, is a very strong oxidizing agent, and can be thought of as super-oxygen, as shown by its reactions: $O_3 \rightarrow O_2 + (O)$. Ozone is too unstable, and too dangerous, to manufacture and transport as a pure material, and so is always made at the point of use from pure oxygen or oxygen in air by an *ozone generator* or *ozonator*. An ozone generator, as shown on Figure 9-23, uses two electrodes connected to a high-voltage AC source, with each electrode separated from the air or oxygen stream by an insulator, usually glass. The high voltage electrical discharge converts the oxygen partially to ozone: $3O_2 \rightarrow 2O_3$. Once made, the ozone/air or ozone/oxygen stream must be dispersed in the wastewater being treated. Although ozone is somewhat more soluble in water than is oxygen, it is still not very soluble, which means that fine bubble dispersion must be used to get effective use of the expensive material. The concentration of ozone in air leaving an ozonator is 0.5-3%, while the concentration in an oxygen-fed system is 1-6%.

Although ozone is quite effective as an oxidizing agent, it is not much used for wastewater treatment because of its high cost. As a general rule, 10-12 kw-hr of electricity are needed to make a pound of ozone from air. This electric power consumption can be reduced by using oxygen instead of air, but then the cost of the oxygen must be added to the total cost (16-100 lbs of oxygen are needed to make a pound of ozone). Ozone generation not only has a high operating cost, but also a high capital cost, since ozone generators are expensive.

Ozone is hazardous to human health, as indicated by air pollution controls on materials which make ozone in the atmosphere. For this reason (as well as economic reasons), the ozone must be efficiently used so as not to vent it. Vents from an ozonation system should be routed to an ozone destruction device, generally an activated carbon canister.

9.12.4 UV OXIDATION

Ultraviolet (UV) light assists hydrogen peroxide or ozone at oxidizing organic materials by activating the oxidant and/or the organic material. Ultraviolet light is generally made with special lamps, and shone into the wastewater through tubes or windows. Since UV light is absorbed by glass, the tubes or windows must be made of quartz.

UV oxidation treatment is very expensive, since the reagents (hydrogen peroxide or ozone, and the UV light itself) are expensive, and the equipment is also quite expensive. However, UV oxidation may be the only means for removing trace levels of resistant organic materials, and so may be justified in some situations.

One of the chief operating problems with using UV oxidation for wastewater treatment is fouling of the quartz windows by materials such as oil, iron, or biological solids in the wastewater. Since the fouling blocks transmission of the light, it is very important to control it, and some commercial systems employ proprietary means for automatically wiping the windows periodically.

As noted in 9.4.2, there may be significant explosion hazard in using a system like this with hot high voltage lamps separated from potentially gasoline-containing wastewater by a breakable quartz window.

9.13 Ammonia Removal Techniques

Ammonia is a common toxic contaminant in petroleum products tank bottoms water, and cannot reliably be completely removed by biological treatment. Some of the special techniques for removing ammonia are as follows:

9.13.1 BREAKPOINT CHLORINATION

Breakpoint chlorination is the reaction of chlorine with ammonia until all of the ammonia is converted to nitrogen gas: $2NH_3 + 3Cl_2 \rightarrow 6HCl + N_2$. Although effective, and relatively simple to operate, it has the significant disadvantage of making chlorinated organic compounds, which are often regulated. Specifically, chlorination converts phenols (normally found in tank bottoms water) to chlorophenols, which are very odorous and foul tasting at low concentrations. The best reagent for chlorination is not chlorine itself, which as a highly toxic gas is very hazardous to use, particularly in populated areas, but sodium or calcium hypochlorite, which are commonly used for swimming pool chlorination.

9.13.2 ALKALINE AIR STRIPPING

Ammonia is very soluble in water, and so is hard to remove by air stripping. The removal can be enhanced by raising the pH of the wastewater to about 10-11 with caustic or lime. Even under these conditions, about 200 cubic feet of stripping air per gallon of water are needed to remove ammonia from water (by contrast, benzene stripping can be done with about 3 cubic feet of air per gallon of water).

9.14 Advanced Metals Removal Techniques

As noted in 4.11.3.17, metals levels in petroleum products terminal wastewaters are usually low, and metals are somewhat removed by treatments intended for removing other contaminants, for example, by biological treatment, activated carbon treatment, or by pH elevation done for other treatments (e.g., alkaline air stripping of ammonia). For those cases where a terminal has very strict discharge limits for metals and its effluent is not brought into compliance by the above means, there are special techniques available, although these have not been much tested on terminal wastewater.

By their nature, metals cannot be destroyed by treatment, but only removed from the water as a solid waste of some type. This solid waste must be disposed of, although not necessarily as a hazardous waste, since the metals may not be leachable under hazardous waste testing conditions.

9.14.1 ALKALINE PRECIPITATION

Most heavy metals are less soluble at higher pH than at lower pH; e.g., the hydroxides or oxides are less soluble than the other metal salts such as chlorides. For this reason, pH elevation is a common technique in some industries for removing wastewater metals. Lime is the usual reagent used for this purpose, although other alkalis can also be used. The usual equipment arrangement is a mix tank for alkali addition, followed by a clarifier for removing the metal-bearing sludge, and finally by a filter for removing the final traces of precipitated metals.

9.14.2 SULFIDE PRECIPITATION

As a rule, heavy toxic metals have very insoluble sulfides; copper sulfide, for example, is not soluble even in strong mineral acid. Sulfide precipitation has been found effective in laboratory testing for removing two common metals, zinc and copper, from terminal bioeffluent water (Hall, 1994), but no commercial process for doing this has been tested. There are two significant disadvantages to using sulfide precipitation despite its effectiveness: the sulfide reagent (e.g., sodium sulfide) can release highly toxic hydrogen sulfide gas if it is accidentally acidified, and aqueous sulfide is very toxic to fish, and so any excess reagent must be removed from a metals precipitation effluent prior to discharge.

9.14.3 COPRECIPITATION

Coprecipitation means the removal of a material as a byproduct of precipitation of another material, and is thought to work by chemical inclusion of the coprecipitated material in the matrix of the main precipitate. Coprecipitation is very useful for removing (and may be the *only* means for removing) metals which are present in wastewater as their oxyanions (as contrasted with the usual cationic form for heavy metals). Metals in this category include the toxic metals arsenic and selenium found in some crude oils, and in tank bottoms water from refined products of those crude oils. Iron salts have been found to be effective (Hall, 1994) coprecipitating agents for arsenic (the main precipitate is iron oxide), and manganese salts to be effective for removing selenium. Commercial processes are available for iron coprecipitation.

9.15 Biological Effluent Polishing

Biological polishing is distinguished from biological treatment mostly by the time scale involved, and by the nature of the treatment system. Biotreatment has a retention time typically of several hours, and is conducted in systems with high population of bacteria. Effluent polishing retention time, on the other hand, can be days or weeks (months, in extreme cases), and usually does not involve densely populated systems. Overall, effluent polishing closely resembles natural mechanisms for removing contaminants from water. It is particularly suited for removing trace quantities of materials which were not removed in upstream treatment (hence the term, polishing).

Because of the long retention time required for effluent polishing systems, they typically require large amounts of land area, which would be a significant disadvantage for many terminals. Also, effluent polishing systems are not particularly suited for cold weather operation. In winter, in northern climates, the systems described below will ice over (or completely freeze) and any exposed plants will be killed by frost.

9.15.1 POLISHING PONDS

A polishing pond is simply a pond through which treated effluent flows on its way to discharge. Since the feed water does not contain much BOD, mechanical aeration is not needed to supplement natural aeration. Because of their long retention time, polishing ponds can sustain bacteria which require long sludge age to grow, which may enable removing materials not removed in upstream treatment. A common problem with polishing ponds is algae growth, particularly in warm weather, which can lead to generation of substantial amounts of algal BOD and to high pH levels (algae consume acidic carbon dioxide).

9.15.2 WETLANDS TREATMENT

Treatment in constructed wetlands of various types has been found to improve effluent quality in several large-scale tests. Wetlands are plant communities which grow in water, either as ponded water (as in a swamp), or as subsurface water in a very porous medium such as a gravel bed. Wetland treatments are thought to achieve their benefits by a combination of plant uptake of contaminants and by bacterial colonies on plant roots and stems.

9.15.3 WATER HYACINTHS

Water hyacinths are nuisance plants in southern waterways and lakes, which float on, and rapidly cover (unless controlled), a water surface. In tests, they have been found to remove organic contaminants and heavy metals in the water which flows under them. They are subject to winter kill, even in southern climates, and must be routinely harvested (disposal of the harvested plants may be a problem) if used to remove significant quantities of metals.

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APPENDIX A

PETROLEUM PRODUCTS TERMINAL WASTEWATER FACT SHEET FORMS

I. GENERAL INFORMATION

1. Terminal Identification

Terminal Name: ______________________________

Location Code: ______________________________

Mailing Address: ______________________________

____

____

2. Persons completing this survey:

Name	Position	Location	Phone	Fax

3. Date survey completed: ______________________________

4. Number of full-time personnel (excluding drivers): ____________

5. Operation time: ____________ hr/day, ____________days/week

6. Please attach a copy of the most recently updated General Arrangement Plan of this terminal, showing locations of buildings, structures, tanks, and other major equipment.

7. Please attach a copy of a facility map showing routing of all water conveyances: intake water lines, underground sewers (show manholes), wastewater piping, wastewater ditches, steam lines, steam condensate lines, and intake water or wastewater ponds.

8. Please attach a copy of the facility wastewater discharge permit or other document specifying the quality, quantity, and charges for the wastewater discharge.

9. Please attach a facility map with stormwater drainage areas marked, along with approximate size (square feet or acres) of each area, and storm runoff destination for each area. The types of area include:
    - Tank basin area
    - Undeveloped land
    - Loading/unloading racks
    - Driveways and parking areas
    - Buildings
    - Other

   The types of storm runoff destination include:
    - Uncontrolled runoff to offsite
    - Spill collection system
    - Other
    - Collected runoff (ditch or sewer) to offsite directly
    - Collected runoff (ditch or sewer) to basin or tank
    - General wastewater collection system

II. COMPLEXITY OF OPERATIONS

1. Wastewater is generated by the following operations or facilities at this terminal (check all that are applicable):

- ☐ Gasoline storage
- ☐ Diesel fuel storage
- ☐ Fuel oil storage
- ☐ Other fuel storage
- ☐ Lube oil blending
- ☐ Lube oil packaging
- ☐ Additive storage
- ☐ Vapor control
- ☐ Warehousing
- ☐ Laboratory
- ☐ Receipt of ballast water
- ☐ Drum cleaning
- ☐ Boiler operation
- ☐ Receipt of offtest product
- ☐ Oxygenate storage
- ☐ Vehicle maintenance
- ☐ Exterior cleaning of
    - ☐ Tank trucks
    - ☐ Rail cars
    - ☐ Barges
    - ☐ Loading rack
    - ☐ Other (specify) ______________________________
- ☐ Interior cleaning of
    - ☐ Tank trucks
    - ☐ Rail cars
    - ☐ Bulk storage tanks
    - ☐ Other (specify) ______________________________
- ☐ Other (specify) ______________________________

____

____

____

____

2. Please provide information on all chemicals (not bulk products) purchased by the facility as shown on Table I (make as many copies as necessary).

TABLE I: PURCHASED CHEMICALS Sheet ______

Make as many copies of this sheet as needed. Do not include bulk products.

*		
1	Chemical Name	
2	Manufacturer	
3	Used For	
4	Annual Consumption	
5	Chemical Components	

1	Chemical Name	
2	Manufacturer	
3	Used For	
4	Annual Consumption	
5	Chemical Components	

1	Chemical Name	
2	Manufacturer	
3	Used For	
4	Annual Consumption	
5	Chemical Components	

1	Chemical Name	
2	Manufacturer	
3	Used For	
4	Annual Consumption	
5	Chemical Components	

*1) Chemical Name is brand name, code, etc., on container
2) Manufacturer is who chemical is made by or formulated by
3) Used For catagories include water treatment chemicals (coagulants, boiler treatment, cooling tower treatment, pH control, etc.), detergents and other cleaning products, pesticides and herbicides, chemicals listed on wastewater permit, and other water-soluble
4) Annual Consumption is amount (give units) purchased in a typical year
5) Chemical Components are ingredients, to be listed if known

III. STORAGE TANKS, TANK WATER BOTTOMS, AND TANK WATER BOTTOMS COLLECTION SYSTEMS

1. Please provide the information requested in Table IIA and IIB concerning bulk storage tank descriptions, product handling, and tank bottoms water handling (make copies of the forms as necessary to include all tanks and vessels). Note the explanation and codes at the bottom of the table.

2. Are tank bottoms water levels gauged routinely, and records kept of the water gauging? _____

3. If tank water bottoms are gauged, what method is used:

   ☐ Gauge stick with water-indicating paste
   ☐ Sample trycocks near tank bottom
   ☐ Sight gauge near tank bottom
   ☐ Other (specify) ______________________________

4. What method is used for draining tank bottoms:

   ☐ Draw tank bottoms until pure product is seen
   ☐ Draw tank bottoms until "cuff" (water/product mixture) layer is seen
   ☐ Draw off a certain volume or height based on water gauge
   ☐ Use an automatic product-detecting shutoff valve

   What type? ______________________________

   ☐ Other (specify) ______________________________

5. During tank water bottoms draining:

   ☐ Operator watches tank draw full-time
   ☐ Operator makes periodic visits to inspect draw

   For the above, drawn water is inspected by:

   ☐ direct inspection (liquid free falls from drain nozzle)
   ☐ liquid goes through sight glass
   ☐ liquid is sampled from side tap on draw line

   ☐ Automatic system makes observation unnecessary
   ☐ Other (specify) ____________________

TABLE II-A: STORAGE TANK INFORMATION, PART A

Sheet ____

Make as many copies of this sheet as needed to include all tanks and vessels. Label each copy in the upper right corner (Sheet ____) as A, B, C. etc.

	Reference: A	B	C	D	E	F
		Tank/Vessel Size				
#	Tank ID Number or Name	Diameter	Height or Length	Product	How Received	Annual Volume Throughput, bbl
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
15						
16						
17						
18						
19						
20						

References:

A) Tank ID: Use standard reference number or name

B) Tank/Vessel Size Diameter: Give units

C) Tank/Vessel Size: Height for vertical tank; Tangent/tangent for horizontal tank; show units

D) Product: Show product name and grade (e.g., super unleaded gasoline, unleaded gasoline, etc.)

E) How Received: Use all codes that apply: PL=pipeline, TT = tank truck, BG = barge, TS = tanker ship, RC = railcar, OT = other (specify)

F) Annual Volume Throughput is last 12-month quantity of product passing through the tank

TABLE II-B: STORAGE TANK INFORMATION, PART B

Sheet _____

Make as many copies of this sheet as needed to include all tanks and vessels. Label each copy in the upper right corner (Sheet ____) as A, B, C. etc.

	Reference: A	G	H	I	J	K
				Tank Bottoms Water		
#	Tank ID Number or Name	Roof Type	Roof Drained To	Water Drained To	Water Volume	Frequency, Weeks
1						
2						
3						
4						
5						
6						
7						
8						
9						
10						
11						
12						
13						
15						
16						
17						
18						
19						
20						

References:

A) Tank ID: Use standard reference number or name (See Table I A)
G) Roof Type: Use all codes which apply: C= fixed cone roof, F = floating roof, D = geodesic dome, N = no roof
H) Roof Drained To: Inside or Outside of tank
I) Tank Bottoms Water Drained To: Tank bottoms water drained to (Codes: TB = tank basin, PC = piped collection, SC = sewer collection, VT = vacuum truck, ND = not drained, OT = other (specify)
J) Tank Bottoms Water Annual Volume (show units)
K) Tank Bottoms Water Drainage Frequency (Typical number of weeks between water draws)

6. Tank bottoms water is drained to:

   - ☐ Ground
   - ☐ Tank bottoms water collection system
   - ☐ Other (specify) ____________________

7. If a tank bottoms water collection system is used, it is:

   - ☐ Hard piped to collection tank

     Lines made of:

     - ☐ Plastic pipe
     - ☐ Steel pipe
     - ☐ Other (specify) ____________________
     - ☐ Concrete sewer pipe
     - ☐ Rubber hose

     Lines are located:

     - ☐ Underground
     - ☐ Above ground

     Lines are drained:

     - ☐ Drained directly to collection tank
     - ☐ Drained to sump, and pumped to tank

     Connections to tanks are:

     - ☐ Permanent
     - ☐ Made when tank is drained

   - ☐ Vacuum truck transport
     - ☐ From sump near tank
     - ☐ From direct connection to tank

   - ☐ Surface ditches
     - ☐ Earthen
     - ☐ Other (specify) ____________________
     - ☐ Concrete lined

8. Tank bottoms water is thought to come mostly from (check all that apply):
    - ☐ Rainwater penetration around floating roof seals
    - ☐ Delivery with product
    - ☐ Tank breathing and condensation in fixed-roof tank
    - ☐ Draining from roof drain into tank
    - ☐ Placement into tank from
        - ☐ Cryogenic vapor recovery system
        - ☐ Haulback of off-spec product from customers
        - ☐ Spill recovery system
        - ☐ Other (specify) ______________________________

          ____

          ____

9. Does tank bottoms water freeze in winter? _____

IV. Loading/Unloading Racks and Spill Prevention Control Tanks

1. Please provide information on the facility spill prevention control tanks (spill collection tanks above and below ground) on Table III.

2. For each loading/unloading rack at the facility, please provide information on copies of Tables IV-A and IV-B.

TABLE III: SPILL COLLECTION TANK INFORMATION

Reference: A	B	C	D	E	F	G
Tank Collects Spills and Water From	Tank Volume	Above or Below Ground?	Tank Water Discharges To	Annual Volume		Product Separated In
				Water	Product	

A) Terminal operation (e.g., truck loading rack) which drains to spill collection tank
B) Effective tank liquid volume (show volume units)
C) If above ground, liquid pumped to tank; if below ground, liquid pumped from tank
D) Receiving point for tank water (e.g., product tank, oil/water separator, sewer)
E) Typical water volume (show if measured or estimated; show volume units)
F) Typical product volume (show if measured or estimated; show volume units)
G) Equipment used to separate water from floating product. Use codes: ST = separated in spill tank itself,
WT = separated in other water tank, PT = separated in product tank,
OW = separated in oil/water separator, NS = not separated, OT = other (specify)

TABLE IV-A
LOADING/UNLOADING RACK

(Please make a copy of this page for each loading/unloading rack at the facility.)

1. This rack is called: ____________________
2. The rack loads/unloads from:
   ☐ Tank trucks ☐ Barges
   ☐ Rail cars ☐ Tanker ships
   ☐ Other (specify) ____________________
3. The rack is used for:
   ☐ Loading ☐ Unloading ☐ Both loading and unloading
4. Method of attaching to transport vessel is:
   ☐ Bottom loading ☐ Top Loading
5. Connection is made with:
   ☐ Hoses ☐ Pipes with swivel joints
   ☐ Other (specify) ____
6. Products handled at this rack include:
   ☐ Gasoline ☐ Diesel ☐ Fuel Oil
   ☐ Lube Oils ☐ Oxygenates ☐ Additives
   ☐ Other (specify) ____
   ____
7. Canopy (roof) over rack covers what percentage of slab area? _____%
8. Does rack have side walls to prevent rain blowing in? _____
9. If rack has a canopy, rainwater drains from canopy:
   ☐ Onto rack slab directly
   ☐ Through downspout onto slab
   ☐ Through downspout off of slab
   ☐ Other (specify) ____

TABLE IV-B

LOADING/UNLOADING RACK

(Please make a copy of this page for each loading/unloading rack at the facility.)

10. Runoff rainwater is prevented from running onto slab by:

☐ Not prevented ☐ Walls ☐ Curbs
☐ Diversion trenches
☐ Other (specify) ______________________________

11. Rack slab is washed:

☐ When needed ☐ After each loading/unloading ☐ Daily
☐ Weekly ☐ Monthly ☐ Never

12. Rack slab is washed with:

☐ Water only ☐ Spill absorbent ☐ Water and detergent
☐ Solvent ☐ Other (specify) ____________________11.

13. Liquid (runoff and spilled product) from slab is sent:

☐ To adjacent ground area
☐ To sewer
☐ To sump with pump
☐ To spill tank (which tank on Table III: ____________________)

☐ Other (specify) ______________________________

14. Is this rack in use during "off-hours" (e.g., is operation automated to allow transport workers to enter and load/offload product in the absence of terminal personnel)? _____

V. WASTEWATER HANDLING

1. Storm water which falls in tank basins is handled as follows:

   - ☐ No tank basins
   - ☐ Soil is porous enough to allow all storm water to percolate
   - ☐ Basin dikes or walls have drains which are kept open to allow storm water to drain from the basin
   - ☐ Basin dikes or walls have drains which are normally kept closed in case of a product spill. After inspecting collected water for spilled product, the drain line valve is opened:
     - ☐ Immediately after storm
     - ☐ Whenever personnel access to basin is needed
     - ☐ When downstream water treatment can accept water
     - ☐ Other (specify) ____________________

2. Storm water which falls outside of tank basins or spill containment areas is handled as follows (following each category, show which plant area is so handled):

   - ☐ Allowed to run offsite without inspection or treatment

     Area: ____________________
   - ☐ Collected and sent offsite

     Area: ____________________
   - ☐ Collected and sent to an oil/water separator

     Area: ____________________
   - ☐ Other (specify) ____________________

     Area: ____________________

3. Provide a diagram showing how the wastewaters listed on page 3 are routed. Show individual wastewater sources, their connection to pipes, ditches, and sewers, and the network of the pipes, ditches, and sewers down to the point of wastewater accumulation, treatment, or disposal.

VI. OIL/WATER SEPARATION

(Please make copies of these 2 pages for each oil/water separator device at the facility)

1. The oil/water separator device is

☐ A standard in-ground site-constructed API design rectangular basin

☐ Covered ☐ Uncovered

☐ With forebay ☐ With inlet water distribution system

☐ With motorized flight scrapers

Skimming is done by

☐ Slotted pipe skimmer
☐ Belt skimmer
☐ Other (specify) ______________________________
☐ Floating skimmer
☐ Adjustable tray skimmer

☐ Holding tank

Product separation is done by

☐ Drawing water from bottom until reaching product, then drawing product
☐ Drawing water and product from nozzles at different elevations
☐ Using an internal swingline to draw liquid from any elevation
☐ An internal skimming device: type ________________
☐ Other (describe) ______________________________

☐ Package separator

Type:
☐ Simple separation chamber type
☐ Parallel plate type
☐ Vertical coalescer
☐ Other (describe) ______________________________

Placement:
☐ Above ground
☐ Below ground (buried)
☐ Other (specify) ______________________________

Skimming done by
  - ☐ Automatic collection of product in a chamber
  - ☐ Other (describe) ____________________________

- ☐ Air flotation unit
  - ☐ Dispersed or induced (mechanical dispersion of air bubbles)
  - ☐ Dissolved (high pressure saturation of air in water)

- ☐ Other (describe) ____________________________

____

____

2. Approximate water volume (give units) ____________________

3. Approximate age, years _______

4. Routine inspections of separator operation are made how often?

   ____

5. The separator is cleaned of settled sludge how often?

   ____

6. Please attach a diagram (particularly a cross-section view) of the oil/water separation equipment

7. Please attach any records for the past year on oil content of separator effluent

8. What are the good features and the problems with this separation equipment?

VII. WASTEWATER TREATMENT

1. Beyond oil/water separation, what type of wastewater treatment is done at this facility?

- ☐ No treatment
- ☐ Contracted mobile unit treatment (brought on-site periodically)
- ☐ Biological treatment
    - ☐ Activated sludge
    - ☐ Rotating biological contactor
    - ☐ Sequencing batch reactor
    - ☐ Aerated lagoon or pond
    - ☐ Trickling filter
    - ☐ Fluidized bed
    - ☐ Other (specify) ____________________
- ☐ Stripping
    - ☐ Air stripping
    - ☐ Sparger stripping
    - ☐ Other gas stripping
    - ☐ Steam stripping
- ☐ Activated carbon treatment
    - ☐ Granular carbon
        - ☐ In replaceable drums or vessels
        - ☐ In columns (loose carbon)
    - ☐ Powdered carbon (mixed with wastewater)
- ☐ Settling or clarification

    Done in a

    - ☐ Tank
    - ☐ Settler
    - ☐ Pond or basin

    Done with

    - ☐ Coagulant chemicals
    - ☐ No chemicals
- ☐ Final polishing treatment
    - ☐ Stabilization pond
    - ☐ Wetlands treatment
- ☐ Other (specify) ____________________

VIII. WASTEWATER DISPOSAL

1. Wastewater other than stormwater is disposed of (final destination) as follows (check all that apply):

- ☐ Sent to adjacent body of water
  - ☐ Ditch ☐ Stream ☐ River ☐ Lake
  - ☐ Estuary ☐ Bay ☐ Ocean
- ☐ Sent to municipal wastewater system (municipal sewer)
- ☐ Sent to offsite treatment system
  - ☐ In pipes or sewers ☐ Hauled in trucks
- ☐ Sent to a waste disposal company
  - ☐ As non-hazardous waste ☐ As hazardous waste
- ☐ Sent to a refinery
  - ☐ As part of off-spec product ☐ As non-hazardous waste
  - ☐ As hazardous waste
- ☐ Placed in an evaporation pond
  - ☐ Lined ☐ Unlined
- ☐ Placed in a percolation pond
- ☐ Other (specify) ______________________________

____

APPENDIX B

SUMMARY OF TREATMENT RESULTS AT TERMINALS

B-1 Introduction

As noted in the introduction to Chapter 9, most of the standard treatment technologies (as well as the more advanced technologies) described in that chapter have not, at this time, been widely applied in petroleum products terminals. Probably for that reason, there is not much information available in the technical literature on the performance of wastewater treatment technologies on petroleum products tank bottoms water (the principal source of contaminants in a terminal). This Appendix summarizes those data which are available, which come from a mixture of long-term pilot unit testing and full-scale wastewater treatment. The pilot unit data were generated in two studies sponsored by the API Marketing Terminal Effluent Task Force. In the first of these studies, an array of treatments were tested in a screening study to determine the basic feasibility of the treatments. The second study was based on the most promising treatments investigated in the first study: RBC and SBR biological treatments, followed by activated carbon adsorption, and was designed to provide practical design and operating data as well as demonstrating treatment performance. Treatment data from full-scale operations were made available to API by two member companies and were based on actual installations at terminals. In the first of these, a combination of trickling filter - activated sludge - activated carbon treatments was used for treating a pipeline terminal wastewater. In the second full-scale Case, SBR treatment was used to treat a marketing terminal wastewater.

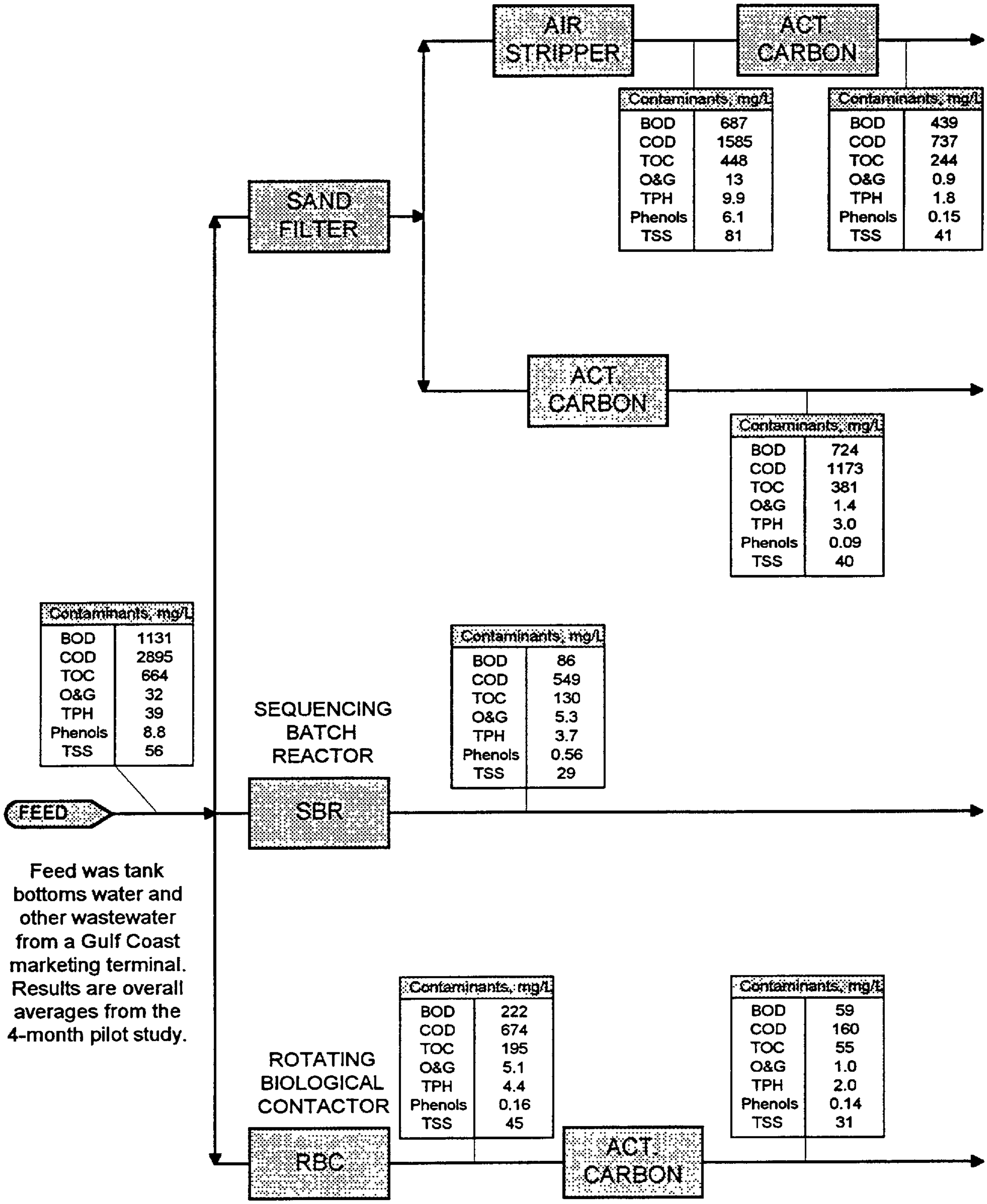
In this Appendix, the performance data for the four Cases are summarized, as well as relevant design and operating data. Although the results from the various treatments can be compared, it should be recognized that tank bottoms waters vary considerably (Hall, 1994) in their contaminants and response to treatment, and that the treatments described here were applied to different degrees (e.g., some of the treatment systems may have been over-designed, and some may have been under-designed). Because of these factors, the results described below should only be taken as an indication of treatment performance, and experimental testing should be done for any given terminal (see 9.4.7) to determine performance and design parameters for any candidate treatment technologies.

B-2 Overview of the Four Cases

In this section, the general nature of the Cases is described, along with some of the conclusions from each Case. In following sections (B-3 and B-4), the treatment results are discussed, and some of the design guidelines from the Cases.

FIGURE B-1

Case 1: Treatment Summary from API 4581, "Evaluation of Technologies for the Treatment of Petroleum Marketing Terminal Wastewater"



Contaminants, mg/L	
BOD	1131
COD	2895
TOC	664
O&G	32
TPH	39
Phenols	8.8
TSS	56

Contaminants, mg/L	
BOD	687
COD	1585
TOC	448
O&G	13
TPH	9.9
Phenols	6.1
TSS	81

Contaminants, mg/L	
BOD	439
COD	737
TOC	244
O&G	0.9
TPH	1.8
Phenols	0.15
TSS	41

Contaminants, mg/L	
BOD	724
COD	1173
TOC	381
O&G	1.4
TPH	3.0
Phenols	0.09
TSS	40

Contaminants, mg/L	
BOD	86
COD	549
TOC	130
O&G	5.3
TPH	3.7
Phenols	0.56
TSS	29

Contaminants, mg/L	
BOD	222
COD	674
TOC	195
O&G	5.1
TPH	4.4
Phenols	0.16
TSS	45

Contaminants, mg/L	
BOD	59
COD	160
TOC	55
O&G	1.0
TPH	2.0
Phenols	0.14
TSS	31

Feed was tank bottoms water and other wastewater from a Gulf Coast marketing terminal. Results are overall averages from the 4-month pilot study.

B-2.1 CASE 1: API 4581 PILOT STUDIES

In these studies (Borey, 1989), a multitude of treatment technologies were applied to the wastewater (mostly tank bottoms water) from a marketing terminal in a 16-week study. As shown on Figure B-1, pilot scale continuous treatments included air stripping followed by activated carbon treatment, activated carbon treatment alone, SBR treatment alone, and RBC treatment followed by activated carbon treatment. Some of the conclusions from this study were

- All of the pilot-scale treatment systems were found to be capable of utilization at most marketing terminals with reasonable levels of attention and manpower. Based on the results for the marketing terminal studied, the overall best treatment for removal of contaminants from wastewater is a biological treatment system with activated carbon polishing. The biological treatment systems regularly produced the effluent with among the lowest general parameters, priority pollutants, oxygenates, and toxicity.

- Air strippers are very effective at removing volatile organics from marketing terminal wastewaters, but biological growth is expected to occur on the stripper packing. Although this growth will remove a portion of the non-volatile fraction, properly designed biological treatment units are more effective for these components and the biological growth may produce blockages which will reduce the efficiency of the stripper.

- Pretreatment of marketing terminal wastewater will maximize treatment efficiency and prolong the life of activated carbon. Results from this study indicate that the best overall treatment with activated carbon was obtained with biological pretreatment.

- All pilot-scale treatments tested appear to be capable of reducing priority pollutants to low or non-detectable levels, but no treatment appears capable of consistently producing effluents with very low or non-detectable levels of all priority pollutants.

- Oxygenates in marketing terminal wastewaters are best treated with biological treatment systems. Activated carbon and chemical oxidation do not reliably treat oxygenates.

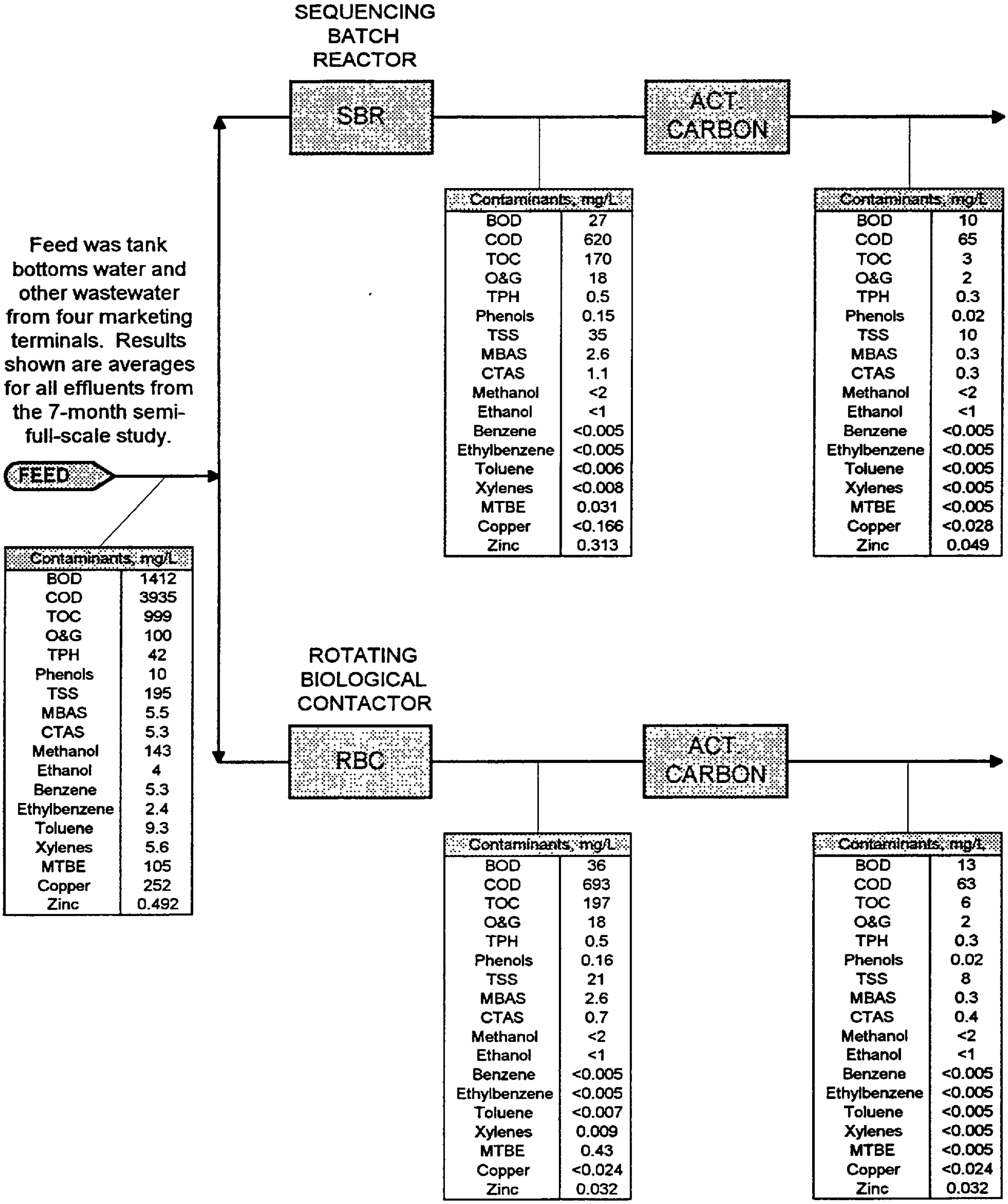
B-2.2 CASE 2: API 4582 PILOT STUDIES

In these studies (Vuong, 1993), two semi-full-scale pilot systems, one with RBC treatment followed by activated carbon drum treatment, and the other with SBR treatment followed by activated carbon drum treatment as shown on Figure B-2, were operated for 40 weeks and treated wastewaters (mostly tank bottoms water) from four marketing terminals. Some of the conclusions from this study were

- Both the SBR and RBC biological treatment processes are effective for removing organic contaminants from four petroleum product terminal wastewaters to make effluents with low acute toxicity.

- Activated carbon treatment at high dosages further removes organic contaminants from the biotreated effluent to minimum levels and enhances chronic toxicity reduction. However, arsenic may leach from the activated carbon into the treated effluent.

FIGURE B-2
Case 2: Treatment Summary from API 4582, "Comparative Evaluation of Biological Treatment of Petroleum Product Terminal Wastewater by the Sequencing Batch Reactor Process and the Rotating Biological Contactor Process"



Feed was tank bottoms water and other wastewater from four marketing terminals. Results shown are averages for all effluents from the 7-month semi-full-scale study.

FEED

Contaminants, mg/L	
BOD	1412
COD	3935
TOC	999
O&G	100
TPH	42
Phenols	10
TSS	195
MBAS	5.5
CTAS	5.3
Methanol	143
Ethanol	4
Benzene	5.3
Ethylbenzene	2.4
Toluene	9.3
Xylenes	5.6
MTBE	105
Copper	252
Zinc	0.492

SBR

Contaminants, mg/L	
BOD	27
COD	620
TOC	170
O&G	18
TPH	0.5
Phenols	0.15
TSS	35
MBAS	2.6
CTAS	1.1
Methanol	<2
Ethanol	<1
Benzene	<0.005
Ethylbenzene	<0.005
Toluene	<0.006
Xylenes	<0.008
MTBE	0.031
Copper	<0.166
Zinc	0.313

ACT. CARBON

Contaminants, mg/L	
BOD	10
COD	65
TOC	3
O&G	2
TPH	0.3
Phenols	0.02
TSS	10
MBAS	0.3
CTAS	0.3
Methanol	<2
Ethanol	<1
Benzene	<0.005
Ethylbenzene	<0.005
Toluene	<0.005
Xylenes	<0.005
MTBE	<0.005
Copper	<0.028
Zinc	0.049

RBC

Contaminants, mg/L	
BOD	36
COD	693
TOC	197
O&G	18
TPH	0.5
Phenols	0.16
TSS	21
MBAS	2.6
CTAS	0.7
Methanol	<2
Ethanol	<1
Benzene	<0.005
Ethylbenzene	<0.005
Toluene	<0.007
Xylenes	0.009
MTBE	0.43
Copper	<0.024
Zinc	0.032

ACT. CARBON

Contaminants, mg/L	
BOD	13
COD	63
TOC	6
O&G	2
TPH	0.3
Phenols	0.02
TSS	8
MBAS	0.3
CTAS	0.4
Methanol	<2
Ethanol	<1
Benzene	<0.005
Ethylbenzene	<0.005
Toluene	<0.005
Xylenes	<0.005
MTBE	<0.005
Copper	<0.024
Zinc	0.032

- The SBR process is slightly better than the RBC process in term of organics removal efficiency, sludge wastage, construction cost, and maintenance. However, the SBR process requires more operating manpower.

- Both the RBC and SBR biological treatment processes are easy to operate and require low manpower. Both are operable by terminal personnel with reasonable levels of attention.
- Overall average treatment data for the biological treatment processes applied to the four wastewaters are:

a. Average Removal (percent)

	SBR		RBC	
Parameter	Avg.	Range	Avg.	Range
BOD	98	95-100	98	92-100
COD	84	65-96	82	63-96
TOC	83	59-93	80	58-93
Oil & Grease	82	50-98	82	43-96
TPH	99	90-100	99	90-100
Phenols	99	74-100	99	63-100
Surfactants	66		70	
Alcohols	99		99	
BTEX	100		100	
MTBE	100		100	

b. Toxicity (percent of test stream concentration)

	SBR	RBC
48-Hour Acute Toxicity to D. Magna		
LC50	96	96
7-Day Chronic Survival to C. Dubia		
NOEC	38	58
LOEC	65	75
7-Day Chronic Reproduction to C. Dubia		
NOEC	21	15
LOEC	41	28

c. Removal Mechanisms (biodegradation and volatilization)

	SBR		RBC	
	Bio	Vol	Bio	Vol
Benzene	89	11	99	1
Toluene	86	14	99	1
Ethylbenzene	93	7	99	1
Xylene	83	17	98	2
MTBE	38	60	70	30

d. Loading: at least 10.8 lb BOD or 25 lb COD or 8.2 lb TOC per week (in 500 gallons per week) for a 500 gallon SBR or a 1500 ft2 RBC.

e. Maximum sludge production in the SBR is 0.25 lb/lb BOD, and maximum sludge wastage for the RBC is 0.18 lb/lb BOD.

f. A set of filter cartridges (one 25 micron and one 5 micron in series) will treat at least 4000 gallons of bioeffluent.

g. Three drums of activated carbon (165 lb of carbon each) can treat at least 4000 gallons of bioeffluent, at a loading of 0.005 lb TOC per lb carbon.

h. Total operator time to operate both treatment trains was about 8 hours per week.

B-2.3 CASE 3: FULL-SCALE TRICKLING FILTER - ACTIVATED SLUDGE - ACTIVATED CARBON TREATMENT

In this Case, a pipeline terminal installed a package trickling filter - activated sludge treatment unit for treating tank bottoms water, and also tested drum activated carbon treatment and UV-ozone treatment for bioeffluent polishing. As shown on Figure B-3, performance data were collected over a seven-month period. Some of the conclusions from a contractor review of the unit performance were

- Performance data show that the wastewater is biologically treatable.

- The existing wastewater treatment plant, without the activated carbon units, removes on average 96 percent of BOD, 59 percent of oil & grease, 74 percent of TOC, and 65 percent of COD. When in use, GAC [granular activated carbon] increased the amounts of TOC, COD, oil & grease, and TSS removed.

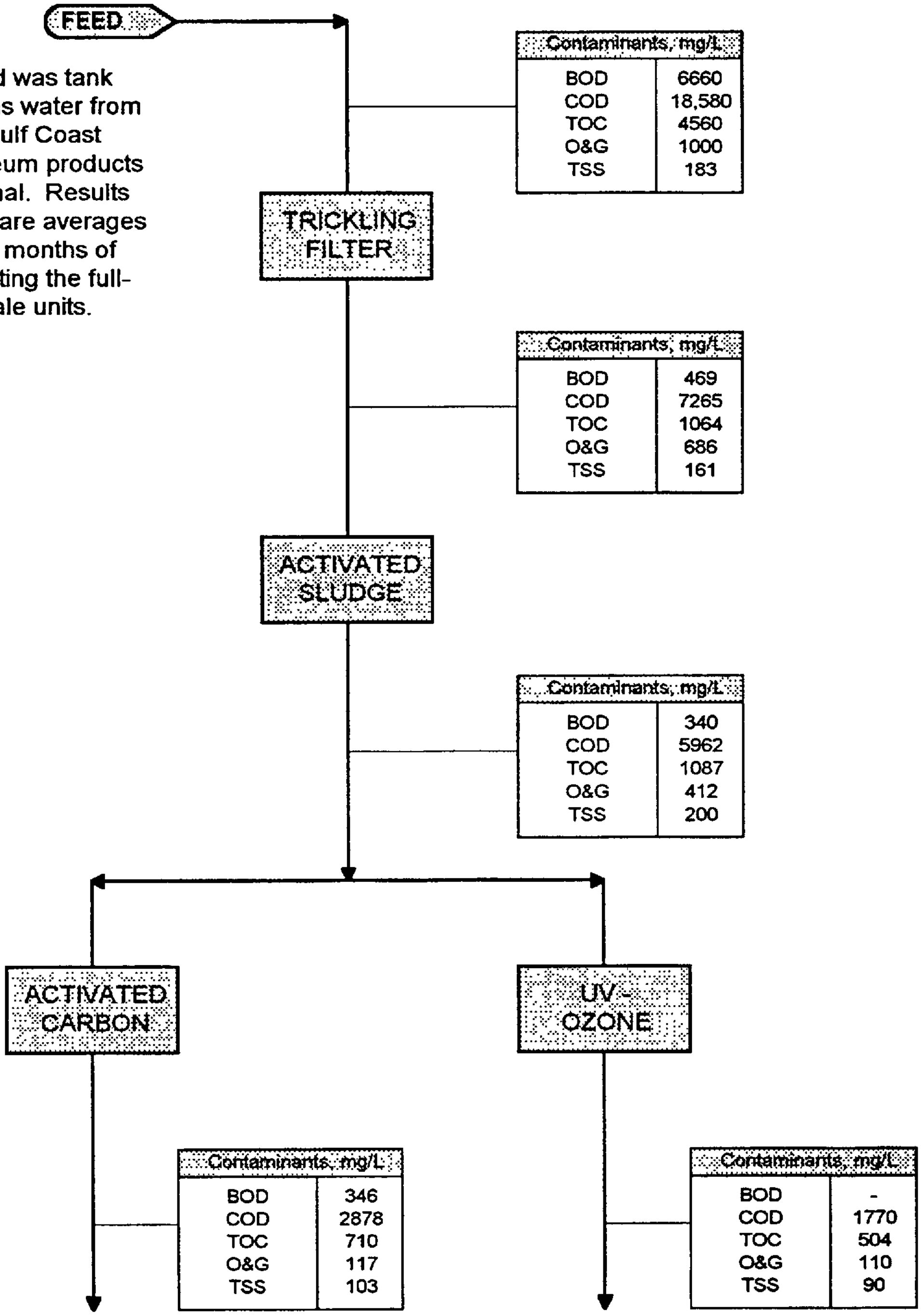
- The trickling filter unit performs quite well, removing about 70 percent of the influent COD and TOC.

B-2.4 CASE 4: FULL-SCALE SEQUENCING BATCH REACTOR TREATMENT

In this Case, a marketing terminal installed a package sequencing batch reactor (SBR) for treating mostly tank bottoms water. The aeration design was somewhat unusual, being a cycle of 30 minutes aeration - 15 minutes non-aeration over the 80-hour aeration period. Average performance data are shown on Figure B-4.

FIGURE B-3

Case 3: Treatment Summary from a Full-Scale Operation of a Trickling Filter - Activated Sludge - Activated Carbon - UV/Ozone Treatment of a Petroleum Products Terminal Tank Bottoms Wastewater



Feed was tank bottoms water from a Gulf Coast petroleum products terminal. Results shown are averages for 7 months of operating the full-scale units.

Contaminants, mg/L	
BOD	6660
COD	18,580
TOC	4560
O&G	1000
TSS	183

Contaminants, mg/L	
BOD	469
COD	7265
TOC	1064
O&G	686
TSS	161

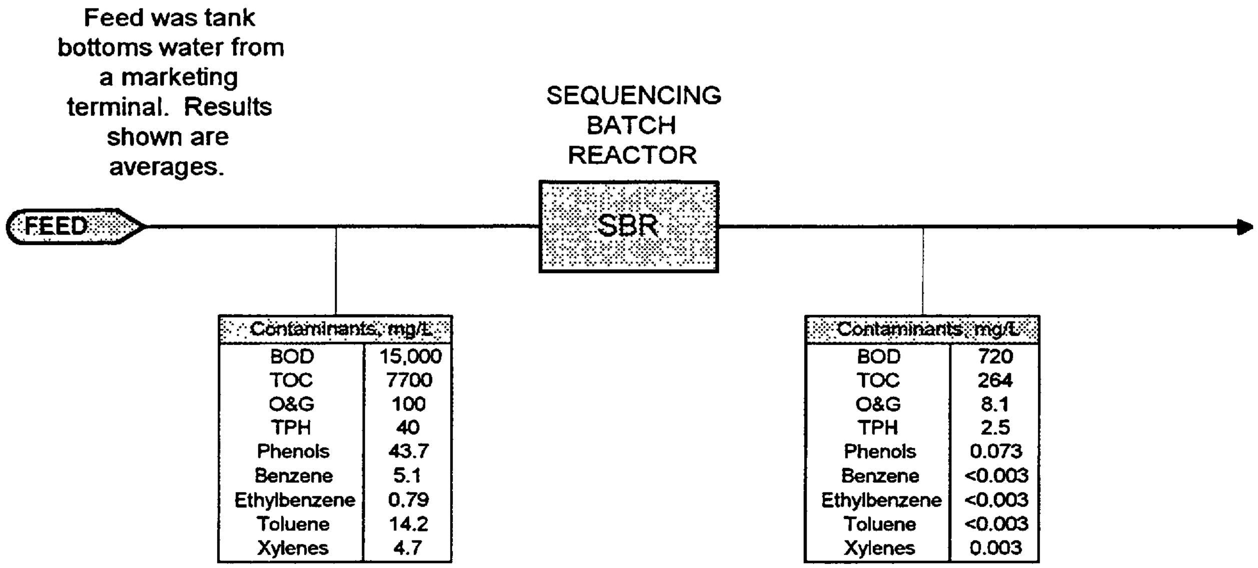
Contaminants, mg/L	
BOD	340
COD	5962
TOC	1087
O&G	412
TSS	200

Contaminants, mg/L	
BOD	346
COD	2878
TOC	710
O&G	117
TSS	103

Contaminants, mg/L	
BOD	-
COD	1770
TOC	504
O&G	110
TSS	90

FIGURE B-4

Case 4: Treatment Summary for Full-Scale Sequencing Batch Reactor Treatment of Marketing Terminal Tank Bottoms Water



Feed was tank bottoms water from a marketing terminal. Results shown are averages.

Contaminants, mg/L	
BOD	15,000
TOC	7700
O&G	100
TPH	40
Phenols	43.7
Benzene	5.1
Ethylbenzene	0.79
Toluene	14.2
Xylenes	4.7

Contaminants, mg/L	
BOD	720
TOC	264
O&G	8.1
TPH	2.5
Phenols	0.073
Benzene	<0.003
Ethylbenzene	<0.003
Toluene	<0.003
Xylenes	0.003

B-3 Treatment Performance

B-3.1 BIOLOGICAL TREATMENT

Figures B-1 through B-4 summarize the biological treatments, as well as secondary treatment by activated carbon, obtained in each of the four Cases. Since the wastewaters all had different strengths, the treatment results were normalized as percent removals as shown on Table B-1.

Some of the conclusions which might be drawn from Table B-1 are

- Biological treatment is effective (more than 93 percent removal in all Cases) at BOD removal from tank bottoms waters.
- Operation of biological treatments in series (TF vs. TF/AC for Case 3) does not produce much better effluent than the first treatment alone.
- Removal of petroleum hydrocarbons (TPH) by biological treatment is quite effective.
- Removal of BTEX components by biological treatment is extremely effective (100 percent removal in all Cases).

Table B-1

Comparison of Secondary Treatments of Petroleum Products Terminals Wastewaters

All values are long-term average Percent Removals

Treatment	SBR	RBC	SBR	RBC	SBR	TF	TF/AS	AC
Case	1	1	2	2	4	3	3	1
BOD	92	80	98	97	95	93	95	36
COD	81	77	84	82		61	68	59
TOC	80	71	83	80	97	77	76	43
Oil & Grease	83	84	82	82	92	31	59	96
TPH	91	89	99	99	94			92
Phenols	94	98	99	98	100			99
MBAS			53	53				
CTAS			79	87				
Methanol			99	99				
Ethanol			75	75				
Benzene			100	100	100			
Ethylbenzene			100	100	100			
Toluene			100	100	100			
Xylenes			100	100	100			
MTBE			100	100				
Copper			34	90				
Zinc			36	93				

TREATMENTS

SBR = Sequencing Batch Reactor (Biological)
RBC = Rotating Biological Contactor
TF = Trickling Filter (Biological)
TF/AS = Trickling Filter + Activated Sludge (Biological)
AC = Activated Carbon Columns

CASES

1 = Pilot-scale treatment of wastewater from a marketing terminal
2 = Semi-full-scale treatment of wastewaters from 4 petroleum products terminals
3 = Full-scale treatment of tank bottoms water from a petroleum products terminal
4 = Full-scale treatment of tank bottoms water from a marketing terminal

B-3.2 ACTIVATED CARBON TREATMENT

B-3.2.1 Performance

In the first 3 Cases, granular activated carbon treatment was tested, as both secondary treatment (Case 1) and as polishing treatment for bioeffluent (Cases 1, 2 and 3). Figures B-1 through B-4 show the treatment performance. Table B-1 shows the percent removals for the Case 1 secondary treatment case, and Table B-2 shows percent removals for Cases 1, 2 and 3 bioeffluent treatment by granular activated carbon. As can be seen, activated carbon was in most cases at least somewhat effective, and frequently very effective, at removing organic constituents from the bioeffluents.

B-3.2.2 Loading

Probably the strongest argument used against the use of activated carbon treatment is the potentially high operating cost for carbon consumption. Carbon consumption is controlled by the capacity of the carbon for holding various contaminants. As described in Section 9.10.1, the usual way of experimentally determining carbon capacity is with adsorption isotherms. Data from these Cases provides an additional method, based on actual required replacement quantities for carbon exhausted during treatment. As noted in Section 9.10, the effective capacity of carbon is controlled by the breakthrough curve, such that a bed of spent carbon is not totally exhausted when breakthrough occurs. Among other things, this means that the effective capacity of carbon is controlled by the definition of breakthrough, i.e., at what effluent concentration must the carbon be replaced. In the sections which follow, the carbon loadings of TOC and COD for each Case, at the point where breakthrough was defined (when the carbon was changed out) is calculated. The loading data are summarized on Figures B-5 and B-6. As can be seen, there appears to be a fairly linear (on a log-log plot) relationship between feed water contaminant concentration and contaminant loading of the exhausted carbon. Although this is not an isotherm plot, it is closely related to such a plot (carbon loading vs. water concentration), being different in that column capacity rather than mixed reactor capacity is being used. These results and usage guidelines are discussed in Section 9.10.3.

Table B-2

Comparison of Activated Carbon Treatments of Bioeffluents

All values are long-term average Percent Removals

Effluent From	RBC	RBC	SBR	TF/AS
Case	1	2	2	3
BOD	73	64	63	0
COD	76	91	90	52
TOC	72	97	98	35
Oil & Grease	80	89	89	72
TPH	55	40	40	
Phenols	13	88	87	
MBAS		89	89	
CTAS		43	73	

TREATMENTS

SBR = Sequencing Batch Reactor
RBC = Rotating Biological Contactor
TF/AS = Trickling Filter + Activated Sludge

CASES

1 = Pilot-scale treatment of wastewater from a marketing terminal
2 = Semi-full-scale treatment of wastewaters fro 4 petroleum products terminals
3 = Full-scale treatment of tank bottoms water from a petroleum products terminal

Case 1 RBC Effluent Polishing Loading: 2 drums (1000 lb) of carbon were used over a 12-week period at a usage rate of about 48 hours per week. At a flow rate of 0.75 L/min, 48 hr/week x 60 min/hr x 0.75 L/min x 12 week = 25,920 L (6848 gallons) were treated. In this time, average TOC removal was from 163 mg/L in RBC effluent down to 36 mg/L in activated carbon effluent. The total TOC removal was 6848 gallon x 8.34 lb/gallon x (163-36) ppm x 10^{-6} = 7.25 lb TOC. The loading of the carbon was 7.25/1000 = 0.00725 lb TOC per lb of carbon. Performing a similar calculation for COD (removal from 616 down to 134 mg/L) gives a loading of 0.0275 lb COD per lb of carbon.

Case 1 Secondary Treatment with Carbon Loading: Three 7.8 lb columns (23.4 lb) of carbon were used over a 4-week period at a usage rate of about 48 hours per week. At a flow rate of 0.1 L/min, 48 hr/week x 60 min/hr x 0.1 L/min x 4 week = 1152 L (304 gallons) were treated. In this time, average TOC removal was from 484 mg/L in sand filter effluent down to 257 mg/L in activated carbon effluent. The total TOC removal was 304 gallon x 8.34 lb/gallon x (484-257) ppm x 10^{-6} = 0.576 lb TOC. The loading of the carbon was 0.576/23.4 = 0.0246 lb TOC per lb of carbon. Performing a similar calculation for COD (removal from 1931 down to 777 mg/L) gives a loading of 0.125 lb COD per lb of carbon.

Case 2 Loading: The SBR and the RBC each were followed by three 500 lb drums of activated carbon in series. The following loadings are based on the maximum operating time for a set of drums (8 weeks) and are *based on the first drum loading and performance only* (effluent from each drum was analyzed). It should be noted that there was no sign of breakthrough of TOC or COD from the first drum in the 8-week run, so the loadings calculated here are conservative (the carbon was not fully loaded). The total amount of water treated was 500 gallons/week x 8 weeks = 4000 gallons (33,360 lb). The average TOC removal for both biotreatment systems was 80.8 mg/L in bioeffluent and 11.5 mg/L in carbon effluent, for a total removal of 2.31 lb. The TOC loading on carbon was 0.0046 lb TOC per lb of carbon. The average COD removal for both biotreatment systems was 263 mg/L in bioeffluent and 40 mg/L in carbon effluent, for a total removal of 7.44 lb. The COD loading on carbon was 0.0149 lb COD per lb of carbon.

Case 3 Loading: 1000 lb of carbon were used per week in treating 1146 gallons per day of water and reducing TOC concentration from 1087 to 710 mg/L. The weekly TOC removal was

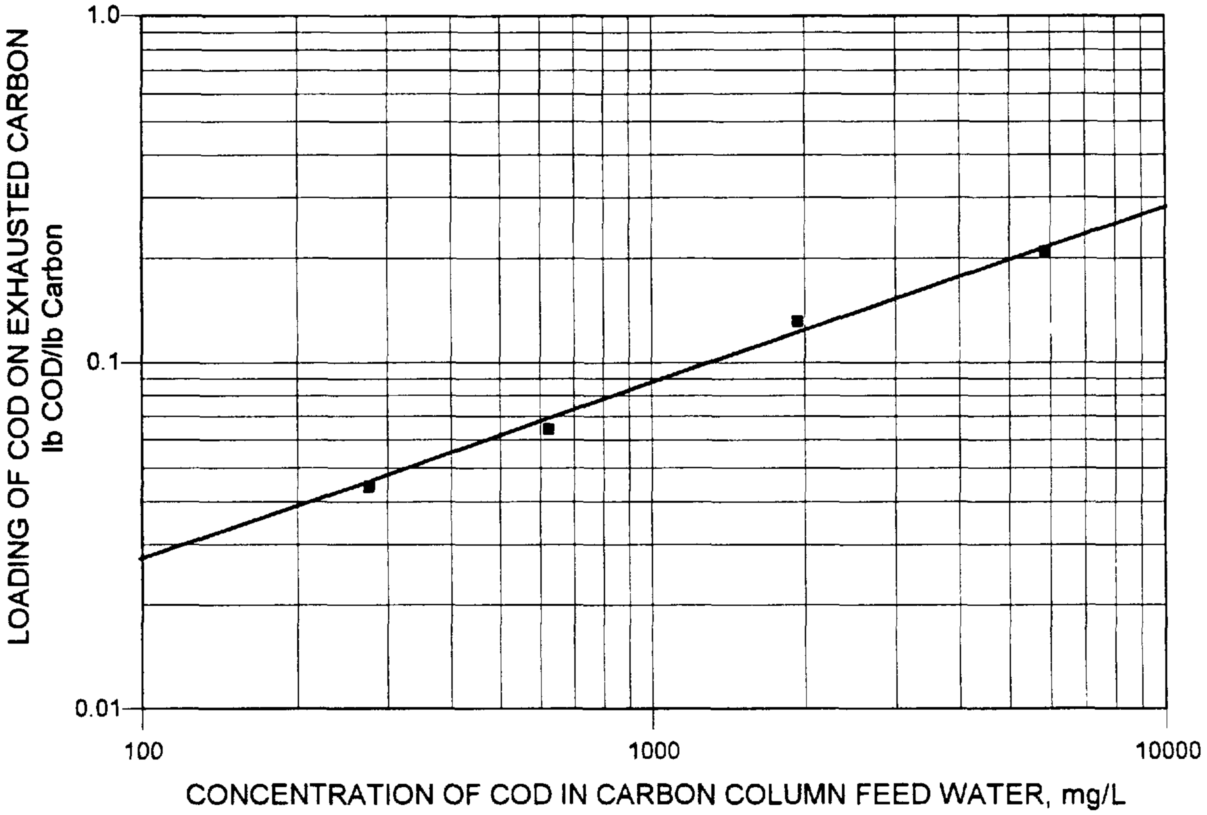
1146 gal/day x 7 day/week x 8.34 lb/gallon x (1087-710)ppm x 10^{-6} = 25.2 lb/week

The loading on the carbon was 25.2/1000 = 0.0252 lb TOC per lb of carbon. Performing a similar calculation for COD (removal from 5962 down to 2878 mg/L) gives a loading of 0.206 lb COD per lb of carbon.

FIGURE B-5

Granular Activated Carbon Column Capacity for COD Based on Exhaustion of Full-Scale and Pilot Scale Activated Carbon Columns

The data and graph on this figure were obtained from actual usage rates for granular activated carbon in columns or drums as determined in full-scale usage or pilot tests on marketing terminal wastewaters in the studies described in Appendix B. "Usage rate" is defined as the amount of carbon used before *breakthrough of contaminants required changeout of the carbon.* The table at the bottom shows the percent of feed COD in the effuent at the time of breakthrough. COD loading was calculated based on the average amount of COD removed from the feed water multiplied by the total volume of water passed through the carbon bed. Figure B-6 shows similar data for TOC loading. Although the data are based on actual experience, they should be used with caution, since different wastewaters have different adsorption characteristics, and different modes of carbon usage can influence usage efficiency.



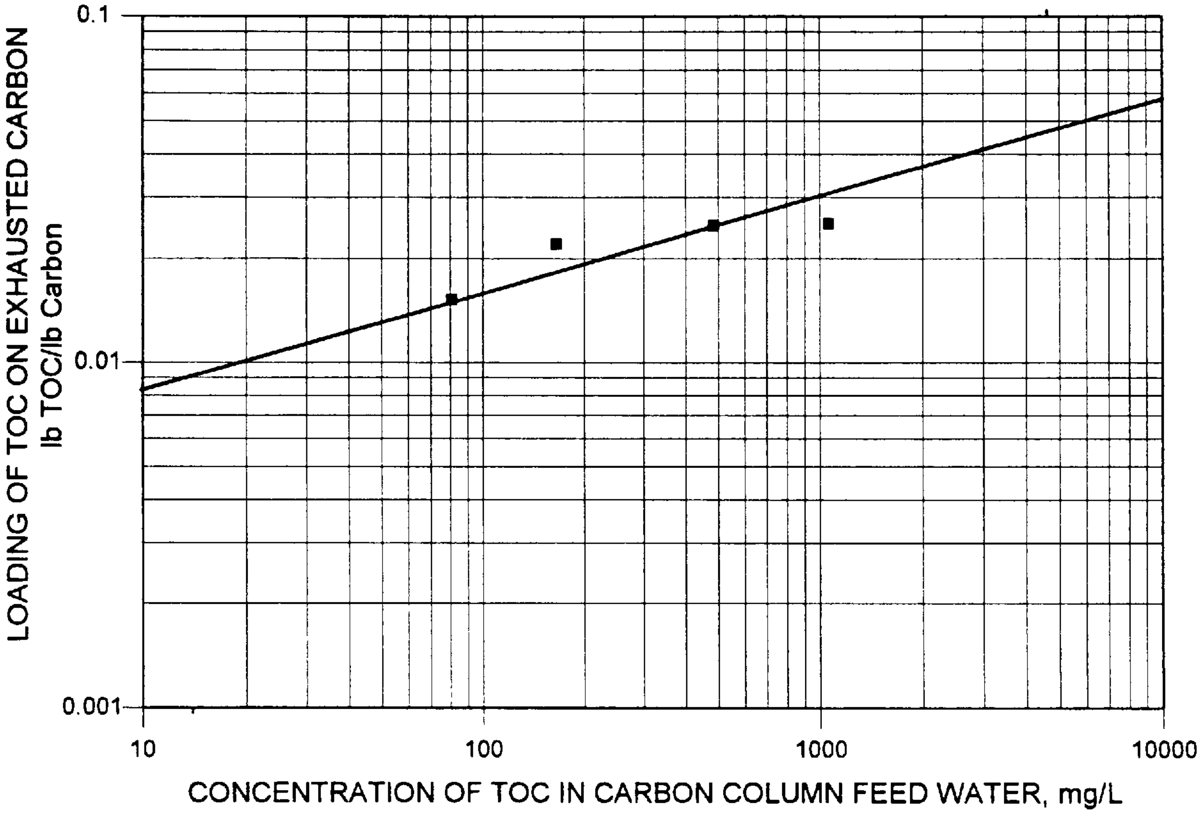
Linear regression equation for best-fit line shown is LW = 2.0060xLC + 5.1353, where LW is log10 of COD concentration in water (mg/L) and LC is log10 of COD loading on exhausted carbon (lb COD/lb carbon).

Water Being Treated	COD		% Effluent COD/Feed COD	
	Conc. in Water	Loading on Carbon, g/g	Initial	At Breakthrough
Trickling Filter / Activated Sludge Effluent	5962	0.206	31	71
RBC Effluent	616	0.06497	17	62
Untreated Wastewater	1931	0.125	21	51
RBC & SBR Effluents	263	0.04509	13	21

FIGURE B-6

Granular Activated Carbon Column Capacity for TOC Based on Exhaustion of Full-Scale and Pilot Scale Activated Carbon Columns

The data and graph on this figure were obtained from actual usage rates for granular activated carbon in columns or drums as determined in full-scale usage or pilot tests on marketing terminal wastewaters in the studies described in Appendix B. "Usage rate" is defined as the amount of carbon used before breakthrough of contaminants required changeout of the carbon. The table at the bottom shows the percent of feed TOC in the effuent at the time of breakthrough. TOC loading was calculated based on the average amount of TOC removed from the feed water multiplied by the total volume of water passed through the carbon bed. Figure B-5 shows similar data for COD loading. Although the data are based on actual experience, they should be used with caution, since different wastewaters have different adsorption characteristics, and different modes of carbon usage can influence usage efficiency.



Linear regression equation for best-fit line shown is LW = 3.6238xLC + 8.5479, where LW is log10 of TOC concentration in water (mg/L) and LC is log10 of TOC loading on exhausted carbon (lb TOC/lb carbon).

Water Being Treated	TOC		% Effluent TOC/Feed TOC	
	Conc. in Water	Loading on Carbon, g/g	Initial	At Breakthrough
Trickling Filter / Activated Sludge Effluent	1087	0.0252	22	57
RBC Effluent	163	0.02197	9	75
Untreated Wastewater	484	0.0246	24	59
RBC & SBR Effluents	80.8	0.0140	15	14

B-4 Treatment System Design Guidelines

Figures B-7, B-8, B-9, and B-10 shown the basic operating conditions (equipment sizes and loadings) for the four Cases. These data, along with the performance data (Figures B-1 through B-4) can be used to arrive at design implications for various biological treatments as was done above for activated carbon treatment. In previous pilot studies (Vuong, 1993, p. 19), it was found that COD removal exceeded BOD removal by a factor of 2.4, i.e., that the BOD test underestimates the amount of biodegradable oxygen demand by a factor of 2.4. For this reason, the following analysis will use COD removal, abbreviated as ΔCOD, as the primary contaminant loading parameter.

B-4.1 CONTAMINANT LOADING

B-4.1.1 Sequencing Batch Reactor Loading

In Case 1, the average SBR ΔCOD over the duration of the study was 2346 mg/L, at a hydraulic loading of 60 gallon/week. This is 1.17 lb/week of ΔCOD, in a 6.016 ft^3 reactor, for a system loading of 0.195 lb/week-ft^3. In Case 2, the overall average SBR ΔCOD was 3315 mg/L, at a hydraulic loading of 500 gallon/week. This is 13.8 lb/week of ΔCOD, in a 66.8 ft^3 reactor, for a system loading of 0.207 lb/week-ft^3. In Case 4, COD removal was not followed, but ΔBOD was 14,280 mg/L, at a hydraulic loading of 6000 gallon/week. This is 715 lb/week of ΔBOD, in a 1203 ft^3 reactor, for a system loading of 0.594 lb/week-ft^3.

B-4.1.2 Rotating Biological Contactor Loading

In Case 1, the average RBC ΔCOD was 2673 mg/L, at a hydraulic loading of 1008 gallon/week. This is 22.5 lb/week of ΔCOD, in a 860 ft^2 reactor, for a system loading of 0.0261 lb/week-ft^2. In Case 2, the overall average RBC ΔCOD was 3242 mg/L, at a hydraulic loading of 500 gallon/week. This is 13.5 lb/week of ΔCOD, in a 1500 ft^2 reactor, for a system loading of 0.00901 lb/week-ft^2.

B-4.1.3 Trickling Filter Loading

In Case 3, the average trickling filter ΔCOD was 11,315 mg/L, at a hydraulic loading of 8022 gallon/week. This is 757 lb/week of ΔCOD, in a 520 ft^3 reactor, for a system loading of 1.46 lb/week-ft^3.

B-4.1.4 Comparison of Loadings

Table B-3 shows a comparison of the biological treatment loadings calculated above. For purposes of comparison, since COD data were not available for all Cases, TOC removal is shown as the performance measure.

With the usual warning that direct comparisons are not possible, since different wastewaters were being treated, it still may be possible to draw some tentative conclusions from the data:

- Although the two pilot SBRs were very similar in their loading and performance, the full-scale unit had about three times the loading, and much better TOC removal. This may lend support to the on/off cycle of aeration employed in the full-scale unit.

- The poorer TOC removal found in the Case 1 pilot RBC may have been caused by its higher loading. In fact, based on disk stage biogrowth patterns for the two Cases, this was the conclusion of the investigators.

- On a loading per cubic foot basis, the trickling filter performed quite well, being about 3 times as "efficient" as the full-scale SBR, and 7 times as "efficient" as the pilot SBRs. On the other hand, its TOC removal was poorer, and it was followed by activated sludge treatment. This is in accord with the popular use of trickling filters as roughing devices for removing organics.

B-4.2 WASTEWATER TREATMENT SYSTEMS DESIGN CRITERIA

Detailed design criteria were obtained only in Case 2, which was a study designed for that purpose. The basic system design parameters for the other Cases described above can also be used to derive bases for design. In reading the following, it should be kept in mind that the Case 2 design (based on Case 1 experience) was deliberately made conservative, i.e., the following guidelines will result in some degree of over-design in most cases.

In Case 2, using the original bases for design used for the demonstration units, and experience gained in operating the equipment, the following design criteria for various types of treatment were developed. The criteria follow the general guidelines of providing units which require minimal operating time, operating cost, and maintenance, but which still have reasonable capital cost. It is recognized that alternative approaches are available for many of the criteria below; the criteria listed are, however, based on fairly long-term successful performance of essentially full-scale equipment, while the success of the alternatives may be less well demonstrated.

TABLE B-3

BIOLOGICAL TREATMENTS LOADING AND PERFORMANCE

TREATMENT	REMOVED COD LOADING		TOC REMOVAL, PERCENT
	LB/CUBIC FOOT	LB/SQUARE FOOT	
Sequencing Batch Reactors			
Case 1 Small Pilot	0.195		80
Case 2 Large Pilot	0.207		83
Case 4 Full-Scale	0.594		97
Rotating Biological Contactors			
Case 1 Large Pilot		0.0261	71
Case 2 Large Pilot		0.00901	80
Trickling Filter			
Case 3 Full-Scale	1.46		77

FIGURE B-7

Case 1: Design and Operating Conditions for the API 4581 Pilot Study

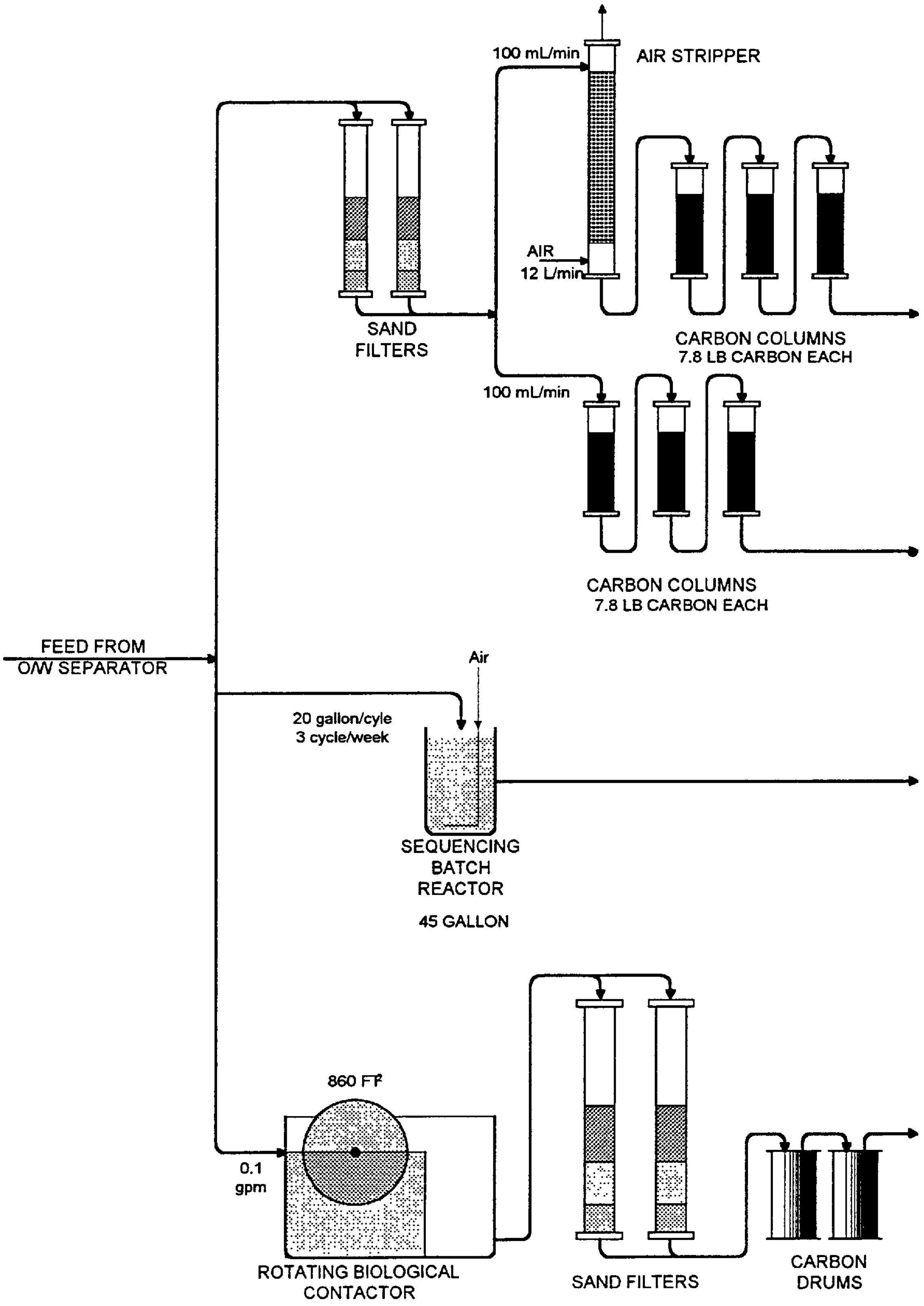


FIGURE B-8

Case 2: Design and Operating Conditions for the API 4582 Pilot Study

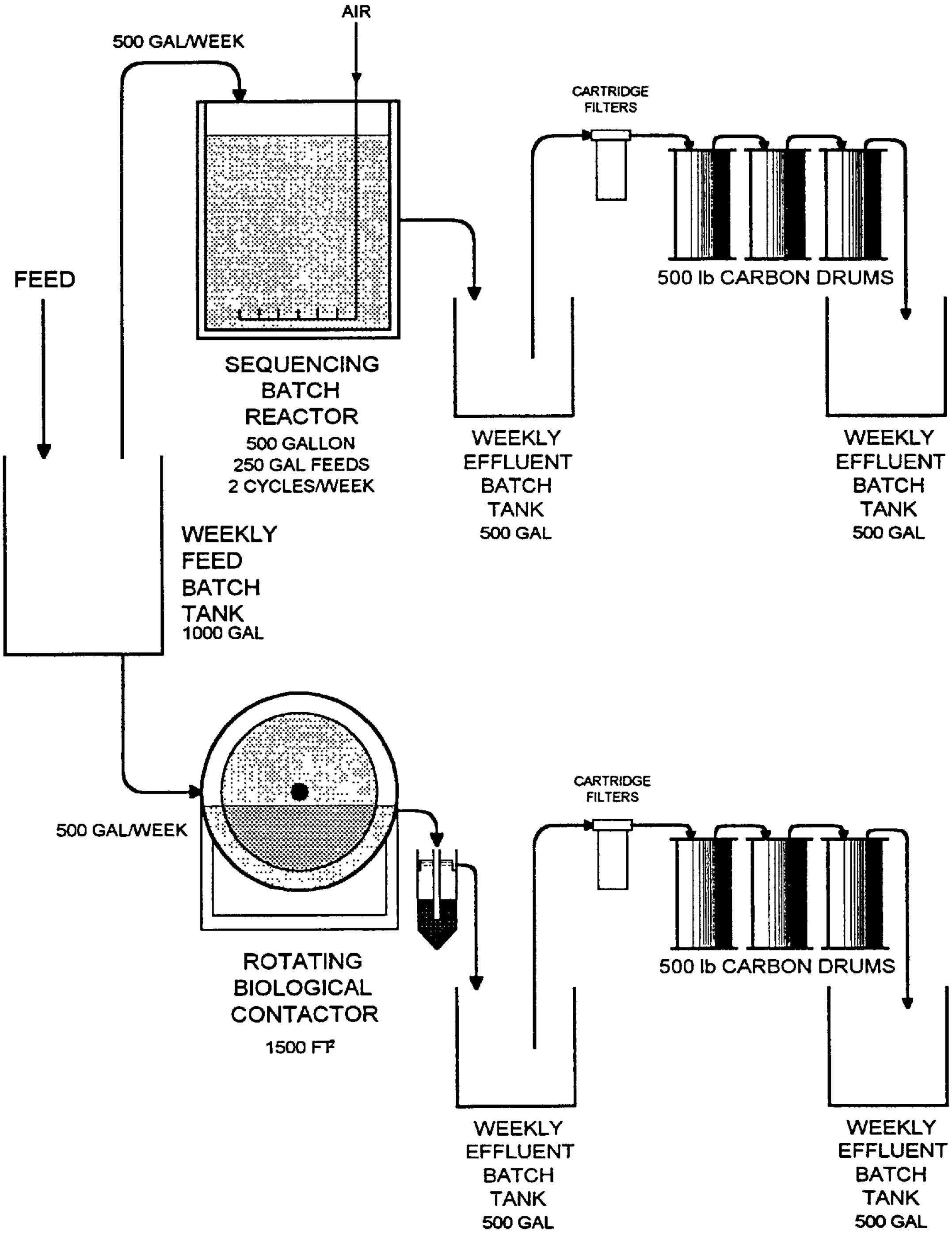


FIGURE B-9

Case 3: Design and Operations of a Full-Scale Trickling Filter / Activated Sludge / Activated Carbon Treatment System for a Petroleum Products Terminal Tank Bottoms Wastewater

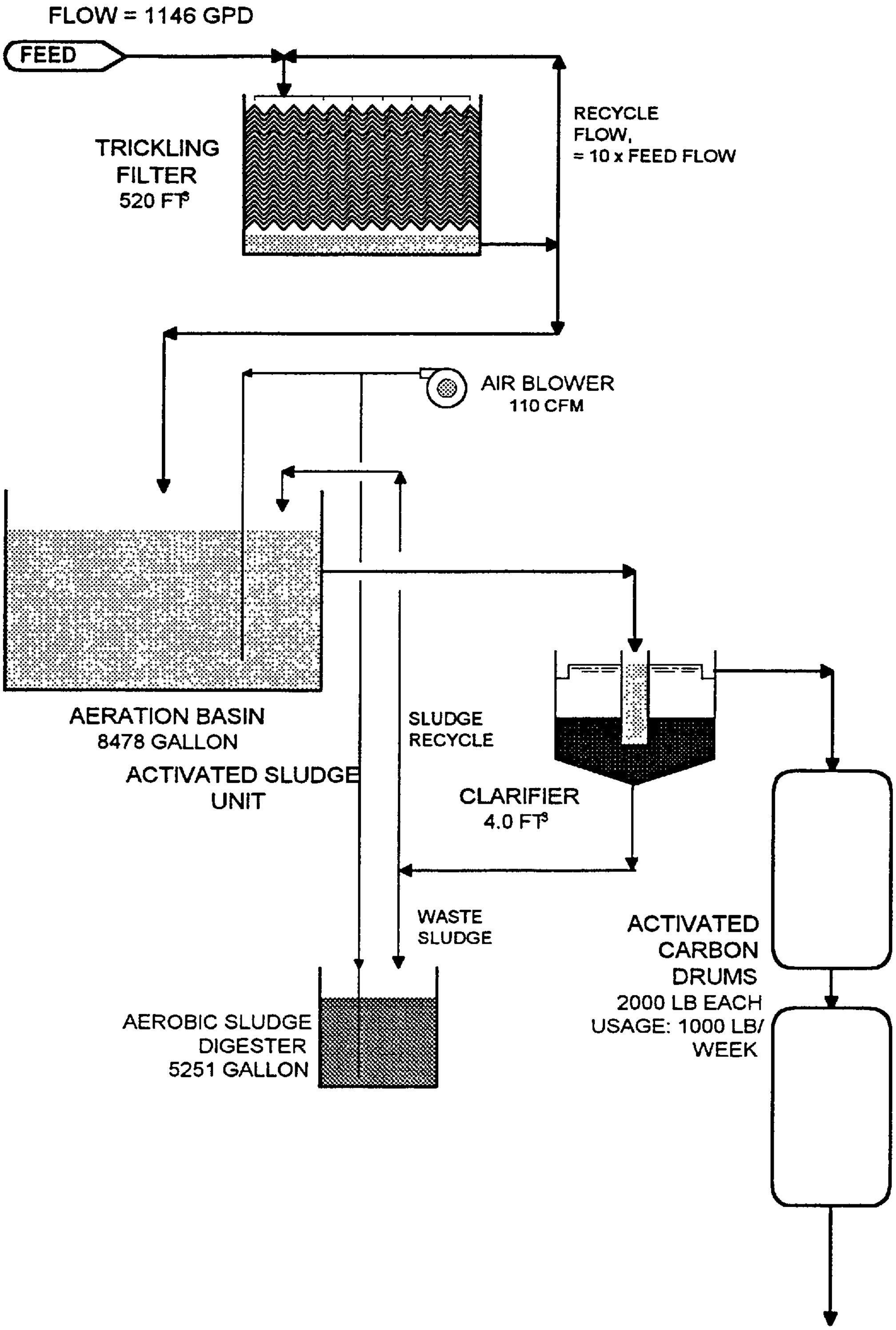
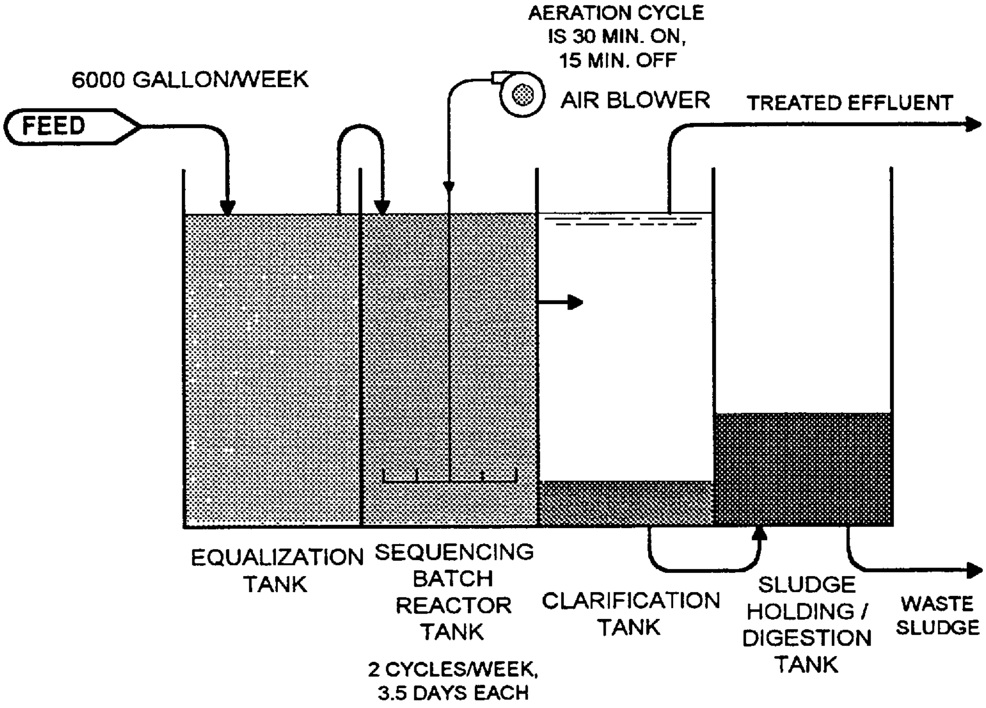


FIGURE B-10

Case 4: Design and Operations of a Full-Scale Sequencing Batch Reactor Treatment System on Marketing Terminal Wastewater



EACH OF THE FOUR TANKS IS 9000 GALLON CAPACITY

B-4.2.1 SEQUENCING BATCH REACTOR DESIGN CRITERIA

a. **Sequencing: Use a 3-day, 4-day sequence.**
Basis: This sequence was used successfully on the API studies. It was designed to allow for a fixed sequencing schedule (the same operations done on the same day of the week). Other sequences could be used, such as 2-2-3 day, or 7-day, or variable. The 2-2-3 day sequence was used successfully in the Case 1 studies; it is not certain, however, that it would have been as good at toxicity removal as the 3-4 day sequence, and it requires, of course, an extra operating day each week. A 7-day sequence, not tested, might be viable. It would, however, expose the bacteria to wider concentration swings (or else require a larger reactor) and may lead to excessive sludge self-digestion in the reactor. A variable sequence could be operated by continuing the aeration until treatment is complete, and then starting the next batch. The problems with this approach are that it is very difficult to determine continuously the degree of biodegradation and a variable sequencing schedule would be more troublesome to operate than a fixed schedule.

b. **Volume: The Reactor volume should be 2.5 gallons per gpm of feed water per ppm of feed water COD.**
Basis: This volume is based on the maximum loading successfully applied in the API studies. The sizing assumes a 50 percent water draw in each batch, and a 3-day, 4-day aeration cycle schedule. As an example, a terminal with 1000 gallons per week of water (0.1 gpm) at a COD level of 6000 ppm should have a (0.1x6000x2.5=) 1500 gallon SBR reactor.

c. **Aeration: Use compressed air with diffusers for aeration, at a rate to satisfy oxygen demand only. The minimum air supply rate is 0.006 SCFM per ppm COD per gpm of wastewater. The air supply should be controllable and metered.**
Basis: Other mechanical types of oxygenation equipment are usually oversized for this application. The aeration rate should be kept at the minimum needed for biodegradation in order to minimize air emissions and foam generation. As an example, a reactor fed 1000 gallons per week (0.1 gpm) of wastewater at a COD level of 6000 ppm should be supplied with (0.006x0.1x6000=) 3.6 SCFM of compressed air. The factor is based on the aeration rate used in the API studies. Compressed air can be supplied from plant compressed air, an air compressor, or a variable-speed blower (with sufficient discharge pressure to overcome the gravity water head and the diffuser losses).

An alternative approach, not tested, would be to use an aspirating aerator, with a recirculating pump taking suction off the aeration basin and discharging through an aspirator into the basin. With such a device, mixing and aeration could be accomplished with the same piece of rotating equipment (the recirculating pump), and the rate of air induction could be controlled with an air valve on the aspirator suction line.

d. **Mixing: Provide the reactor with a variable-speed mixer with sufficient mixing power to keep biosolids suspended. Mixer sizing should be based on shaft rotational speed N (rpm), impeller diameter D (ft), reactor volume V (ft^3), and an impeller constant, K. The formula is $(N^3)(D^5)K/V = 15{,}000$ to $123{,}000$. The mixer shaft horsepower formula is power (HP) = $1.63x10^{-8}K(N^3)(D^5)$. Also, at least 3 baffles, with widths of at least 0.1 times the tank diameter, should mounted on the tank wall.**
Basis: Although aeration air could be used for mixing, the need to minimize air flow (see c) requires that mixing be done mechanically.

The formula is based on an established mixing relationship* and on lab trials of an SBR mixer in an 1800 (241 ft^3) gallon reactor with a 2.25-foot diameter 3-blade propeller operating over a 40-80 rpm speed range. This mixer, driven by a 1.0 HP variable speed motor, provided adequate mixing without undue surface agitation. K values for the impeller are listed below. As an example, it is desired to calculate the speed range for a mixer with a 4-foot diameter propeller in a 4000 gallon (535 ft^3) tank:

$(N^3)(4.0^5)\text{x}1.0/535 = 15{,}000$ to 123,000.
$N^3 = 7837$ to 64,263
$N = 19.9$ to 40.1 rpm

The mixer shaft horsepower at the higher speed will be
$P = 1.63\text{x}10^{-8}\text{x}1.0\text{x}(40.1^3)(4.0^5)$
$= 1.08$ horsepower

Note that motor horsepower will be greater than shaft horsepower due to efficiency losses in the motor and in any transmission equipment.

Impeller K values (assuming 4 tank wall baffles):

Propeller, square pitch, 3-blade	0.32
Propeller, pitch two, 3-blade	1.00
Turbine, six flat blades	6.30
Turbine, six curved blades	4.80
Turbine, six arrowhead blades	4.00
Fan Turbine, six blades	1.65
Flat Paddle, two blade	1.70
Shrouded Turbine, two curved blades	1.08
Shrouded Turbine with stator (no baffles)	1.12

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*Amirtharajah, A., Chapter 11, "Design of Flocculation Systems" in Sanks, R.A., "Water Treatment Plant Design", Ann Arbor Science.

e. Heater: Provide sufficient heat to maintain a reactor temperature of 70 F. If an immersion heater is used, it should be explosion-proof and located below the minimum water elevation.

Basis: 70 F is a comfortable minimum temperature for biological treatment reactions. Heater sizing is based on the reactor wall and roof heat losses, and on the need to heat the incoming feed batch. If the reactor is insulated or located in an enclosure, the feed batch heating will be the dominant requirement. As a rule of thumb, the heater should be sized to heat one feed batch at the minimum temperature to 70 F in about 7 hours (10 percent of the 3-day aeration time). Since the feed water might contain gasoline, an electric immersion heater should be kept submerged at all times (located below the lowest water draw elevation) and should be used with auxiliary controls (using level or temperature detection) to shut off the heater in case the water level drops below it.

f. Level Control: The reactor should have a fill line automatic liquid level shutoff valve, and a liquid-seal liquid overflow line above the normal liquid level.

Basis: This system uses a fixed operating level. After batch draining, the fill pump is turned on, and feed water enters the reactor until shut off by the automatic liquid level valve. This can be either a float valve, or a control valve connected to a liquid level control. The liquid overflow, used for failure of the fill shutoff valve, has a liquid seal to prevent air from exiting from it. This can be conveniently done by piping the overflow from the top of the reactor down to grade, then up to the top of the reactor and then down to grade, with a water fill nozzle provided to enable making the water seal.

g. Sealing: Provide the option of sealing the top of the reactor (including hatchways and mixer seal), and providing a vent pipe for offgases.

Basis: Current or future air emission regulations for hydrocarbons or other volatile materials such as MTBE may require capturing and treating offgases. If air regulations do not exist, but are anticipated, then providing the top seals initially may be less expensive than retrofitting.

h. **Pressure Relief: The reactor, if sealed, should have a pressure relief valve on top.**
Basis: If the reactor is closed (except for the vent) and is supplied with air, a pressure relief valve is necessary in case of vent plugging or shutoff. If adequately sized, the liquid overflow line can serve this function.

i. **Draw Taps: The side of the reactor should be fitted with 6 draw taps, spaced at 30, 40, 50, 60, 70, and 80 percent of normal liquid level elevation.**
Basis: Feed rate to the reactor is controlled by the amount of clear water drained from the previous treatment batch. Multiple taps allow this rate to be adjusted for varying wastewater contaminant concentration and flow, without requiring operator attention (or electronic controls) to set the drain level. Other variables which could have been used for this adaptation (aeration time and aeration liquid level) are kept constant in this system.

j. **Window: The side of the reactor should be fitted with window(s) which span the elevations of the draw taps (20-90 percent of normal liquid level), and are located adjacent to the draw taps. The top of the reactor should have a source of light (window or electric light). Access (platform and hatchway) should be provided to enable scrubbing the window from the top of the reactor.**
Basis: The SBR operates by batch settling, and it is essential to determine that the biosludge has settled to below the draw tap before that tap is opened. Fouling by biosludge will occur, and so the window needs to be periodically scrubbed with a brush.

k. **Venting: If the SBR is inside an enclosure (building), it must be tightly sealed and vented outside. In addition, the enclosure should be positively ventilated at all times with an exhaust fan.**
Basis: Most of the wastewater in a petroleum product terminal originates in a fuel/water system (product tanks and spill containment tanks), and there is, therefore, a significant probability that at times the wastewater will contain gasoline. If, under those circumstances, the SBR vents directly into the enclosure, there is a strong possibility of generating an explosive atmosphere. The lower explosive limit concentration for gasoline components is about 1.0 volume percent. For example, an enclosure 8 ft x 8 ft x 40 ft could thus be rendered explosive by vaporization of 6.6 lb, or about 1 gallon, of gasoline. Although less likely, it is possible that piping and other equipment could leak gasoline into the enclosure, and thus a ventilation fan is needed to guard against that. The reactor and fan should vent upwards from the top of the enclosure, and the enclosure air intake vent should be near the floor on the other end of the enclosure (to prevent vapor recycle).

l. **Freeze Protection: In climates which experience freezing temperatures, special provisions must be made for freeze protection.**
Basis: Petroleum product terminals typically produce very low flows of wastewater, and treatment systems will be small and above-ground. Under these circumstances, there is considerable danger of freezing of small lines, pumps not in service, and so forth. There are, of course, a variety of methods for guarding against freezing. The "standard" approach would be to steam or electric trace all equipment, but this would be expensive to install and troublesome to operate and maintain. The techniques outlined below should provide relatively low-cost and effective alternatives.

- Place the entire treatment system inside a heated building. This alternative may be the least expensive approach for the small treatment units utilized at terminals. For example, an 1800 gallon SBR unit with auxiliary tankage and sludge handling equipment, was built to fit on a 15 ft x 33 ft slab, and could have been covered with a 10 ft high roof. If the SBR is enclosed, it should be vented outside as described above.

- Place lines, pumps, and other small equipment inside a heated building, with the SBR unit and tanks outside of, but immediately adjacent to, the building. Make an opening in the building wall to allow the SBR window to be observed, and the SBR draw taps to be operated, from within the building. Insulate outside equipment. This alternative was utilized in the API studies. By locating the tanks and treatment units immediately adjacent to the building, water transfers between feed tanks, treatment units, and effluent tanks, was done without exposing lines to outside weather.

- Do not use outside sight gauges on tanks, provide heaters for any feed and effluent tanks, and insulate the SBR vent pipe well.

  Basis: These bases for these items are self-evident; note that the vent air will be water-saturated, and thus prone to icing if not insulated.

B-4.2.2 ROTATING BIOLOGICAL CONTACTOR DESIGN CRITERIA

a. Disk Area: The total disk area should be at least 7.56 square feet per gpm of feed water per ppm of feed water COD.
Basis: This area is based on the maximum loading successfully applied in the API studies. As an example, a terminal with 1000 gallons per week of water (0.1 gpm) at a COD level of 6000 ppm should have a (0.1x6000x7.56=) 4536 square foot RBC.

b. Staging: Use four stages of treatment, with equal area in each stage.
Basis: This arrangement was used successfully in the API studies. Other stage arrangements might work just as well, or better, but these were not tested.

c. Speed: Provide a variable-speed drive for the disk shaft, adjustable over the range of 1.0 - 2.0 rpm.
Basis: Disk rotational speed controls oxygen transfer and biomass sloughing rate (both are higher at higher rpm). In general, the higher the BOD loading on the disks (lb BOD/day), the higher the rotational speed should be. At low loadings, excessive speed may lead to excessive sloughing, so the speed should be adjustable.

d. Feed Pump: Feed the RBC with a positive-displacement adjustable-flow pump.
Basis: The RBC is a continuous-flow low-flow treatment unit. Typical feed rates for petroleum product terminal wastewaters are in the range of 500-2000 gallons per week, or 188-751 mL/min. It is necessary to feed the unit at a controlled steady rate to prevent upsets, but the only practical means for doing flow control at these low rates is to use positive displacement pumps. Since the rate needs to be changed to handle varying wastewater concentrations and flows, the pump rate should be adjustable. There are two approaches on pump utilization. The first approach uses a continuously-operated low-flow pump. This is generally workable, as found in the API studies, but periodic plugging of the small openings due to accumulated solids in the lines can be expected. Another approach, not tested, would be to use a larger pump (and larger suction and discharge lines) which would be operated periodically by a timer (e.g., to be turned on for 1 minute out of every 10 minutes). A larger pump would be less susceptible to fouling. If the timing sequence is frequent enough, the effects of pulsing the feed to the RBC should have only a small effect on its performance. For both approaches, various types of positive displacement pumps (progressing cavity, piston, diaphragm) can be used, but progressing cavity pumps, not having check valves, would probably be the least susceptible to malfunctioning due to solids.

e. **Cover: The RBC unit should have a reasonably tight cover. Small hatchways should be provided in the cover to allow access to each disk stage.**
Basis: If the RBC is outside, it is necessary to cover the disks to protect them from weather and to minimize air emissions of volatile contaminants. Access into each stage is required to inspect the disks and to take dissolved oxygen measurements in the basin water. If the RBC is inside, safety considerations require (see item j) that the disk unit be sealed.

f. **Heating: Provide sufficient heat to maintain a basin temperature of 70 F using a recirculated hot water system.**
Basis: 70 F is a comfortable minimum temperature for biological treatment reactions. Heater sizing is based on the unit wall heat losses, and on the need to heat the incoming feed water. A convenient and safe way of providing heat to an RBC is to place a heating coil made of half-inch stainless steel tubing into the first stage basin (near the end wall or the stage divider), and to circulate hot water through the coil. The hot water can be provided by a small household water heater, with a centrifugal pump taking suction off the bottom of the heater, and with cooled water returning from the RBC coil back to the water heater (recirculated closed-loop system). Temperature control is done with a thermocouple in the last stage connected to a temperature controller which turns the water circulating pump on and off.

g. **Elevation: The RBC unit should be elevated such that its effluent can flow by gravity to the clarifier inlet.**
Basis: In order to simplify equipment and operations, and to avoid sludge shearing, it is very desirable not to pump the RBC effluent to the clarifier.

h. **Clarifier: Provide an effluent clarifier with a cross-sectional area of at least 3.6 square feet per gpm. The sludge draw nozzle should have a diameter of at least 1.5 inches.**
Basis: This is the standard size for RBC clarifiers. Since the minimum size is very small (0.36 ft^2 for a 1000 gallon per week flow), it may be preferred to oversize the clarifier somewhat (as was done in the API studies). The minimum 1.5-inch size for the sludge draw nozzle is to ensure that it is not blocked ("bridged") by settled sludge.

i. **Sludge Pump: Provide a positive-displacement, preferably progressing cavity, sludge pump operated with a timer and located directly under the clarifier sludge nozzle.**
Basis: The main challenge in removing sludge from a clarifier is keeping sludge levels sufficiently low to prevent the sludge from becoming anaerobic (and thus causing odor problems and sludge flotation) while not pumping excessive water with the sludge. An additional challenge for a very small clarifier is keeping sludge passages large enough to prevent plugging while removing very small flows of sludge. The best way to handle these constraints is to use a fairly large pump, with an adjustable timer which will turn on the pump for a short time during a set interval (e.g., to pump for 20 seconds every hour). A progressing cavity pump is preferred based on its successful operation in this application in several pilot studies. The pump should be located directly under the clarifier to minimize the likelihood of pump suction line plugging by sludge.

j. **Sealing: If the RBC and clarifier are inside an enclosure (building), they must be tightly sealed and vented outside. In addition, the enclosure should be positively ventilated at all times with an exhaust fan.**
Basis: As described above for SBR units (item g), gasoline accidentally fed to the treatment system can result in an explosive atmosphere in an enclosure if the units (RBC unit and clarifier) vent directly into the enclosure. RBC units, which do not have positive aeration, are less likely to have this problem, but an explosion is still possible. Sealing and venting an RBC and clarifier, while still allowing access, is somewhat challenging. It is possible to attach a vent to the RBC cover, seal all openings except the shaft drive end, and

use a vent fan (explosion-proof) to pull air through the unit and discharge it outside (note that this eliminates one of the RBC advantages: low air emissions compared to SBR). Any access hatches would have to be sealable. The clarifier could be sealed, preferably with a transparent cover, and vented to outside. To handle the possibility of piping and other equipment leaking gasoline into the enclosure, an enclosure ventilation fan is recommended.

k. **Freeze Protection: In climates which experience freezing temperatures, special provisions must be made for freeze protection.**
See the writeup for SBR freeze protection for the design guidelines.

Cover photo: Gasoline and heating oil are stored in vast waterfront distribution centers such as Sun Company's Newark, New Jersey bulk terminal.

Photo courtesy of Sun Company of NJ

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