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Industrial Wastewater Management, Treatment, and Disposal

THIRD EDITION

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MANUAL OF PRACTICE No. FD-3

INDUSTRIAL WASTEWATER MANAGEMENT, TREATMENT, AND DISPOSAL

Prepared by **Industrial Wastewater Management, Treatment, and Disposal Task Force** of the **Water Environment Federation**

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Under the Direction of the **Industrial and Hazardous Wastes Subcommittee** of the **Technical Practice Committee**

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WEF Press

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Manuals of Practice of the Water Environment Federation

The WEF Technical Practice Committee (formerly the Committee on Sewage and Industrial Wastes Practice of the Federation of Sewage and Industrial Wastes Associations) was created by the Federation Board of Control on October 11, 1941. The primary function of the Committee is to originate and produce, through appropriate subcommittees, special publications dealing with technical aspects of the broad interests of the Federation. These publications are intended to provide background information through a review of technical practices and detailed procedures that research and experience have shown to be functional and practical.

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Preface

The focus of this book is exclusively on management of industrial wastewater; how wastewater characteristics varies by industry; what methods of treatment are used in industry, developing trends; and how industrial design, construction, and operations services are or could be procured.

This Manual of Practice is a totally revised and expanded edition of the 1994 WEF bestseller *Pretreatment of Industrial Wastes.* Besides an overall updating and editing of the technical material, this edition contains:

- An update on current regulations,
- A greatly expanded section on biological treatment of industrial wastes,
- A new section on organoclays,
- A new chapter on instrumentation and control of industrial waste treatment processes, and
- A new chapter on innovative methods for procuring services related to facility design, construction, and operation.

This book is intended to appeal to a wide range of professionals responsible for regulating, monitoring, and designing industrial waste facilities. Engineering consultants, industrial waste managers and purchasing department managers, government regulators, and graduate students will find this book invaluable.

The book has been written by a diverse group of professionals experienced in the particular area of concern. Design engineers, industrial managers, university professors, and regulators have combined their efforts to produce a book that is thoroughly grounded in theory but is a practical resource for those who need to apply industrial wastewater principles to facility design or even to retaining an engineers or contractor.

Industrial Wastewater Management, Treatment, and Disposal was produced under the direction of Terence P. Driscoll, *Chair.*

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Chapter 1

Introduction

INTRODUCTION

Municipal and industrial wastewater treatment are very different. Compared to municipal wastewater, industrial wastewater contains different pollutants and is often more variable, concentrated, and toxic. The nature of the design, construction, and operations services are also different, as are the procurement techniques.

This book focuses on how to manage industrial wastewater and residuals, how its characteristics vary by industry, what treatment methods are used, and how industrial design, construction, and operations services typically are procured. It also discusses emerging pretreatment trends.

NEW IN THIS EDITION

This is a totally revised and expanded edition of the 1994 WEF Manual of Practice titled *Pretreatment of Industrial Wastes.* Besides an overall update of preexisting technical material, this edition contains:

- Updated regulatory information;
- New sections on organoclays and the latest methods for removing heavy metals, especially arsenic, selenium, and mercury;

- A greatly expanded section on biological treatment methods, including sequencing batch reactors; and
- New chapters on industrial waste characteristics, industrial wastewater sampling, treatability studies, instrumentation and control of treatment processes, and innovative procurement methods.

This book is intended to appeal to professionals responsible for regulating, monitoring, and designing industrial waste facilities. Engineering consultants, industrial waste managers, purchasing department managers, government regulators, and graduate students will find this book invaluable.

The book was written by a diverse group of experts. Design engineers, industrial managers, university professors, and regulators worked together to produce a practical resource for industrial wastewater professionals.

LAYOUT OF THE BOOK

The book has two sections:

- Planning and managing industrial wastewater pretreatment processes and
- Designing, operating, and procurement of industrial pretreatment facilities.

SECTION 1: PLANNING AND MANAGING INDUSTRIAL WASTEWATER PRETREATMENT PROCESSES. The first half of the book discusses:

- The issues related to pretreatment;
- The regulations governing discharges of industrial wastewater;
- The types of industrial wastewaters and their characteristics;
- The steps involved in characterizing a given waste and devising an appropriate treatment scheme via site-specific treatability studies; and
- Management strategies for minimizing the size and cost of pretreatment facilities.

Chapter 1 demonstrates the need for pretreatment guidance and provides a framework for later waste-specific discussions.

Chapter 2 provides an introduction to U.S. pretreatment regulations and notes what prompts various technology selections.

Chapter 3 outlines representative sampling techniques for industrial wastewater when developing wastewater characteristics, designing pretreatment facilities, and demonstrating compliance with regulatory requirements.

Chapter 4 describes methods for conducting an in-house industrial wastewater survey and toxicity characterizations, including regulatory submittals for sampling and analysis.

Chapter 5 suggests approaches for developing treatability studies for specific wastestreams, whether performed in-house or by a contractor. It also describes treatability studies for aerobic and anaerobic biological treatment, physical treatment, and chemical treatment.

Chapter 6 notes typical characteristics for various industrial wastes, based on both established databases and the authors' own expertise. It provides a starting point for industrial consultants, designers, and managers to determine a specific facility's wastewater characteristics and can help them specify the processes needed to meet pretreatment objectives and regulations.

Chapter 7 addresses wastewater management alternatives (e.g., in-plant pollution prevention and waste minimization). It is designed to help pretreatment professionals minimize the investment needed to achieve pretreatment requirements.

SECTION 2: DESIGN, OPERATION, AND PROCUREMENT OF INDUSTRIAL PRETREATMENT FACILITIES. Section 2 provides guidance on process selection and system design to meet pretreatment requirements and accurately control the system. The chapters are organized by waste characteristics, as follows:

- Chapter 8: Flow and Load Equalization;
- Chapter 9: Solids Separation and Handling;
- Chapter 10: Removal of Fats, Oil, and Grease;
- Chapter 11: pH Control;
- Chapter 12: Removal of Inorganic Constituents;
- Chapter 13: Removal of Organic Constituents;
- Chapter 14: Process Instrumentation and Control; and
- Chapter 15: Project Procurement.

Chapters 8 through 13 outline various pretreatment processes and their applications, advantages, disadvantages, and expected performance. They also provide basic design criteria to be used when sizing each process.

Chapter 14 provides guidance on controlling pretreatment processes via key process variables (e.g., flow, dissolved oxygen, pH, oxidation-reduction potential, and total organic carbon). It also outlines process-control strategies for both batch- and continuous-flow systems, and discusses the design and use of feedback and feed-forward control loops.

Chapter 15 describes various methods for procuring design, construction, and operations services and equipment. It describes the nature of the design process, highlighting the need for project planning and feasibility studies, and noting the advantages and disadvantages of in-house design. The chapter also discusses project construction issues (e.g., bonds, shop drawing reviews, inspections, change orders, startup, and warranty issues during operations). In addition, it describes a number of procurement methods, including the design-bid-build, construction manager-at-risk, design-build-operate, and design-build-own-operate-transfer methods. Lastly, Chapter 15 lists operations options (e.g., contract operations) and outlines predictive maintenance programs that ensure continuous operations and avoid catastrophic equipment failure.

PURPOSE AND SCOPE OF THE BOOK

This book provides guidance on selecting processes and designing systems for pretreating industrial wastes. It is written for

- Consultants who specialize in industrial waste treatment;
- Industrial engineers and managers responsible for wastewater pretreatment facilities; and
- Municipal, state, and federal regulators who oversee and enforce pretreatment programs.

The book includes a general approach to pretreatment system design and operations, specific design values for various treatment processes, and suggestions for optimizing process operations. It also discusses pollution prevention techniques as the first step in pretreatment planning and design.

THE NEED FOR PRETREATMENT

Industries may directly discharge their treated wastewater to a receiving waterbody (if they have the appropriate permit) or indirectly discharge it to a publicly owned treatment works (POTW). Direct discharge typically involves more treatment. The technologies discussed in this book may be used whether the effluent will be directly or indirectly discharged, but because indirect discharge is more common, it is the principal focus of the book.

In this book, *pretreatment* is defined as reducing, eliminating, or altering pollutants in industrial wastewater before discharging the wastewater to a POTW. Industries discharging to a POTW may have to pretreat their wastewater to

- Comply with the General Pretreatment Regulations issued by the U.S. Environmental Protection Agency;
- Comply with Categorical Pretreatment Standards;
- Comply with local municipal sewer ordinances;
- Reduce sewer use fees (when they are based on the mass loading of one or more pollutants); and
- Improve their public images or reduce the stigma associated with publicly reported pollutant discharges, such as the Toxics Release Inventory under the Superfund Amendment and Reauthorization Act.

To meet typical pretreatment requirements, industries typically must invest in a wastewater pretreatment system. This book provides general guidance on selecting and designing pretreatment facilities. Readers should not apply the typical values given in this manual to specific industrial applications. To ensure proper design, the book describes site-specific evaluations and appropriate treatability testing that should be used instead. If more information is needed, readers should refer to the detailed wastewater design texts included in the references at the end of each chapter.

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Chapter 2

Discharge and Disposal Regulations

(continued)

This chapter presents the regulations related to the disposal of industrial wastewater and its treatment residuals as of March 31, 2007. Wastewater disposal options include indirect discharge, direct discharge, subsurface injection, land application, and incineration. *Indirect discharge* involves sending untreated or partially treated (pretreated) wastewater to a municipal wastewater treatment plant [publicly owned treatment works (POTW)] for further treatment. *Direct discharge* is a matter of treating wastewater (if required) and then discharging it to a body of water (e.g., river, lake, or ocean).

Wastewater treatment residuals disposal options include subsurface injection, land application, landfilling, and incineration. This chapter only presents the landfilling and incineration requirements that pertain to the waste generator. For more regulatory information on designing, permitting, operating, and closing landfills and incinerators, see Parts 239, 240, 257, 258, and 264 of Title 40 of the *Code of Federal Regulations* (40 *CFR* 239, 240, 257, 258, and 264).

Each industrial facility should review the federal, state, and local regulations that apply to its specific wastewater and residual disposal procedures to ensure that all requirements are met and all options that could reduce disposal costs are used.

PRETREATMENT REGULATIONS

FEDERAL PRETREATMENT REGULATIONS. The Federal Water Pollution Control Act amendments of 1972 [also called the Clean Water Act (CWA)] give the U.S. Environmental Protection Agency (U.S. EPA) the authority to establish and enforce pretreatment standards for indirectly discharged industrial wastewater. The agency's pretreatment program has three objectives (40 *CFR* 403.2):

1. "To prevent the introduction of pollutants into POTWs which will interfere with the operation of a POTW, including interference with its use or disposal of municipal sludge;"
2. "To prevent the introduction of pollutants into POTWs which will pass through the treatment works or otherwise be incompatible with such works;" and
3. "To improve opportunities to recycle and reclaim municipal and industrial wastewaters and sludge."

These objectives originated from the fact that POTWs are required to treat only domestic wastewater, which resulted in industrial wastewater discharged to POTWs not being appropriately treated. The Clean Water Act categorizes pollutants as conventional, nonconventional, and toxic. The *conventional pollutants* are those expected to be present in domestic wastewater and include biochemical oxygen demand (BOD); total suspended solids (TSS); pH; fecal coliforms; and oil and grease (U.S. EPA, 1999a and 40 *CFR* 401.16). *Nonconventional pollutants* are those that are neither conventional nor toxic, such as ammonia, nitrogen, phosphorus, chemical oxygen demand, aluminum, manganese, acidity, and whole effluent toxicity (WET). *Toxic pollutants* originally were a list of 65 categories of chemicals negotiated in a 1975 lawsuit (see 40 *CFR* 401.15). According to the lawsuit settlement, the U.S. Environmental Protection Agency had to establish effluent standards for these chemicals by July 1, 1980. The list was later modified to show the compounds in each of the organic categories and the specific inorganic elements of concern only (not their compounds) and to delete three chemicals and became the list of *priority pollutants* (Table 2.1). Under Section 307(a)(1) of the CWA, the U.S. Environmental Protection Agency has the authority to add other toxic pollutants of concern to the effluent standards regulations for particular industries, and it has done so (e.g., carbamates) as it developed standards for the different industrial categories. These additional parameters, though, are not part of the priority pollutant list.

Table 2.1 List of priority pollutants (Appendix A to 40 *CFR* Part 423: Steam Electric Power Generating Point Source Category).

Code	Priority pollutant[a]	Code	Priority pollutant[a]
001	Acenaphthene	038	Ethylbenzene
002	Acrolein	039	Fluoranthene
003	Acrylonitrile	040	4-Chlorophenyl phenyl ether
004	Benzene	041	4-Bromophenyl phenyl ether
005	Benzidine	042	bis(2-Chloroisopropyl) ether
006	Carbon tetrachloride (tetrachloromethane)	043	bis(2-Chloroethoxy) methane
007	Chlorobenzene	044	Methylene chloride (dichloromethane)
008	1,2,4-Trichlorobenzene	045	Methyl chloride (dichloromethane)
009	Hexachlorobenzene	046	Methyl bromide (bromomethane)
010	1,2-Dichloroethane	047	Bromoform (tribromomethane)
011	1,1,1-Trichloroethane	048	Dichlorobromomethane
012	Hexachloroethane	051	Chlorodibromomethane
013	1,1-Dichloroethane	052	Hexachlorobutadiene
014	1,1,2-Trichloroethane	053	Hexachlorocyclopentadiene
015	1,1,2,2-Tetrachloroethane	054	Isophorone
016	Chloroethane	055	Naphthalene
018	bis(2-Chloroethyl)ether	056	Nitrobenzene
019	2-Chloroethyl vinyl ether (mixed)	057	2-Nitrophenol
020	2-Chloronaphthalene	058	4-Nitrophenol
021	2,4, 6-Trichlorophenol	059	2,4-Dinitrophenol
022	Parachlorometa cresol	060	4,6-Dinitro-o-cresol
023	Chloroform (trichloromethane)	061	n-Nitrosodimethylamine
024	2-Chlorophenol	062	n-Nitrosodiphenylamine
025	1,2-Dichlorobenzene	063	n-Nitrosodi-n-propylamine
026	1,3-Dichlorobenzene	064	Pentachlorophenol
027	1,4-Dichlorobenzene	065	Phenol
028	3,3-Dichlorobenzidine	066	bis(2-Ethylhexyl) phthalate
029	1,1-Dichloroethylene	067	Butyl benzyl phthalate
030	1,2-trans-Dichloroethylene	068	di-n-Butyl phthalate
031	2,4-Dichlorophenol	069	di-n-Octyl phthalate
032	1,2-Dichloropropane	070	Diethyl phthalate
033	1,2-Dichloropropylene (1,3-dichloropropene)	071	Dimethyl phthalate
034	2,4-Dimethylphenol	072	1,2-Benzanthracene (benzo[a]anthracene
035	2,4-Dinitrotoluene	073	Benzo(a)pyrene (3,4-benzo-pyrene)
036	2,6-Dinitrotoluene	074	3,4-Benzofluoranthene (benzo[b]fluoranthene)
037	1,2-Diphenylhydrazine	075	11,12-Benzofluoranthene (benzo[b]fluoranthene)

Code	Priority pollutant[a]	Code	Priority pollutant[a]
076	Chrysene	102	Alpha-BHC
077	Acenaphthylene	103	Beta-BHC
078	Anthracene	104	Gamma-BHC (lindane)
079	1,12-Benzoperylene (benzo[ghi]perylene)	105	Delta-BHC
080	Fluorene	106	PCB–1242 (Arochlor 1242)[b]
081	Phenanthrene	107	PCB–1254 (Arochlor 1254)
082	1,2,5,6-Dibenzanthracene (dibenzo[a,h]anthracene)	108	PCB–1221 (Arochlor 1221)
		109	PCB–1232 (Arochlor 1232)
083	Indeno (1,2,3-cd) pyrene (2,3-o-phenylene pyrene)	110	PCB–1248 (Arochlor 1248)
		111	PCB–1260 (Arochlor 1260)
084	Pyrene	112	PCB–1016 (Arochlor 1016)
085	Tetrachloroethylene	113	Toxaphene
086	Toluene	114	Antimony
087	Trichloroethylene	115	Arsenic
088	Vinyl chloride (chloroethylene)	116	Asbestos
089	Aldrin	117	Beryllium
090	Dieldrin	118	Cadmium
091	Chlordane (technical mixture and metabolites)	119	Chromium
		120	Copper
092	4,4-DDT	121	Cyanide, total
093	4,4-DDE (p,p-DDX)	122	Lead
094	4,4-DDD (p,p-TDE)	123	Mercury
095	alpha-Endosulfan	124	Nickel
096	beta-Endosulfan	125	Selenium
097	Endosulfan sulfate	126	Silver
098	Endrin	127	Thallium
099	Endrin aldehyde	128	Zinc
100	Heptachlor		
101	Heptachlor epoxide (BHC-hexachlorocyclohexane)	129	2,3,7,8-Tetrachloro-dibenzo-p-dioxin (TCDD)

[a] There were originally 129 priority pollutants, but three had been removed from the list by the time the source regulation was issued.

[b] PCB = polychlorinated biphenyls.

The general pretreatment regulations (40 *CFR* 403) on which pretreatment programs nationwide are based establish the procedures, responsibilities, and requirements for industries and federal, state, and local regulatory agencies. Control authorities, which may be POTWs if authorized by their respective states, or the state itself, are primarily responsible for enforcing the pretreatment regulations. The regulations include "prohibited discharge standards" for all nondomestic (industrial) POTW users (40 *CFR* 403.5) and "categorical pretreatment standards" for specific industries (40 *CFR* 405–471).

Pretreatment programs are not limited to priority pollutants. For example, the Miami, Florida, Water and Sewer Department's program establishes limits for all toxic organics in wastewater (Miami-Dade County, Florida, 2006), and the pretreatment standards for petroleum refineries (40 *CFR* 419.15) address only conventional pollutants. Pretreatment standards for conventional pollutants ensure that a POTW's treatment capacity is not overwhelmed by industrial discharges. [For more information on the pretreatment program, see U.S. EPA's *Introduction to the National Pretreatment Program* (U.S. EPA, 1999a).]

Prohibitions. The general pretreatment regulations list several discharge prohibitions (40 *CFR* 403.5). In general, an industrial user's discharge to a POTW may not interfere with treatment plant processes or sludge disposal options, or pass through the plant untreated. Nor can the following eight types of pollutants be introduced to a POTW [40 *CFR* 403.5(b)]:

1. "Pollutants which create a fire or explosion hazard in the POTW, including, but not limited to, wastestreams with a closed cup flashpoint of less than 140° F or 60° C using the test methods specified in 40 *CFR* 261.21;
2. Pollutants which will cause corrosive structural damage to the POTW, but in no case Discharges with pH lower than 5.0, unless the works is specifically designed to accommodate such Discharges;
3. Solid or viscous pollutants in amounts which will cause obstruction to the flow in the POTW resulting in Interference;
4. Any pollutant, including oxygen demanding pollutants (BOD, etc.) released in a Discharge at a flow rate and/or pollutant concentration which will cause Interference with the POTW;
5. Heat in amounts which will inhibit biological activity in the POTW resulting in Interference, but in no case heat in such quantities that the temperature at

the POTW Treatment Plant exceeds 40° C (104° F) unless the Approval Authority, upon request of the POTW, approves alternate temperature limits;

6. Petroleum oil, nonbiodegradable cutting oil, or products of mineral oil origin in amounts that will cause interference or pass through;
7. Pollutants which result in the presence of toxic gases, vapors, or fumes within the POTW in a quantity that may cause acute worker health and safety problems;
8. Any trucked or hauled pollutants, except at discharge points designated by the POTW."

If a POTW determines that these prohibitions are not enough to protect it against interference or pass-through via industrial users, it can set and enforce the local pollutant limits deemed necessary [40 *CFR* 403.5(d)]. For more information, see the "Local Pretreatment Limits" section of this chapter.

Categorical Pretreatment Standards. As of March 31, 2007, the U.S. EPA had established pretreatment standards for 35 categories of industrial facilities (Table 2.2). For details of the most current pretreatment standards, see 40 *CFR* Chapter I, Subchapter N.

There are basically two types of categorical pretreatment standards:

- Pretreatment standards for existing sources (PSES), which the U.S. Environmental Protection Agency (U.S. EPA) establishes taking into account the cost of upgrading existing systems versus the benefits obtained; and
- Pretreatment standards for new sources (PSNS), which require new sources to install the best available technology when constructing their facilities.

U.S. EPA promulgates categorical pretreatment and direct-discharge standards for new sources at the same time [40 *CFR* 401.1(g)], so they are found in the same regulatory section. However, the electroplating industry has only pretreatment standards because regulators determined that electroplating facilities do not discharge directly to waterbodies (40 *CFR* 413).

Categorical pretreatment standards may include concentration (expressed in mass per volume of wastewater) and/or mass limits (expressed as mass per unit of production) for specific pollutants [40 *CFR* 403.6(c)]. They usually specify maximum daily limits, a maximum monthly average, or a 4-day average standard. If only one type of limit (i.e., either concentration or mass) is listed, local regulators

TABLE 2.2 Industries with categorical pretreatment standards (U.S. EPA, 1999; *CFR* Parts 405 through 471, as of March 31, 2007).[a]

Point source category	40 CFR part number	Subcategory[b]	
		PSES	PSNS[c]
Aluminum forming	467	A–F	A–F
Battery manufacturing	461	A–G	A–G
Carbon black manufacturing	458	—	A–D
Centralized waste treatment	437	A–D	A–D
Coil coating	465	A–D	A–D
Concentrated animal feeding operations	412	A–D	A–D
Copper forming	468	A	A
Electrical and electronic components	469	A–D	A–D
Electroplating	413	A–B, D–H	—
Fertilizer manufacturing	418	—	A–G
Glass manufacturing	426	—	H, K–M
Grain mills	406	—	A
Ink formulating	447	—	A
Inorganic chemicals manufacturing	415	A–BO	A–BO
Iron and steel manufacturing	420	A–F, H–J, L	A–F, H–J, L
Leather tanning and finishing	425	A–I	A–I
Metal finishing	433	A	A
Metal molding and casting	464	A–D	A–D
Nonferrous metals forming and metal powders	471	A–J	A–J
Nonferrous metals manufacturing	421	B–AE	B–AE
Oil and gas extraction	435	D	D
Organic chemicals, plastics, and synthetic fibers	414	B–H, K	B–H, K
Paint formulating	446	—	A
Paving and roofing materials (tars and asphalt)	443	—	A–D
Pesticide chemicals	455	A, C, E	A, C, E
Petroleum refining	419	A–E	A–E
Pharmaceutical manufacturing	439	A–D	A–D
Porcelain enameling	466	A–D	A–D
Pulp, paper, and paperboard	430	A–G, I–L	A–G, I–L
Rubber manufacturing	428	—	E–K
Soap and detergent manufacturing	417	—	O–R
Steam electric power generating	423	Established	Established
Timber products processing	429	F–H	F–H
Transportation equipment cleaning	442	A–C	A–C
Waste combustors	444	A	A

[a] Categories shown are those with numerical pretreatment standards or prohibition of discharge to publicly owned treatment works, either complete or partial. The other categories regulated under 40 *CFR* Parts 405 through 471 either have no pretreatment requirement or are only required to meet the 40 *CFR* Part 403 requirements.

[b] — = not established in the regulations; A through AE = subparts assigned to the subcategories within each point source category (see Chapter 6); Established = the category has pretreatment standards, even though there are no subcategories; PSES = pretreatment standards for existing sources; PSNS = pretreatment standards for new sources.

[c] New sources are regulated processes for which construction *started after* the date the PSNS were proposed. See 40 *CFR* Part 122.2 for the distinction between a "new source" and a "new discharger."

may calculate equivalent limits based on the industrial user's average production rate or daily regulated process wastewater flow rate [40 *CFR* 403.6(c)(3) to (5)]. The equivalent limits are then that user's pretreatment standards [40 *CFR* 403.6(c)(7)].

Industrial users may not use dilution to meet the pretreatment standards [40 *CFR* 403.6(d)]; in fact, local regulators may impose mass limits to ensure that adequate pretreatment is provided. If process effluents are mixed with other wastestreams before treatment, the control authority may establish alternate concentration or mass limits based on the dilution provided by the non-process effluents [40 CFR 403 *CFR* 6(e)]. However, the alternate limits may not be used if they are below a pollutant's analytical detection limit; in this case, the control authority may require segregation of the wastewater to allow its proper monitoring [40 *CFR* 403.6(e)(2)]. Also, the monitoring location will be different if an alternate pretreatment standard is being used [40 *CFR* 403.6(e)(4)].

Industrial User Definitions. The pretreatment regulations currently have requirements for both categorical and significant non-categorical industrial users. To determine whether an industrial user is covered by a categorical pretreatment standard, see 40 *CFR* 403.6 and the appropriate subchapters of 40 *CFR* Chapter N (Table 2.2 shows the currently regulated industries). When new categorical standards are promulgated, industrial users and POTWs have until 60 days after its effective date to request the U.S. EPA to issue a written certification on whether a specific user fits in the category and must meet its requirements [40 *CFR* 403.6(a)(1)]. If a POTW makes this request, it must submit a copy to the affected industrial user, which has 30 days to comment on the request.

Industrial users that are not categorical users may still be significant non-categorical industrial users, which must meet the pretreatment limits established by the local regulators. According to 40 *CFR* 403.3(v)(1), there are two types of significant industrial users:

- Those covered by a categorical pretreatment standard (40 *CFR* 403.3(v)(1)(i); and
- Those that discharge more than 95 m^3/d (25 000 gpd) of process wastewater—excluding sanitary, noncontact cooling and boiler blowdown wastewater—on average, contribute process wastewater at more than 5% of the POTW's average dry-weather hydraulic or organic capacity, or are reasonably likely to adversely affect POTW operations or violate a pretreatment requirement (as determined by regulators) [40 *CFR* 403.3(v)(1)(ii)].

The regulators may make a determination that significant users that meet 40 *CFR* 403.3(v)(1)(i) or (1)(ii) are non-significant users if they meet the conditions specified in 40 *CFR* 403.3(v)(2) or (3), respectively.

The publicly owned treatment works must notify each significant industrial user of its status and the related requirements [40 *CFR* 403.8(f)(2)(iii)]. Users must be notified within 30 days once the appropriate authority (typically the regional U.S. EPA office) has approved the POTW's list of significant industrial users [which is required under 40 *CFR* 403.8(f)(6)].

Requirements for All Industrial Users. Every industrial user must meet certain requirements of the general pretreatment regulations. For example, all industrial users must allow the POTW to randomly sample and analyze their discharges for possible violations [40 *CFR* 403.8(f)(2)(v)], report various data on their discharges at a POTW-specified schedule [40 *CFR* 403.12(h)], immediately notify the POTW about any discharge that could cause problems for the treatment works [40 *CFR* 403.12(f)], and notify the POTW of any pretreatment standard violation within 24 hours of becoming aware of it [40 *CFR* 403.12(g)(2)].

Also, all industrial users must notify the POTW, the state's hazardous waste authorities, and the U.S. EPA Regional Waste Management Division Director in writing about any discharge that would be considered a hazardous waste if disposed via another method [40 *CFR* 403.12(p)]. The requirements contain specific directions on exemptions, the contents of the written notice, and the signed certification statement.

Users discharging stormwater associated with certain industrial activities [40 *CFR* 122.26(a)(14)] to large or medium municipal separate storm sewer systems [40 *CFR* 122.26(b)(4) and (7)] must provide the following information to the municipal authority [40 *CFR* 122.26(a)(4)]:

- Facility name,
- Contact name and telephone number,
- Location of the discharge,
- A description of its principal products or services, and
- Any existing National Pollutant Discharge Elimination System (NPDES) permits.

For more information on NPDES permits, see the "Direct-Discharge Regulations" section of this chapter.

Reporting Requirements for Categorical Industrial Users. Categorical industrial users have certain reporting, recordkeeping, and other obligations. The reporting requirements for existing categorical industrial users include the following (40 *CFR* 403.12):

- A baseline monitoring report within 180 days after a categorical pretreatment standard takes effect or after the POTW makes a formal determination that the industrial user is subject to pretreatment standards and notifies the industrial user. It includes a brief process description, the pretreatment standards applicable to each regulated process, the flowrate and analytical data for the wastewater from each regulated process, a statement certifying that the user is either in compliance with the standards or will adhere to a schedule (to be provided in the report) bringing it in compliance by the applicable date (40 *CFR* 403.12[b]).
- If a compliance schedule is necessary, a progress report within 14 days of each milestone date. The milestones must be less than 9 months apart, and each report must be filed within 9 months of the previous one [40 *CFR* 403.12(c)].
- A compliance report within 90 days of the compliance date (the day that the industrial user first meets the relevant categorical pretreatment standards, which must be less than 3 years after they were promulgated). It must certify that compliance has been achieved and include appropriate monitoring data supporting this assertion [40 *CFR* 403.12(d)].
- Continued compliance reports every June and December. They contain monitoring results of flows and pollutant concentrations or mass, depending on the applicable limits [40 *CFR* 403.12(e)(1)]. Regulators may require users to submit these reports more frequently. They also may reduce the reporting frequency to once a year if the industrial user meets the conditions in 40 *CFR* 403.12(e)(3).

Categorical industrial users that are new sources must meet similar reporting requirements, but the deadlines are different (40 *CFR* 403.12).

Industrial users also may have to meet other significant reporting requirements, including signatory and recordkeeping requirements (see 40 *CFR* 403.12). Although the federal categorical pretreatment regulations sometimes require industrial users to monitor for long lists of parameters, POTWs may waive the requirement to monitor some pollutants if an industrial user demonstrates that it meets the conditions in 40 *CFR* 403.12(e)(2).

According to 40 *CFR* 403.12(q), non-significant categorical industrial users only have to submit an annual certification that they met the conditions in 40 *CFR* 403.3(v)(2).

Reporting Requirements for Significant Noncategorical Industrial Users. Significant industrial users must file special reports every 6 months, even if they are not categorical users [40 *CFR* 403.12(h)]. These reports contain much of the same information specified above for categorical users. The reporting deadlines are specified by the POTWs.

Other Provisions. The general pretreatment regulations contain other provisions that all industrial users should evaluate.

Removal Credits. Industrial users subject to categorical pretreatment standards may apply for removal credits at POTWs that meet certain requirements; if the removal credit is approved, the industrial user will receive pretreatment standards that are greater than the corresponding categorical limits because the removal achieved at the POTW for the pollutants is taken into account. Only POTWs that have received approval of a petition to grant removal credits to U.S. EPA (or a U.S. EPA-authorized state) may elect to issue removal credits [40 *CFR* 403.7(a)(3)]. The POTW can only receive such approval if it meets the conditions in 40 *CFR* 403.7(a)(3), which include having an approved pretreatment program or awaiting approval of an approved pretreatment program, consistently removing the related pollutants as specified under 40 CFR 403.7(b), and not exceeding any federal, state, or local sludge requirements for the sludge management method it uses. Removal credits are available for the following pollutants:

- Those included in Table 2.3 when a POTW's solids disposal practices meet 40 *CFR* 503's requirements.
- Those included in Table 2.4 if the pollutants' concentrations in the POTW's solids are less than those in this table.
- Any pollutant in the POTW's wastewater treatment residuals if the POTW sends them to a municipal solid waste landfill that meets 40 *CFR* 258 requirements.

Pretreatment Program Requirements. The regulatory provisions pertaining to establishing or modifying a POTW's pretreatment program (40 *CFR* 403.8 and 403.9) have certain spin-off requirements for industrial users. Therefore, industrial users should

Table 2.3 Regulated pollutants in 40 *CFR* Part 503 eligible for a removal credit (40 *CFR* Part 403, Section 403.7 and Appendix G, Section I).

	Use or disposal practice		
Pollutant	**Land application**	**Surface disposal**[a]	**Incineration**[b]
Arsenic	X	X	X
Beryllium	—[c]	—	X
Cadmium	X	—	X
Chromium	—	X	X
Copper	X	—	—
Lead	X	—	X
Mercury	X	—	X
Molybdenum	X	—	—
Nickel	X	X	X
Selenium	X	—	—
Zinc	X	—	—
Total hydrocarbons	—	—	X[d]

[a] Surface disposal site without a liner and leachate collection system.

[b] Firing of sludge in an incinerator.

[c] — = value not specified.

[d] The following organic pollutants are eligible for a removal credit if the requirements for total hydrocarbons in Subpart E of 40 *CFR* Part 503 are met when sludge is fired in an incinerator: acrylonitrile, aldrin/dieldrin (total), benzene, benzidine, benzo(a)pyrene, bis(2-chloroehtyl)ether, bis(2-ethylhexyl)phthalate, bromodichloromethane, bromoethane, bromoform, carbon tetrachloride, chlordane, chloroform, chloromethane, DDD, DDE, DDT, dibromochloromethane, dibutyl phthalate, 1,2-dichloroethane, 1,1-dichloroethylene, 2,4-dichlorophenol, 1,3-dichloropropene, diethyl phthalate, 2,4-dinitrophenol, 1,2-diphenylhydrazine, di-n-butyl phthalate, endosulfan, endrin, ethylbenzene, heptachlor, heptachlor epoxide, hexachlorobutadiene, alpha-hexachlorocyclohexane, beta-hexachlorocyclohexane, hexachlorocyclopentadiene, hexachloroethane, hydrogen cyanide, isophorone, lindane, methylene chloride, nitrobenzene, n-nitrosodimethylamine, n-nitrosodi-n-propylamine, pentachlorophenol, phenol, polychlorinated biphenyls, 2,3,7,8-tetrachlorodibenzo-p-dioxin, 1,1,2,2-tetrachloroethane, tetrachloroethylene, toluene, toxaphene, trichloroethylene, 1,2,4-trichlorobenzene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, and 2,4,6-trichlorophenol.

provide comments on proposed new programs or modifications, if appropriate. Industrial users should consult U.S. EPA's guidance materials on preparing pretreatment programs (U.S. EPA, 2004a) and U.S. EPA's "model pretreatment ordinance" document before commenting, to ensure that the local POTW is applying the regulations correctly (U.S. EPA, 2007a).

Table 2.4 Additional pollutants eligible for a removal credit (mg/kg-dry weight basis) (40 *CFR* Part 403, Section 403.7 and Appendix G, Section II).

	Use or disposal practice			
		Surface disposal		
Pollutant	Land application	Unlined[a]	Lined[b]	Incineration
Arsenic	—c	—	100 000	—
Aldrin/dieldrin (total)	2.7	—	—	—
Benzene	16 000	140	3 400	—
Benzo(a)pyrene	15	100 000	100 000	—
Bis(2-ethylhexyl)phthalate	—	100 000	100 000	—
Cadmium	—	100 000	100 000	—
Chlordane	86	100 000	100 000	—
Chromium (total)	100 000	—	100 000	—
Copper	—	46 000	100	1 400
DDD, DDE, DDT (total)	1.2	2 000	2 000	—
2,4-Dichlorophenoxy-acetic acid	—	7	7	—
Fluoride	730	—	—	—
Heptachlor	7.4	—	—	—
Hexachlorobenzene	29	—	—	—
Hexachlorobutadiene	600	—	—	—
Iron	78 000	—	—	—
Lead	—	100 000	100 000	—
Lindane	84	28 000	28 000	—
Malathion	—	0.63	0.63	—
Mercury	—	100 000	100 000	—
Molybdenum	—	40	40	—
Nickel	—	—	100 000	—
n-Nitrosodimethylamine	2.1	0.088	0.088	—
Pentachlorophenol	30	—	—	—
Phenol	—	82	82	—
Polychlorinated biphenyls	4.6	50	50	—
Selenium	—	4.8	4.8	4.8
Toxaphene	10	26 000	26 000	—
Trichloroethylene	10 000	9 500	10 000	—
Zinc	—	4 500	4 500	4 500

[a] Active sludge unit without a liner and leachate collection system.

[b] Active sludge unit with a liner and leachate collection system.

[c] — = value not specified.

Variances. Variances from categorical pretreatment standards (40 *CFR* 403.13) can only be used to modify standards for individual pollutants. They are based on a demonstration that an industrial user's factors (e.g., volume of wastewater, type of processes, or compliance costs) are fundamentally different from those considered when establishing the applicable standard.

Other. Four other sections worthy of consideration include 40 *CFR* 403.14 (Confidentiality), 40 CFR 403.15 (Net/Gross Calculations), 40 *CFR* 403.16 (Upset Provision), and 40 *CFR* 403.17 (Bypass). Careful review of these provisions is important to ensure that proprietary information is adequately protected while enforceable requirements are met.

Regulatory Outlook. This discussion pertains to the national pretreatment program that existed as of March 31, 2007. For details on U.S. EPA's plans regarding future effluent limitations, see the "Direct-Discharge Regulations" section of this chapter. Readers should supplement the references in this manual with any new U.S. EPA regulations in existence when design and facility development activities are undertaken.

LOCAL PRETREATMENT LIMITS. A publicly owned treatment works must have a pretreatment program if

- Its design flow is more than 0.22 m^3/s (5 mgd) and its industrial users' discharges are subject to pretreatment standards or contain pollutants that may pass through or interfere with POTW operations; or
- Regulators have determined that it needs a pretreatment program because of the nature or volume of industrial user discharges or because of POTW upsets, biosolids contamination, or other circumstances [40 *CFR* 403.8(a)].

The pretreatment program may be administered by a private company. For example, the Indianapolis, Indiana, pretreatment program is administered by United Water, the city's POTW operations contractor.

Limits. Before deciding to install a new plant or increase production, industrial users should consult the general, categorical, and local pretreatment standards and determine how much wastewater pretreatment will be required. Local limits must take into account both the area's water quality management plans [40 *CFR* 403.9(g)] and the U.S. EPA's general pretreatment standards. Publicly owned treatment works also may develop best management practices (BMPs) to achieve local pretreatment limits, and these BMPs are considered to be pretreatment standards, according to a federal rule promulgated on October 15, 2005 [40 *CFR* 403.5(c)(4)]. (For more information on BMPs, see the "Direct-Discharge Regulations" section in this chapter.)

Local limits may be more stringent than categorical or general pretreatment standards. They are established at the POTW's discretion, based on its treatment system, effluent or biosolids disposal options, and NPDES permit. So, local limits may differ from city to city (Table 2.5). These limits may be based on maximum concentrations at any time, monthly averages, daily maximums, grab samples, composite samples, or even total mass. Following are examples of differences in local limits and pretreatment ordinances:

- In Des Moines, Iowa, industrial users are prohibited from discharging certain pollutants (such as BOD, arsenic, phenols, cyanide) in quantities that, when combined with the discharges from all other sources, will exceed a certain mass per day in the POTW's influent. They also must meet daily maximum limits on benzene alone and combined with toluene, ethylbenzene, and xylenes (BTEX) in gasoline-cleanup projects (Des Moines, Iowa, 2006).
- Chicago has stringent mercury limits because the states in the Great Lakes basin are required to reduce bioaccumulative, toxic, and persistent substances in their wastewater discharges (Metropolitan Water Reclamation District of Greater Chicago, 2005a).
- Hampden Township, Pennsylvania, has established local limits for BOD, TSS, ammonia as nitrogen, and total phosphorus as phosphate (PO_4) (Hampden Township, Pennsylvania, 2006).
- Miami has daily mass limits for BOD and TSS discharges, and instantaneous limits for chlorinated hydrocarbons (e.g., carbon tetrachloride, 1,2-cis-dichloroethylene, tetrachloroethylene, trichloroethylene, and vinyl chloride) (Miami-Dade County, 2006).
- Houston does not have pretreatment standards for toxic organic pollutants because it demonstrated, in accordance with 40 *CFR* 403.8(f)(4), that they were unnecessary. (For more information, see http://www.infosolinc.net/edischargepermits/houston_site and click on "Local Limits.")
- Los Angeles may require BMPs to reduce POTW pollutant loadings and pretreatment to remove compounds that may interfere with the ability to reuse treated wastewater (City of Los Angeles, 2001).

Table 2.5 Examples of local pretreatment instantaneous maximum limits (Chicago, 2005b; Des Moines, Iowa, 2006; Hampden Township, Pennsylvania, 2006; Houston, Texas, 2006A; Los Angeles, 2001; Miami Dade, 2006).

Pollutant	Chicago, Illinois	Des Moines, Iowa	Hampden Township, Pennsylvania	Houston, Texas	Los Angeles, California[a]	Miami, Florida
Ammonia, mg/L	—[b]	[c]	40 (as nitrogen)	—	—	100 (un-ionized)
Arsenic (total), mg/L	—	0.0069d	—	3[e]	3	0.325
Barium (total), mg/L	—	6.18[d]	—	—	—	—
Benzene (for gasoline remediation projects), mg/L	—	0.05	—	—	None	200[f]
Benzene, ethylbenzene, toluene, and xylenes (sum, for gasoline remediation projects), mg/L	—	0.75	—	—	None	—
Biochemical oxygen demand, mg/L	—	[c]	500[g]	—	—	200[f]
Cadmium, mg/L	2	0.24[d]	0.14	0.4[e]	15	0.187
Carbon tetrachloride, mg/L	—	—	—	—	None	0.22
Chromium (total), mg/L	25	6.0[d]	0.84	3[e]	10	7.6
Chromium (hexavalent), mg/L	10	3.9[d]	—	—	—	—
Copper (total), mg/L	3	0.75[d]	0.22	3[e]	15	0.5
Cyanide (free), mg/L	—	—	—	—	2	—
Cyanide (total), mg/L	5	0.2[d]	17.6	g	10	0.5
1,2-cis-Dichloroethylene	—	—	—	—	None	3.75
Fats, oils, and greases (total), mg/L[j]	250	—	140	400[i]	—	100
Fluoride (total), mg/L	—	11.37[d]	—	—	—	—
Iron (total), mg/L	250	—	—	—	—	—
Lead (total), mg/L	0.5	1.07[d]	7.0	1.5[e]	5	0.7
Manganese (total), mg/L	—	6.36[d]	—	—	—	1.9
Mercury (total), mg/L	0.0025 10	0.35[d]	0.04	0.02[e]	None	0.01
Molybdenum (total), mg/L	—	—	—	—	—	0.4
Nickel (total), mg/L	10	1.28d	0.72	3[e]	12	0.39
Oil and grease (mineral), mg/L	—	100	—	—	—	—
Oil and grease (dispersed, total), mg/L	—	400	—	—	600	—
Oil and grease (floatable)	—	—	—	—	None visible	—
Organics, man-made 11	—	—	—	—	None	—
pH range, standard units	5–10 12	5–12	5–9	5–11	5.5–11	5.5–11.5
Phenols (total), mg/L	—	7.82[d]	94.4	—	—	—

(continued on next page)

TABLE 2.5 *(Continued)*

Pollutant	Chicago, Illinois	Des Moines, Iowa	Hampden Township, Pennsylvania	Houston, Texas	Los Angeles, California[a]	Miami, Florida
Phosphorus as phosphate (total), mg/L	—	—	40	—	—	—
Polychlorinated biphenyls, mg/L	—	—	—	—	—	0.008
Selenium (total), mg/L	—	0.59d	—	5[e]	—	0.65
Silver (total), mg/L	—	0.68d	0.48	2[e]	5	0.60
Sulfides, mg/L	—	—	—	5[e]	0.1 (dissolved)	—
Temperature, °C	< 66	< 66	< 66	< 45	< 60	< 66
°F	< 150	< 150	< 150	< 113	< 140	< 150
Tetrachloroethylene, mg/L	—	—	—	—	None	0.125
Thallium, mg/L	—	—	—	—	—	0.0005
Total Kjeldahl nitrogen, mg/L	—	[c]	—	—	—	—
Total petroleum hydrocarbon, mg/L	—	10.0	—	—	—	50[n]
Total suspended solids, mg/L	—	[c]	500	—	—	200[f]
Trichloroethylene, mg/L	—	—	—	—	None	0.16
Vinyl chloride, mg/L	—	—	—	—	None	0.08
Zinc (total), mg/L	15	1.5[d]	4.9	6[e]	25	6.8

[a] Additional limits may be imposed for other compounds if they would interfere with the reclamation or reuse of the treated wastewater or biosolids or with the POTW's compliance with its air quality limits.

[b] — = value not specified.

[c] Only 30-day average mass limits for the aggregate of all industrial discharges to the POTW established.

[d] Monthly averages and daily maximum mass limits also established.

[e] The ordinance also establishes limits for composite samples.

[f] For a total of 65.9 kg/d (145 lb/d), not to exceed the concentration shown unless allowed by the POTW.

[g] Average 5-day BOD (no time period specified).

[h] Less than what would liberate hydrogen cyanide gas over 2 mg/L as cyanide (including cyanogens).

[i] Average concentration (no time period specified).

[j] Hexane-extractable materials, U.S. EPA Method 1664.

[k] Value shown is an instantaneous limit; other limits include 0.001 mg/L for daily composites and 0.0005 mg/L for monthly averages. Higher concentrations allowed in certain cases.

[l] Includes total identifiable chlorinated hydrocarbons not already indicated in the table, gasoline, kerosene, naphtha, ethers, alcohols, ketones, aldehydes, peroxides, chlorates, perchlorates, bromates, carbides, hydrides, solvents, pesticides or jet fuel.

[m] Continuously monitored discharges may exceed upper pH by less than 0.5 unit for a maximum of 4 hours in any calendar day.

[n] Recoverable, silica gel-treated hexane-extractable materials, U.S. EPA Method 1664.

Sometimes, local regulations prohibit industrial wastewater from being discharged without a permit or approval from the pretreatment authority.

Industrial users can and should comment on proposed local limits to prevent them from becoming onerous—especially if they are unnecessary for the POTW to meet its NPDES discharge limits and dispose of its sludge cost-effectively [40 *CFR* 403.5(c)(3)]. Industrial users also can cooperate with the POTW to improve the treatment works' performance and thereby ameliorate pretreatment requirements.

Fees or Surcharges. Publicly owned treatment works typically charge fees or surcharges for treating industrial wastewater (see Table 2.6 for examples). Some fees correspond proportionally (based on flow rate) to the cost of constructing, operating, and maintaining the POTW. Others reflect the additional effort required compared to a POTW that treats only domestic wastewater. Surcharges may be applied to flow rates above certain values, excess BOD and TSS, or concentrations of other pollutants (e.g., total Kjeldahl nitrogen and oil and grease). Other fees may be applied for such items as sewer connections, permitting, and wastewater effluent analysis.

When designing a pretreatment system, industrial users should select the most cost-effective option based on a comparison of pretreatment costs with the applicable surcharges and fees.

Permitting. According to 40 *CFR* 403.8(f)(1)(iii), significant industrial users must have a permit, an equivalent individual control mechanism, or a general control mechanism for meeting the conditions specified in 40 *CFR* 403.8(f)(1)(iii)(A). (An *equivalent control mechanism* is something with as much specificity and control as a permit.) The permit or control mechanism must be renewed every 5 years (or sooner), be enforceable, and contain requirements for:

- Effluent limits,
- Self-monitoring,
- Sampling,
- Reporting,
- Notification, and
- Recordkeeping.

Permits also must include applicable civil and criminal penalties for noncompliance. However, compliance with the permit terms does *not* shield an industrial user from liability for failing to comply with federal pretreatment requirements that were not noted in the permit.

Table 2.6 Example of user fees or surcharges (Chicago, Illinois, 2005b; Des Moines, Iowa, 2006; Hampden Township, Pennsylvania, 2006; Houston, Texas, 2006a; City of Los Angeles, California, accessed May, 28, 2006; City of Los Angeles, California, 1997; Miami-Dade, 2002).

City, state	Type of charge	Charge[a]	
Chicago, Illinois	User charge[b]	TSS	= \$0.40/kg (\$0.18/lb)
		BOD	= \$0.53/kg (\$0.24/lb)
		Flowrate	= \$59.70/1 000 m^3 (\$225.80/MG)
Des Moines, Iowa	Surcharge	TSS	= \$0.35/kg (\$0.16/lb) over 250 mg/L
		BOD[c]	= \$0.24/kg (\$0.11/lb) over 200 mg/L
		TKN[d]	= \$1.34/kg (\$0.61/lb) over 30 mg/L
		O&G	= \$0.13/kg (\$0.06/lb) over 100 mg/L
Hampden Township, Pennsylvania	Sewer rate (SR)	\$75.28/q for first 45.42 m^3/q (12 000 gal/q), plus \$1.52/(m^3/q) (\$5.75/1 000 gal/q) over 45.42 m^3/q (12 000 gal/q)	
	Surcharge	BOD	= 0.002 × SR × BOD over 250 mg/L
		TSS	= 0.001 × SR × TSS over 250 mg/L
		P	= 0.003 × SR × P over 20 mg/L
		N	= 0.006 × SR × N over 20 mg/L
		O&G	= 0.002 × SR × O&G over 70 mg/L
Houston, Texas	Sewer service charge[e]	Minimum	= \$12.17 for 7.57 m^3 (2 000 gal) or less, plus
		\$1.23/m^3 (\$4.64/1 000 gal) for > 7.57 m^3 (2 000 gal)	
	Surcharge[f]	BOD	= \$0.46/kg (\$0.21/lb) over 350 mg/L
		TSS	= \$0.97/kg (\$0.44/lb) over 375 mg/L
Los Angeles, California	Sewer service charge	\$0.94/m^3 (\$2.66/748 gal)	
	Surcharge	BOD	= \$0.57/kg (\$0.26/lb) over 215 mg/L
		TSS	= \$0.75/kg (\$0.34/lb) over 205 mg/L
Miami, Florida	Sewer rate	Base charge	= \$3.00, plus
		\$0.45/m^3 (\$1.28/ccf) for 0–14 m^3 (0–5 ccf)	
		\$0.73/m^3 (\$2.06/ccf) for 17–48 m^3 (6–17 ccf)	
		\$0.90/m^3 (\$2.55/ccf) for 51 m^3 (18 ccf) and over	

[a] Rounded to two decimal figures; N = ammonia as nitrogen; O&G = oil and grease; P = total phosphorus as phosphate; q = quarter (3 months); TKN = total Kjeldahl nitrogen.

[b] Under certain conditions, the total user charge is reduced by a percentage (56.8%) of the real estate taxes paid on the previous year.

[c] Chemical oxygen demand may be used instead of BOD.

[d] Ammonia nitrogen may be used instead of TKN.

[e] For users taking city water.

[f] Surcharge adjusted annually on April 1.

Some POTWs monitor industrial users' effluent (for a fee), while others require the industry to monitor itself. If the POTW collects all the data required for periodic reports (e.g., flows and concentrations in effluent samples), industrial users do not have to meet the periodic reporting requirements of 40 *CFR* 403.12(e).

If local pretreatment regulations allow effluent trading, then industrial users can meet their local limits by establishing a trading agreement with another industrial user that has a treatment facility and has or can produce pollutant credits (New Jersey Chemical Industry Project—Effluent Trading Team, 1998). (Pollutant credits are excess removal of pollutants over the local requirements, and must be certified by the regulatory agency.) However, industrial users still need to meet their federal categorical pretreatment standards. The trading agreement would typically consist of a purchasing industrial user paying another user for the extra operation and maintenance cost of reducing pollutant concentrations below its local requirements. This results in a net reduction of the pollutant mass discharged to the POTW at a lower cost than if the purchaser of pollutant credits were to install a new wastewater treatment plant or process to remove that pollutant. The local authority must approve the agreement between the trading partners.

DIRECT-DISCHARGE REGULATIONS

PROHIBITIONS AND DEFINITIONS. The Clean Water Act forbids point sources from discharging pollutants to navigable U.S. waters without a permit [CWA Sec. 301(a)]. According to 40 *CFR* 401.11(d), a *point source* is an entity that discharges wastewater into waters of the United States via a discrete conveyance (e.g., a pipe, ditch, or channel). Point sources that discharge directly into waters of the United States are "direct dischargers" and must obtain an NPDES permit for this activity.

According to 40 *CFR* 401.11(l), *waters of the United States* include navigable waters; tributaries of navigable waters; interstate waters; and intrastate lakes, rivers, and streams that are

- Used by interstate travelers for recreation and other purposes,
- Sources of fish or shellfish sold in interstate commerce, or
- Used for industrial purposes by industries engaged in interstate commerce.

The Clean Water Act requires wastewater to be treated via at least the "best treatment technology economically achievable," regardless of the receiving waterbody's condition. However, if the receiving waters still do not meet water quality standards, more stringent limits may be imposed [CWA Sec. 301(b)]. So, the discharge location can be critical in designing a cost-effective wastewater treatment system.

CATEGORICAL REQUIREMENTS. The Clean Water Act required U.S. EPA to develop effluent limitations for a number of non-municipal dischargers. As of March 31, 2007, the agency had issued effluent limitations for 56 categories of point sources (see Table 2.7 and 40 *CFR* 405–471). Electroplating is the only category without direct-discharge effluent limitations because such facilities invariably send their wastewater to POTWs.

Types of Technology-Based Limitations. There currently are four technology-based categories of limitations:

- *Best Practicable Control Technology Currently Available (BPT).* These limitations apply to existing direct dischargers of conventional, nonconventional, and toxic pollutants. When establishing BPT limitations, the U.S. EPA must consider the age of the industry's facilities and equipment, the processes used and changes needed, the cost of the treatment process(es) required, non-water-quality environmental effects, the anticipated benefits, and any other appropriate factors. Typically, BPT limitations are based on the average of the best performing facilities in the industry, although they may be stricter if existing performances are inadequate [CWA Sec. 304(b)(1)].
- *Best Conventional Pollutant Control Technology (BCT).* These are stricter limitations for existing direct dischargers of conventional pollutants. When establishing BCT limitations, the U.S. EPA must conduct a two-part test that involves comparing the cost of treating these pollutants at a POTW and determining whether meeting these limitations would cost more than 129% of BPT costs [CWA Sec. 304(b)(4)].
- *Best Available Technology Economically Achievable (BAT).* These are stricter limitations for existing direct dischargers of toxic and nonconventional pollutants. When establishing BAT limitations, the U.S. EPA must consider the same factors used for BPT limitations, as well as economic achievability (i.e., the overall financial effect on the industry). These limitations can include requirements for process and operational changes [CWA Sec. 304(b)(2)(B)].

Table 2.7 Regulations on industrial effluent limitations (as of May 26, 2006).

Point source category	40 CFR part number
Aluminum forming	467
Asbestos manufacturing	427
Battery manufacturing	461
Canned and preserved fruits and vegetables processing	407
Canned and preserved seafood processing	408
Carbon black manufacturing	458
Cement manufacturing	411
Centralized waste treatment	437
Coal mining	434
Coil coating	465
Concentrated animal feeding operations	412
Concentrated aquatic animal production	451
Copper forming	468
Dairy products processing	405
Electrical and electronic components	469
Electroplating	413
Explosives manufacturing	457
Ferroalloy manufacturing	424
Fertilizer manufacturing	418
Glass manufacturing	426
Grain mills	406
Gum and wood chemicals manufacturing	454
Hospital	460
Ink formulating	447
Inorganic chemicals manufacturing	415
Iron and steel manufacturing	420
Landfills	445
Leather tanning and finishing	425
Meat and poultry products	432
Metal finishing	433
Metal molding and casting	464
Metal products and machinery	438
Mineral mining and processing	436
Nonferrous metals forming and metal powders	471
Nonferrous metals manufacturing	421
Oil and gas extraction	435
Ore mining and dressing	440

(continued on next page)

TABLE 2.7 *(Continued)*

Point source category	40 CFR part number
Organic chemicals, plastics, and synthetic fibers	414
Paint formulating	446
Paving and roofing materials (tars and asphalt)	443
Pesticide chemicals	455
Petroleum refining	419
Pharmaceutical manufacturing	439
Phosphate manufacturing	422
Photography	459
Plastics molding and forming	463
Porcelain enameling	466
Pulp, paper, and paperboard	430
Rubber manufacturing	428
Soap and detergent manufacturing	417
Steam electric power generating	423
Sugar processing	409
Textile mills	410
Timber products processing	429
Transportation equipment cleaning	442
Waste combustors	444

- *New Source Performance Standards (NSPS).* These limitations apply to new direct dischargers of conventional, nonconventional, and toxic pollutants. They are based on the best available demonstrated control technology, taking into account the related costs, non-water quality effects, and energy requirements (CWA Sec. 306).

The pretreatment standards for existing and new sources (PSES and PSNS, respectively) are established concurrently. (For more information, see the "Categorical Pretreatment Standards" section in this chapter.)

Numerical Limits. These effluent limitations can be based on pollutant concentration or mass (e.g., mass per unit of product, mass per unit of raw material, mass rate). In fact, according to 40 *CFR* 122.45(f)(1), all permit limits, standards, or prohibitions must be expressed in terms of mass units (e.g., pounds, kilograms, or grams) except for:

- Temperature, pH, radiation, and other pollutants that cannot be measured via mass;

- Applicable standards and limitations expressed in other units of measurement; or
- Pollutants that cannot be related to a measure of production (when establishing site-specific technology-based permit limits).

However expressed, all numerical limits must ensure that dilution will not be used as a substitute for treatment.

Compliance Schedule. All direct-discharge limitations—except those in rules promulgated after the deadline—were to be met by March 31, 1989 [40 *CFR* 125.3(a)(2)]. New categorical effluent limitations must be met by their specified deadlines, which typically are no more than 3 years after the relevant regulation was promulgated [CWA Sec. 301(b)(2)]. However, a new source whose wastewater treatment facility was built to meet all existing NSPS at the time of construction cannot be required to meet more stringent standards until:

- 10 years after construction was completed or discharge began, or
- The facility is depreciated or amortized.

This protection does not apply to toxic pollutants without NSPS before the facility was completed or to permit conditions that are not technology-based [40 *CFR* 122.29(d)(1)].

Other Potential Requirements. The effluent limitations for some industrial categories [e.g., pharmaceutical manufacturing (40 *CFR* 439) and electrical and electronic components (40 *CFR* 469)] specify monitoring requirements that may include sampling locations, monitoring parameters, and procedures for obtaining permission to reduce the number of monitored parameters.

Other regulations assume the use of pollution prevention, water use minimization, and waste minimization procedures [e.g., those for aluminum forming (40 *CFR* 467); iron and steel manufacturing (40 *CFR* 420); and pulp, paper, and paperboard (40 *CFR* 430)]. Industrial facilities should evaluate these procedures to determine whether they can help the facility meet the numerical effluent limits. (For more information on pollution prevention, water use minimization, and waste minimization procedures, see Chapter 7.)

Need to Determine Applicable Requirements. Sometimes a manufacturing facility or process has to meet effluent limitations for multiple industrial categories, subcategories, or processes. The Metal Products & Machinery (MP&M) regulations

(40 *CFR* 438), for example, apply to facilities that generate oily wastewater when manufacturing, rebuilding, or maintaining finished metal products, parts, or machines. Many diverse industries—aerospace, bus and truck, electronic equipment, hardware, household equipment, instruments, miscellaneous metal products, mobile industrial equipment, motor vehicle, office machine, precious metals and jewelry, ordnance, railroad, ships and boats, and stationary industrial equipment—must met these requirements. All facilities that operate a process regulated under the MP&M limitations must comply with these rules, even if a pollutant is not regulated under the industry's categorical rules.

So, to determine which rules apply to their wastewaters, industrial facilities must thoroughly evaluate not only the standards for their specific category or subcategory but also those for each process (whether specific to the industry's products or ancillary).

NPDES PERMITS. The National Pollutant Discharge Elimination System program was created in 1972 to regulate wastewater discharges to U.S. waters (CWA Sec. 402). Stormwater discharges were added to the NPDES program in 1990. The related regulations can be found in 40 *CFR* 122. Industries also should review 40 *CFR* 123 (State Program Requirements), 40 *CFR* 124 (Procedures for Decisionmaking), 40 *CFR* 125 (Criteria and Standards for the National Pollutant Discharge Elimination System), and 40 *CFR* 129 (Toxic Pollutant Effluent Standards).

National Pollutant Discharge Elimination System permits are issued by either the U.S. EPA or an agency-authorized state. Individual NPDES permit applications for construction activities that disturb land [40 *CFR* 122.26(b)(14)(x) and (b)(15)(i)] must be submitted at least 90 days before the discharge begins, in accordance with 40 *CFR* 121(c)(1). Applications for all other new discharges must be submitted at least 180 days before the discharge is expected to begin and for permit renewal at least 180 days before the permit expiration date. Applications are submitted to the applicable authority on standard forms that include the requirements under 40 *CFR* 122, Subpart B, typically available from the permitting authority. NPDES permits last a maximum of 5 years.

Industrial facilities must apply for coverage under a stormwater general permit at least two days before the discharge commences under the current general permit for industrial activities (U.S. EPA, 2000). However, the 2005 proposed stormwater permit includes a 30-day wait period after coverage application (U.S. EPA, 2005a). Other requirements for this type of permit are covered under the Types of NPDES Permits section of this chapter.

General Requirements. All industries must have an NPDES permit to discharge any wastewater directly into a receiving waterbody. However, only some need an NPDES permit to discharge stormwater to a receiving waterbody or a large or medium municipal separate storm sewer system [see Table 2.8 and 40 *CFR* 122.26(b)(14)]. Large and medium municipal separate storm sewer systems are located in places with populations of 250,000 people or more and between 100,000 and 250,000 people, respectively, or in places that meet other requirements listed under 122.26(b)(4) and (7). All industries must notify the municipal authority if they discharge to a separate storm sewer system. They do not need a permit to discharge stormwater to combined sewer systems; such discharges are covered under the pretreatment or NPDES permits.

Types of NPDES Permits. NPDES permits can be individual or general, depending on such factors as geographical area, type of operation, and whether the permit is for wastewater or stormwater (40 *CFR* 122.28). An individual permit may include both wastewater and stormwater conditions. General permits typically are for stormwater discharges. To apply for coverage under such permits, qualified industrial facilities must submit a relevant notice of intent (NOI) after meeting all applicable requirements of the general permit, because a certification of compliance is required in the NOI (U.S. EPA, 2000). No stormwater permit is required for facilities that meet the requirements for "no exposure" specified in 40 *CFR* 122.26(g).

To qualify for coverage under a general stormwater permit, a facility must have a stormwater pollution prevention or management plan (based on BMPs) to minimize pollutant concentrations in stormwater, among other requirements. Stormwater BMPs may include installing a roof over an open dumpster, establishing spill-prevention and -response procedures, and implementing good-housekeeping measures. (For more information on BMPs, see the "Permit Contents" section in this chapter.)

Comment Periods. A major NPDES permitting requirement is a 30-day public comment period so interested citizens can evaluate a new or renewed permit (40 *CFR* 124.10). The public also must be given 30-days notice of an NPDES permit-related public hearing, which may be called at the regulators' discretion or public's request (40 *CFR* 124.12). In addition, if the state is authorized to issue NPDES permits, the U.S. EPA must be given up to 90 days to review and comment on each draft permit (40 *CFR* 123.44). Comment periods and hearings are one reason why most NPDES permit applications must be submitted 180 days before a new facility should begin discharging or the existing permit expires [40 *CFR* 122.21(c)(1)].

Table 2.8 Industries that must obtain stormwater NPDES permits (U.S. EPA, 1997).

Category	Description[a]
(i)	Facilities subject to stormwater effluent limitation guidelines, new source performance standards, or toxic pollutant effluent standards under 40 *CFR* subchapter N (except facilities with toxic pollutant effluent standards which are exempted under category [xi]). The list below shows the existing 40 *CFR* Part Number for each of the industrial categories for which effluent limitations have been issued.[b] 405 Dairy products processing 406 Grain mills 407 Canned and preserved fruits and vegetable processing[c] 408 Canned and preserved seafood processing 409 Beet, crystalline and liquid cane sugar refining 410 Textile mills 411 Cement manufacturing 412 Feedlots[e] 414 Organic chemicals plastics and synthetic fibers 415 Inorganic chemical manufacturing[c] 417 Soap and detergent manufacturing 418 Fertilizer manufacturing 419 Petroleum refining 420 Iron and steel manufacturing 421 Nonferrous metal manufacturing 422 Phosphate manufacturing[c] 423 Steam electric power 424 Ferroalloy manufacturing[c] 425 Leather tanning and finishing 426 Glass manufacturing[c] 427 Asbestos manufacturing 428 Rubber manufacturing 429 Timber products processing 430 Pulp, paper, and paperboard[c] 431 Builder's paper and board mills[d] 432 Meat products 433 Metal finishing 434 Coal mining[c] 436 Mineral mining and processing[c] 439 Pharmaceutical manufacturing[c] 440 Ore mining and dressing[c] 443 Paving and roofing materials 446 Paint formulating 447 Ink formulating 455 Pesticide chemicals[c] 458 Carbon black manufacturing 461 Battery manufacturing 463 Plastics molding and forming 464 Metal molding and casting 465 Coil coating 466 Porcelain enameling 467 Aluminum forming 468 Copper forming[c] 469 Electrical and electronic component 471 Nonferrous metal forming and powders
(ii)	Facilities classified by the SIC codes below: 24 Lumber and wood products (except 2434 wood kitchen cabinets, see [xi]) 26 Paper and allied products (except 265 Paperboard containers, 267 Converted paper, see [xi]) 28 Chemicals and allied products (except 283 Drugs, see [xi]) 29 Petroleum and coal products 311 Leather tanning and finishing 32 Stone, clay and glass production (except 323 Products of purchased glass, see [xi]) 33 Primary metal industry 3441 Fabricated structural metal 373 Ship and boat building and repair

Category	Description[a]
(iii)	Mineral industry Facilities classified as SIC codes 10–14, including active or inactive mining operations (except for areas of coal mining operations no longer meeting the definition of a reclamation area under 40 *CFR* 434.11[1] because the performance bond issued to the facility by the appropriate SMCRA authority has been released, or areas of non-coal mining operations that have been released from applicable state or federal reclamation requirements after December 17, 1990), and oil and gas exploration, production, processing, or treatment operations, or transmission facilities that discharge stormwater contaminated by contact with or that has come into contact with, any overburden, raw material, intermediate products, finished products, byproducts or waste products located on the site of such operations (inactive mining operations are mining sites that are not being actively mined, but which have an identifiable owner/operator; inactive mining sites do not include sites where mining claims are being maintained prior to disturbances associated with the extraction, beneficiation, or processing of mined materials, nor sites where minimal activities are undertaken for the sole purpose of maintaining a mining claim). 10 Metal mining (metallic mineral/ores) 12 Coal mining 13 Oil and gas extraction[f] 14 Non-metallic minerals except fuels Oil and gas operations that discharge contaminated stormwater at any time between November 16, 1987, and October 1, 1992, and that are currently not authorized by an NPDES permit, must apply for a permit. Operators of oil and gas exploration, production, processing, or treatment operations or transmission facilities, that are not required to submit a permit application as of October 1, 1992 in accordance with 40 *CFR* 122.26(c)(1)(iii), but that after October 1, 1992, have a discharge of a reportable quantity of oil or a hazardous substance (in a stormwater discharge) for which notification is required pursuant to either 40 *CFR* 110.6, 117.21, or 302.6, must apply for a permit.[f]
(iv)	Hazardous waste Hazardous waste treatment, storage, or disposal facilities, including those that are operating under interim status or a permit under Subtitle C of RCRA.
(v)	Landfills Landfills, land application sites, and open dumps that receive or have received any industrial waste (waste that is received from any of the facilities described under categories [i]–[xi]) including those that are subject to regulations under Subtitle D of RCRA.
(vi)	Facilities involved in the recycling of materials, including metal scrap yards, battery reclaimers, salvage yards, and automobile junkyards, including but limited to those classified as SIC 5015 (used motor vehicle parts) and 5093 (scrap and waste materials).
(vii)	Steam electric plants Steam electric power generating facilities, including coal-handling sites.

(continued on next page)

Table 2.8 *(Continued)*

Category	Description[a]
(viii)	Transportation Transportation facilities classified by the SIC codes listed below which have vehicle maintenance shops, equipment cleaning operations, or airport deicing operations. Only those portions of the facility that are either involved in vehicle maintenance (including vehicle rehabilitation, mechanical repairs, painting, fueling, and lubrication), equipment cleaning operations, airport deicing operations, or which are otherwise identified under categories (i)–(vii) or (ix)–(xi) are associated with industrial activity, and need permit coverage. 40 Railroad transportation 41 Local and interurban passenger transit 42 Trucking and warehousing (except 4221-25, see [xi]) 43 U.S. postal service 44 Water transportation 45 Transportation by air 5171 Petroleum bulk stations and terminals
(ix)	Treatment works Treatment works treating domestic wastewater or any other wastewater sludge or wastewater treatment device or system, used in the storage, treatment, recycling, and reclamation of municipal or domestic wastewater, including land dedicated to the disposal of sludge, that are located within the confines of the facility, with a design flow of 4 164 m^3/d (1.0 mgd) or more, or required to have an approved pretreatment program under 40 *CFR* 403. Not included are farm lands, domestic gardens or lands used for sludge management where sludge is beneficially reused and which are not physically located in the confines of the facility, or areas that are in compliance with section 405 of the Clean Water Act.
(x)	Construction Construction activity including clearing, grading, and excavation activities except: operations that result in the disturbance of less than 2 ha (5 ac) of total land area that are not part of a larger common plan of development or sale. [The construction "operator" must apply for permit coverage under the General Storm Water Permit for Construction Activities. The "operator" is the party or parties that either individually or taken together meet the following two criteria: (1) they have operational control over the site specification; (2) they have the day-to-day operational control of those activities at the site necessary to ensure compliance. For a typical commercial construction site, the owner and general contractor must both apply. For a typical residential development, the developer and all builders must apply. Each builder must apply even if they individually disturb less than 2 ha (5 ac) if the overall development is 2 or more ha (5 or more ac). Only one pollution prevention plan is required per site even though there may be multiple parties.]

Category	Description[a]
(xi)	Light industry Facilities classified by the SIC codes listed below (and which are not otherwise included in categories [ii]–[x]) with stormwater discharges from all areas (except access roads and rail lines) where material handling equipment, or activities, raw materials, immediate products, final products, waste materials, byproducts, or industrial machinery are exposed to stormwater. Material handling activities include the storage, loading and unloading, transportation, or conveyance of any raw material, intermediate produce, finished product, byproduct, or waste product. 20 Food and kindred product 21 Tobacco products 22 Textile mill products 23 Apparel and other textile product 2434 Wood kitchen cabinets 25 Furniture and fixtures 265 Paperboard containers and boxes 267 Miscellaneous converted paper products 27 Printing and publishing 283 Drugs 285 Paints and allied products 30 Rubber and miscellaneous plastic 31 Leather and products (except 311) 323 Products of purchased glass 34 Fabricated metal products (except 3441) 35 Industrial machinery and equipment 36 Electronic and other electric equipment 37 Transportation equipment (except 373) 38 Instruments and related products 39 Miscellaneous manufacturing 4221 Farm product storage 4222 Refrigerated storage 4225 General warehouse and storage

[a] NAICS = North American Industry Classification System; RCRA = Resource Conservation and Recovery Act; SIC = Standard Industrial Classification; SMCRA = Surface Mining Control and Reclamation Act; links to the 2002 NAICS codes and to tables with conversions from the SIC to 1997 NAICS codes and with the correspondence between the 1997 NAICS and 2002 NAICS codes can be found at http://www.census.gov/epcd/www/naics.html.

[b] The list of industries with categorical standards is based on the regulations as of September 4, 1997. See 40 *CFR* subchapter N to determine if additional industries are covered.

[c] Some facilities in this group do not have limits or standards; see 40 *CFR* subchapter N to verify.

[d] Combined with 40 CFR 430: Pulp, Paper, and Paperboard.

[e] Now "concentrated animal feeding operations."

[f] U.S. EPA exempted the oil and gas exploration, production, processing, or treatment operations, or transmission facilities from the stormwater NPDES requirements in January 2006.

Notices of intent for stormwater general permits do not require a public comment period because the general permit has already undergone this process.

Permit Contents. A wastewater NPDES permit typically contains a cover page, effluent numerical limitations, monitoring and reporting requirements, standard conditions, and special conditions (U.S. EPA, 1996). All permits include standard conditions, which are described in 40 *CFR* 122.41 under the following subsection titles: duty to comply, duty to reapply, need to halt or reduce activity is not a defense, duty to mitigate, proper operation and maintenance, permit actions, property rights, duty to provide information, inspection and entry, monitoring and records, signatory requirement, reporting requirements, bypass, and upset.

Special conditions may include implementing BMPs, additional monitoring activities, ambient stream surveys, and toxicity reduction evaluations (TREs) (U.S. EPA, 1996). For some facilities, a special condition is to notify regulators if a toxic pollutant for which there are no effluent limitations in the facility's NPDES permit is in the effluent or may be discharged in the future at concentrations greater than the notification levels specified in 40 *CFR* 122.42(a). The permit also may specify the location, design, construction, and capacity of cooling-water intake structures to minimize adverse environmental effects (40 *CFR* 125.84).

Sometimes the NPDES permit also contains variances and waivers, as indicated in the "Variances and Waivers" section of this chapter.

Stormwater general permits typically require that an industrial facility monitor its stormwater discharges visually or analytically and that it meet certain compliance-monitoring requirements.

Best Management Practices. Regulators may include BMPs in an NPDES permit when the facility cannot otherwise meet its numerical effluent limitations or when BMPs are required in the CWA [40 *CFR* 122.44(k)]. In accordance with their definition in 40 *CFR* 122.2, BMPs may consist of:

- "...schedules of activities, prohibitions of practices, maintenance procedures, and other management practices to prevent or reduce the pollution of 'waters of the United States'"; and
- "...treatment requirements, operating procedures, and practices to control plant site runoff, spillage or leaks, sludge or waste disposal, or drainage from raw material storage."

Best management practices are also required in a facility's pollution prevention or management plans to obtain coverage under a stormwater general permit.

Even if the NPDES permit does not require BMPs, industrial facilities can take advantage of the information available via the Pollution Prevention Act of 1990 (42 U.S.C. 133) to reduce pollutants in their wastewaters, which typically results in a short- or medium-term reduction of treatment and disposal costs. The Pollution Prevention Act established the following national policy:

> *"The Congress hereby declares it to be the national policy of the United States that pollution should be prevented or reduced at the source whenever feasible; pollution that cannot be prevented should be recycled in an environmentally safe manner, whenever feasible; pollution that cannot be prevented or recycled should be treated in an environmentally safe manner whenever feasible; and disposal or other release into the environment should be employed only as a last resort and should be conducted in an environmentally safe manner."*

To promote pollution prevention practices, the act included provisions to:

- Provide matching funds for state and local programs that encourage businesses to implement pollution prevention techniques, and
- Operate a source-reduction clearinghouse.

The Pollution Prevention Information Clearinghouse provides telephone references and referrals, distributes U.S. EPA documents, and has a collection of pollution prevention references available for interlibrary loan. In addition, the U.S. EPA and state and local agencies have prepared multiple documents on demonstrated pollution prevention options for specific industries. The agency also started a waste minimization partnership program to reduce the number of priority chemicals in hazardous wastes. (For more information, see the list of Web site addresses at the end of this chapter.)

Variances and Waivers. Some of the variances and waivers that can be included in NPDES permits are:

- Water quality-related variances from BAT; economic variances from BAT; or thermal variances from BPT, BCT, and BAT [as specified in 40 *CFR* 125.3(b)(1)(ii) and (iii)]. These variances are allowed only if the industrial facility meets all the requirements specified in CWA Sec. 301(c), 301(g), or 316(a), respectively.

- Deadline extensions for compliance with categorical limitations for BPT and BAT, which an industrial facility can request in accordance with 40 *CFR* 125.3(b)(2)(ii).
- A monitoring waiver for pollutants listed in the categorical effluent limitation guidelines if the industrial facility has demonstrated that its discharge does not contain such pollutants or only contains background levels of them [40 *CFR* 122.44(a)(2)]. This waiver can only be requested during permit renewals and is only good for the duration of the permit. Each time an industrial facility applies for a permit renewal, it must request and demonstrate that it qualifies for the waiver.

Reporting Requirements. National Pollutant Discharge Elimination System permit holders must report the following information [40 *CFR* 122.41(l)]:

- Any planned physical alteration or addition to the permitted facility, if they meet the conditions specified in 40 *CFR* 122.41(l)(1).
- Any anticipated noncompliance events resulting from planned changes or activities.
- Requests for permit transfers (the permit may have to be reissued).
- Monitoring results at least once per year (in a discharge monitoring report form), except for stormwater discharges associated with industrial activities, which are due every 3 years. Regulators also may provide monitoring report forms for sludge use or disposal practices.
- Reports required by compliance schedules included in the permit, which are due within 14 days of each compliance date.
- Any noncompliance event (e.g., unanticipated bypasses, upsets that exceed effluent limitations, or violations of maximum limitations for permit-specified pollutants) that may endanger human health or the environment. Permittees must report this verbally within 24 hours of the time they became aware of the event, and follow up with a written report in less than 5 days from the noncompliance event.
- Other instances of noncompliance must be included in the annual or triannual monitoring report.

- Any relevant facts not submitted with the permit application or any corrections to information in a permit application or monitoring report.

Other reporting requirements include:

- Unanticipated noncompliance events for stormwater discharges associated with industrial activities must be reported annually [40 *CFR* 122.44(i)(5)].
- Any activity that resulted or would result in the discharge of a toxic pollutant for which the permit does not specify limits at concentrations exceeding the notification levels specified in 40 *CFR* 122.42. Notification must be given even if the discharges would occur infrequently.

Numerical Limits. When establishing NPDES permit limits, permit writers consider the relevant categorical standards, applicable BAT requirements, and the discharge's effects on receiving waters. If there are no categorical standards for a facility's process, or the categorical standards only apply to certain operational aspects or pollutants, then permit writers must use their best professional judgment to establish site-specific technology-based standards using all reasonably available and relevant data [CWA Sec. 402(a)(1)]. However, they first must ensure that the processes, operations, or pollutants not specifically addressed by the categorical standards were not evaluated during standards development and determined to be addressed appropriately by the limitations established in the effluent guidelines. Technology-based limits must also be established for wastewater treatment residues (e.g., grit, sludge, or filter backwash) [40 *CFR* 125.3(g)].

When using best professional judgment, permit writers must evaluate the same factors that the U.S. EPA considers when establishing categorical standards (see the "Categorical Requirements" section in this chapter). Best-professional-judgment limits must be met immediately [40 *CFR* 125.3(a)(2)].

Often, the receiving water's water quality standards determine the permit limits. In fact, an NPDES permit cannot be issued or renewed if the permit conditions "cannot ensure compliance with the applicable water quality requirements of all affected States" [40 *CFR* 122.34(d)].

The permit must have limitations for all wastewater parameters that regulators determine may exceed any state water quality criteria [40 *CFR* 122.44(d)(1)(i)]. One critical permit limitation is WET, which the U.S. EPA developed to evaluate the effects of toxic chemicals for which no specific numerical limits have been developed.

To measure WET, the facility must conduct toxicity tests, using the species, organism age and growing conditions, dilution water, industrial facility's effluent concentration, water temperature and composition, and duration specified in the permit. Available testing methods are listed in Table 1A of 40 *CFR* 136.3. If the tests show exceedances of the WET limits or the permit writer makes a determination that a pollutant in the facility effluent will impact the receiving water body, then the permittee must perform a TRE in accordance with U.S. EPA-specified procedures (U.S. EPA, 1989, 1991, 1992, 1993a, 1993b, 2001). The cause of WET exceedances can be difficult to identify when toxicity is detected sporadically.

Permit applications requesting ocean discharge must demonstrate that the discharger has no other alternatives and that the discharge will not unreasonably degrade the marine environment (40 *CFR* 125.121–125.124).

REGULATORY OUTLOOK. In the first 9 months of 2004, U.S. EPA finalized effluent guidelines for the concentrated aquatic animal production category, issued more requirements for the meat and poultry products category, and determined that the construction and development category did not need effluent guidelines because existing stormwater management programs and regulations were sufficiently protective of the environment. These actions completed the agency's obligations under a 1992 consent decree with the Natural Resources Defense Council to establish effluent limitations for a group of "primary industry categories."

However, CWA Sec. 304(m) requires that the U.S. EPA publish a plan every 2 years that includes a schedule for reviewing and revising existing effluent guidelines, identifies industrial categories discharging toxic or nonconventional pollutants that have no established effluent limitations, and establishes a schedule for issuing effluent limitation guidelines for these categories. (This section of the CWA applies only to direct dischargers.) The draft *Strategy for National Clean Water Industrial Regulations* (U.S. EPA, 2002) describes how the agency planned to meet the CWA requirements for the biennial plans. According to this document, which the agency has been using since published (even though it has not been finalized), the U.S. EPA would use the following criteria to determine whether existing effluent guidelines must be revised:

- "The extent to which the industry category is discharging pollutants that pose a risk to human health or the environment.
- The identification of an applicable and demonstrated technology, process change, or pollution prevention approach beyond current industry performance that could control pollutants to reduce the risk.

- The cost, performance, and affordability of a demonstrated technology, process change, or pollution prevention approach beyond current industry performance that could control pollutants to reduce the risk.
- Implementation/efficiency considerations."

At the time the agency started its evaluation, there were 55 industrial categories subject to effluent guidelines. (The guidelines for aquatic animal production were finalized in June 2004.) The *Effluent Guidelines Program Plan for 2004/2005* (U.S. EPA, 2004b and 2004c) presented the results of U.S. EPA's evaluation in accordance with the above Strategy document. After the required public comment period, the following four categories were selected:

- Airport deicing operations (a new category);
- Drinking water supply and treatment (a new category);
- Vinyl chloride manufacturing, a potential subcategory of the organic chemicals, plastics, and synthetic fibers category; and
- Chlor-alkali manufacturing, a potential subcategory of the inorganic chemicals category.

The U.S. Environmental Protection Agency expects to propose a rule for airport deicing operations in December 2007 (U.S. EPA, 2007b). The agency also plans to evaluate responses to the survey submitted to drinking water treatment facilities in 2007 (U.S. EPA, 2007c). The vinyl chloride and chlor-alkali manufacturing subcategories were merged into the chlorine and chlorinated hydrocarbon manufacturing category in the *Final 2006 Effluent Guidelines Program Plan* (U.S. EPA, 2006a), and the agency plans to send a questionnaire to these manufacturers to gather more data and determine whether more effluent limitation guidelines are warranted (U.S. EPA, 2007d).

Also, in response to a Second Circuit Court of Appeals order, the U.S. EPA proposed modifications to the effluent limitation guidelines for concentrated animal feeding operations (40 *CFR* 412) on June 30, 2006. (The deadline for comments was August 29, 2006, but the U.S. EPA did not publish any update before March 31, 2007.)

The *Preliminary 2006 Effluent Guidelines Program Plan* (U.S. EPA, 2005b) indicated that the agency plans to study three categories: pulp, paper, and paperboard (40 *CFR* 430) and steam electric power generating (40 *CFR* 423) for possible guideline revisions; and tobacco products for new effluent guidelines. However, when the U.S. EPA issued the *Final 2006 Effluent Guidelines Program Plan* (U.S. EPA, 2006a and 2006b), the agency had finished studying the tobacco products and pulp, paper, and paperboard categories, deciding that no new or revised guidelines were necessary for these two categories. Instead, the U.S. EPA would evaluate steam electric power generators and three other categories for possible guideline revisions: coal mining (40 *CFR* 434), oil and gas extraction (40 *CFR* 435), and hospitals (and other health services facilities) (40 *CFR* 460).

Meanwhile, the U.S. EPA issued two stormwater-related proposed rulemaking notices between December 2005 and January 2006:

- A proposed NPDES general permit for stormwater discharges from industrial activities (U.S. EPA, 2005a); and
- An amendment to exempt stormwater discharges associated with oil and gas exploration, production, processing, or treatment operations, as well as transmission facilities, from the NPDES permit requirements (U.S. EPA, 2006c).

The 2000 NPDES general permit for stormwater discharges from industrial activities expired in October 2005, and as of March 2007, the proposed permit had not been finalized. In 2006, U.S. EPA issued an automatic administrative continuance of permit coverage for permitted facilities (U.S. EPA, 2006d). The agency also indicated that, although unpermitted facilities could not apply for coverage under the general permit until a new one was issued, they should develop and implement pollution prevention plans in accordance with the 2000 general permit.

OTHER DISPOSAL REGULATIONS FOR WASTEWATER AND ITS TREATMENT RESIDUALS

Besides discharging it directly or indirectly to surface waterbodies, wastewater can be managed via subsurface disposal (wells), land application (for agricultural purposes or for treatment), and incineration. Landfilling of liquid wastes is prohibited under the current regulations, except under very limited circumstances (40 *CFR* 258.28 and 40 *CFR* 264.314).

Residuals of wastewater treatment can be disposed via subsurface injection, land application, landfilling, or incineration. (The applicable regulations depend on whether the waste is hazardous.)

DEFINITIONS AND APPLICABLE REGULATIONS. Wastewater and its treatment residuals disposed via subsurface injection are regulated under 40 *CFR* 144–148. Industrial wastewater and its treatment residuals disposed via land application or landfilling (residuals only) at a disposal facility owned or controlled by the industrial facility are considered "solid wastes" subject to 40 *CFR* 257 unless the following is true (40 *CFR* 257.2, 261.2, and 261.4):

- The wastewater is nonhazardous and subject to a pretreatment or NPDES permit under 40 *CFR* 122, 124, and 403;
- The residuals were generated at an industrial facility's wastewater treatment system designated as "treatment works treating domestic sewage" [in accordance with 40 *CFR* 122.1(b)(3)] and so are subject to the technical standards for sewage sludge use and disposal in 40 *CFR* 503; or
- The wastewater and residuals are classified as hazardous wastes—they exhibit a hazardous waste characteristic, have been mixed with hazardous waste, or are generated during treatment of hazardous waste or wastewater (40 *CFR* 261.3)—and so are regulated under 40 *CFR* 261–268.

Some wastewaters that meet the definition of "hazardous waste" (40 *CFR* 261.3) do not have to meet the requirements in 40 *CFR* 261–268 if the generators have a pretreatment or NPDES permit [40 *CFR* 261.3(a)(2)(iv)]. The requirements for municipal solid waste landfills and incinerators can be found in 40 *CFR* 258 and 240, respectively. The state permit program requirements for solid waste disposal are listed in 40 *CFR* 239.

SUBSURFACE INJECTION REGULATIONS. Industrial wastewater and its treatment residuals can be disposed via subsurface injection through a well. The Safe Drinking Water Act's underground injection control (UIC) program regulates the placement of fluids underground (40 *CFR* 144–148). The UIC and NPDES permitting regulations are codified in the same place: 40 *CFR* 124.

The UIC program lists five categories of wells (40 *CFR* 144.6–144.81):

- Class I—wells used to inject liquids into isolated formations beneath the lowest underground source of drinking water,
- Class II—wells used to inject fluids related to oil and gas production activities,
- Class III—wells used to inject fluids associated with solution mining of minerals,
- Class IV—wells used to inject hazardous or radioactive waste into or above formations within one-quarter mile of underground sources of drinking water, and

- Class V—all other wells (e.g., recharge wells, large-capacity cesspools, dry wells used to inject waste, septic system wells serving multiple dwellings or businesses, and wells used to return spent brine—after halogens or their salts are extracted—to the same formation from which it was withdrawn).

General Requirements. The underground injection control program is designed to prevent the contamination of current or potential underground sources of drinking water, so a UIC permit is required to inject any type of fluid into the subsurface (40 *CFR* 144.11). Industrial facilities may not use Class IV wells unless authorized to do so for groundwater remediation projects under the conditions specified in 40 *CFR* 144.13. Subsurface injection of industrial wastewater occurs through either Class I or Class V wells.

Class I Wells. The owner or operator of a nonhazardous Class I well must meet the following installation, operation, and monitoring requirements (40 *CFR* 146.12 and 40 *CFR* 146.13):

- Install the well in a location free of faults or other geological features that would allow contaminated fluids to migrate into underground sources of drinking water.
- Make the well deep enough so fluids will be injected into a formation that cannot be used as an underground source of drinking water and is separated from such sources by impermeable formations.
- Isolate the well from the formations it crosses by putting one pipe (tubing) inside another (casing) and cementing the casing on the outside to fill any voids between it and the hole drilled for the well.
- Test the well's mechanical integrity when it is completed and every 5 years thereafter.
- Monitor the well and the injected fluids continuously to ensure the well integrity and document the characteristics of the injected fluids, respectively. Well integrity monitoring requires continuous recording of the fluid injection pressure, flow rate, and volume; pressure in the annulus between the tubing and casing; and pressure in the injection zone. Injected fluid monitoring must occur at an adequate frequency to yield representative data of its characteristics.

Class I wells must be operated and maintained to ensure that underground sources of drinking water are not contaminated. Once injection stops, the owner or operator must properly plug and abandon the well to prevent contaminants from migrating to drinking water sources (40 *CFR* 146.10).

Owners or operators of hazardous Class I wells have more requirements (see 40 CFR 146.61–146.73).

Class V Wells. Class V wells are typically "authorized by rule," meaning the well owner or operator must meet all UIC requirements but does not have to obtain an individual permit, except under certain conditions (40 *CFR* 144.84). Such conditions include:

- Contaminated fluid is moving into an underground source of drinking water,
- The well is a large-capacity cesspool or a Class V motor vehicle waste disposal well in a groundwater-protection or other sensitive area,
- The owner or operator failed to submit inventory information to regulators (see the Reporting Requirements subsection of the Subsurface Injection Regulations section in this chapter for the information required),
- Regulators have requested that the owner or operator get a permit for the well, or
- Regulators requested additional information about the well and the owner or operator failed to provide it on a timely manner.

If a Class V well owner or operator must obtain a permit, then the well must be designed, installed, and operated so it does not contaminate an underground source of drinking water or adversely affect the health of persons using the aquifer (40 *CFR* 144.82). The well also must be properly closed when no longer in use (40 *CFR* 144.80). Other requirements are listed in 40 *CFR* 144–148.

Reporting Requirements. Owners or operators of new Class V wells must submit a one-time "inventory" form (OMB No. 2040–0042) containing information about their wells to the underground injection control program director before starting operation of the well (40 *CFR* 144.83). The inventory form must include the following information: "facility name and location; name and address of legal contact; ownership of facility; nature and type of injection well(s); and operating status of injection well(s)" [40 *CFR* 144.83(a)(2)(i)]. Additional information [40 *CFR* 144.83(a)(2)(iii)] may be required for certain wells [40 *CFR* 144.83(a)(2)(ii)]. Owners or operators of permitted wells must meet the reporting requirements listed under the "NPDES Permits" section of this chapter, with the following modifications:

- Monitoring results must be submitted quarterly, and
- The 24-hour verbal, 5-day written reporting requirement applies to data indicating that injection operations may endanger an underground drinking water source or cause fluid to migrate into or between such sources [40 *CFR* 144.51(l)].

The quarterly monitoring report must include the injected fluids' characteristics; the monthly average, maximum, and minimum values of annulus pressure, injection pressure, flow rate, and volume; and the analytical results of any well sampling done to monitor possible fluid migration into drinking water sources. Also, results of mechanical integrity tests, results of any other required test(s), and data on well repairs must be submitted with the first quarterly report after such information is obtained.

Permitting. Regulators issue UIC and NPDES permits under the conditions specified in 40 *CFR* 124. The permit requirements are similar, but UIC permits also include the following conditions (40 *CFR* 144.51): requirements before injection begins, duty to establish and maintain the well's mechanical integrity, prior notification of well conversion or abandonment, well-plugging and -abandonment procedures and reports, and financial assurance instruments to ensure that the well will be properly plugged and abandoned when no longer needed (40 *CFR* 144.52 and 146.14). Because UIC permits are subject to the same public comment requirements as NPDES permits, the applications must be submitted a "reasonable time" before construction begins (40 *CFR* 144.31), but no specific time is indicated in the regulation.

LAND-APPLICATION REGULATIONS FOR SITES CONTROLLED BY THE WASTE PRODUCERS. If industrial wastewater or its treatment residuals are disposed on land owned, managed, or otherwise controlled by the industrial facility, the activity (e.g., land application for agricultural purposes, land application for waste treatment, or landfilling) must meet the following environmental protection requirements (40 *CFR* 257.3):

- It cannot restrict the base flood's flow, reduce the floodplain's temporary water storage capacity, or result in a solid waste washout that would pose a hazard to human life, wildlife, or land or water resources;

- It cannot destroy or adversely modify the critical habitats of endangered or threatened species as identified in 40 *CFR* 17;
- It must meet both NPDES requirements and any area-wide management plan approved by the U.S. EPA;
- It cannot contaminate an underground source of drinking water beyond the solid waste boundary;
- When applied to land used for food-chain crops, it cannot exceed the cadmium numerical limitations specified in 40 *CFR* 257.3–5;
- Onsite disease vectors must be minimized;
- Open burning is not allowed, and the operation must meet the requirements of the state implementation plan and the Clean Air Act; and
- Explosive gases must be minimized, fire hazards and hazards to aircraft from birds must be prevented, and public access must be controlled as necessary to protect human health and safety.

States regulate the land application of industrial wastewater, and a permit is typically required. Industrial facilities should consult state regulations to determine the specific requirements, which may include application rate, minimum distance to residences, groundwater monitoring, and reporting.

Residuals-disposal conditions may be included in the NPDES permit as a sludge management plan or in a state-issued solid waste management permit. Regulators may require an industrial facility to control the sites where its wastewater treatment residuals are land applied (e.g., used as fertilizers or soil amendments). Such "control" may occur via a sales contract or other agreement.

A publicly owned treatment works' residuals (also called "sewage sludge" or "biosolids") must be used or disposed in accordance with 40 *CFR* 503. If an industrial facility's wastewater management system is designated a "treatment works treating domestic sewage," its residuals would also have to meet the specific technical requirements of 40 *CFR* 503.12–503.15, 503.32, and 503.33, which include:

- Limits on the concentrations of metals (e.g., arsenic, cadmium, copper, lead, mercury, molybdenum, nickel, selenium, and zinc) in residuals to protect crops, public health, and the environment;
- Use of a stabilization method [e.g., pH adjustment (alkaline stabilization), digestion, composting, or heat drying] to destroy pathogens, minimize odors, and make the residuals less attractive to vectors (e.g., flies, mosquitoes, rodents, and birds);

- Safe distances between land-application sites and U.S. waters; and
- Specific operating practices (e.g., timing of application, depth of biosolids application, and annual application rate).

The U.S. Environmental Protection Agency has developed guidelines that specify a tiered evaluation to determine whether a land-application program would contaminate groundwater (U.S. EPA, 1999b). This evaluation includes comparing the wastewater treatment residuals' pollutant concentrations to default concentration tables, performing a location-adjusted assessment, and completing a comprehensive risk assessment. Basically, evaluators model whether, if land applied, the residuals' constituents would migrate to the groundwater. The results can be used to demonstrate to regulators that the selected disposal method meets 40 *CFR* 257 requirements.

Hazardous industrial wastewater or residuals must be disposed in accordance with 40 *CFR* 264. (Readers should consult the regulations related to the chosen disposal method to ensure that the industrial facility meets all applicable requirements.)

REGULATIONS FOR DISPOSAL AT THIRD-PARTY FACILITIES. Third-party disposal facilities include municipal solid waste landfills, municipal solid waste incinerators, and hazardous waste disposal facilities.

Municipal Solid Waste Landfills. To dispose wastewater treatment residuals in municipal solid waste landfills that meet 40 *CFR* 258 requirements, industrial facilities only need an agreement with the landfill operator. However, the landfill operator may require certain tests to ensure that the material is acceptable, such as analyses of the residuals to ensure that they are not hazardous (40 *CFR* 258.20) and do not contain free liquids, which cannot be landfilled (40 *CFR* 258.28).

Municipal Solid Waste Incinerators. To dispose residuals in municipal incinerators, industrial facilities need an agreement with the owner or operator. Owners or operators of municipal incinerators must meet 40 *CFR* 240 requirements, so they may require the facility to test its residuals for pollutants that the incinerator is not designed to handle, or to assess whether their residuals are excluded from the incinerator's permit.

Hazardous Waste Disposal Facilities. To dispose of hazardous materials in hazardous waste disposal facilities, industrial facilities need to obtain approval of their wastes by the owner or operator of the disposal facility. This process usually requires either testing a representative sample of the facility's waste or using generator knowledge. Generators of hazardous wastes must meet the 40 *CFR* 262 requirements applicable to their conditions. An industrial facility that produces more than 1000 kg/mo (2200 lb/mo) of hazardous wastewater or residuals—a "large quantity generator"—must meet the following generator requirements (40 *CFR* 262):

- Determining the type of hazardous waste generated;
- Applying for a U.S. EPA identification number and using it in all hazardous waste-related documentation;
- Using a manifest to transport or offer for transportation hazardous waste for offsite treatment, storage, or disposal;
- Packaging, labeling, marking, and placarding the hazardous waste in accordance with the regulations;
- Accumulating hazardous waste onsite for less than 90 days without a storage-facility permit;
- Meeting reporting requirements on the amount of waste generated and whether the waste reached the intended facility; and
- Keeping manifests, reports, and test results for at least 3 years.

Industrial facilities that generate between 100 and 1000 kg/mo (220 and 2200 lb/mo) of hazardous waste—"small quantity generators"—have special requirements, such as being allowed to accumulate wastes for up to 180 days and meeting less stringent recordkeeping and reporting requirements [40 *CFR* 262.34(d) and 262.44]. According to 40 *CFR* 261.5, industrial facilities that generate less than 100 kg/mo (220 lb/mo) of hazardous waste or less than 1 kg/mo (2.2 lb/mo) of acute hazardous waste—"conditionally exempt small quantity generators"—are exempt from regulation if they dispose such wastes at facilities that meet the requirements of 40 *CFR* 240 and 258.

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http://cfpub.epa.gov/npdes/home.cfm?program_id=3 (Pretreatment regulations)

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Chapter 3

Wastewater Sampling and Analysis

GENERAL REQUIREMENTS

Data generated during wastewater sampling and analysis may be used for one or more of the following purposes: compliance monitoring, process control and troubleshooting, wastewater characterization, treatability testing, wastewater treatment system design, and chemical-source tracking.

The choice of sampling approaches, techniques, equipment, and analysis methods depends on the data's intended use, so the first step in a successful sampling and analysis program is to establish clear data objectives. Otherwise, the analytical results may be useless because the wrong methods were used, the reporting limits were inadequate, or the samples were not representative of the wastewater. To be a success, a sampling and analysis program must meet the following minimum criteria:

- The data it generates must be able to address the questions that initially prompted the sampling and analysis effort. The data type and quality must be able to answer specific questions (e.g., Is the treatment system meeting permit limits? Is this upsetting treatment operations? Is this where the toxic chemical originated?).
- The data must be representative of the sampled wastewater's content, flow, and variability. Intermittent discharges (batch processes), campaign-based discharges, continuous discharges, equalized wastestreams, and unequalized wastestreams require different sampling approaches.
- The analytical methods must be appropriate for program goals. Detection limits, potential interferences, and the need for regulator-approved methods are all important considerations when selecting analytical methods.
- The sampling and analysis program must be economical. Extraneous data and data collected only to satisfy personal curiosity while contributing little to the data objectives should be avoided. The analytical and sampling methods should only be as complex, accurate, and expensive as needed to meet program goals—no more, no less.

A well thought out sampling plan is essential. The plan's contents, details, and overall length depend on the magnitude of the sampling and analysis effort and how the resulting data will be used. It typically contains goals and data objectives, site-specific information, program scope, proposed methodology, sampling containers and sample handling, field and laboratory analytical methods, health and safety requirements, field and laboratory quality assurance/quality control (QA/QC) procedures, and relevant appendices (e.g., sampling checklist, maps and figures, chain-of-custody forms, field instrument-calibration forms, equipment decontamination procedures, and standard field analysis and sampling procedures). The sampling plan's content, format, and organization will vary based on specific project requirements and the author's style, but all serve the same purpose: they are working documents to help field personnel implement the sampling programs. So, instructions and statements that are open to interpretation are problematic.

FLOW MEASUREMENT

Flow measurements are required for many reasons, including:

- Developing a design basis for a new or upgraded wastewater treatment plant,
- Determining hydraulic loads on existing wastewater treatment units,
- Determining compliance with mass-based limits in NPDES permits,
- Determining compliance with flow reporting requirements in permits,
- Determining flow-proportioned chemical dosing requirements,
- Developing flow and mass balances (required for permit applications or source control/monitoring efforts),
- Collecting a flow-proportioned sample, and
- Determining stormwater runoff volumes.

Flow is expressed in units of volume per a unit of time (e.g., m^3/d, L/min, gpm, mgd, and cu ft/sec). Expressing flow in familiar units (e.g., mgd, gpm, m^3/day, and L/min) makes it easier to make quick calculations without the need for conversion tables. For example, given the concentration of a wastewater constituent (e.g., total suspended solids or biochemical oxygen demand) and the wastewater flow in mgd, one could easily calculate the mass loading (lb/d) using the following formula:

$$\text{lb/d} = \text{Flow (mgd)} \times \text{Concentration (mg/L)} \times 8.34$$

In this equation, 8.34 is a conversion factor that only works for dilute aqueous solutions; the assumption is that water density is 8.34 lb/gal.

In metric units, mass loading is expressed as follows:

$$\text{kg/d} = \text{Flow (m}^3\text{/d)} \times \text{Concentration (mg/L)} \times 10^{-3}$$

Basically, there are two types of flow systems: closed channel flow and open channel flow (Figure 3.1). *Closed channel flow* is flow in completely filled pressure conduits or pipes (e.g., a pressurized potable water line, a sewer forcemain, or an industrial pressurized process line). *Open channel flow* is flow that can interact with the atmosphere (e.g., rivers, ditches, or partially filled conduits or pipes). Different methods are used to measure flow in each system.

Flow measurements can be classified as instantaneous or average. Instantaneous flow is measured at a particular moment in time. Average flow is based on

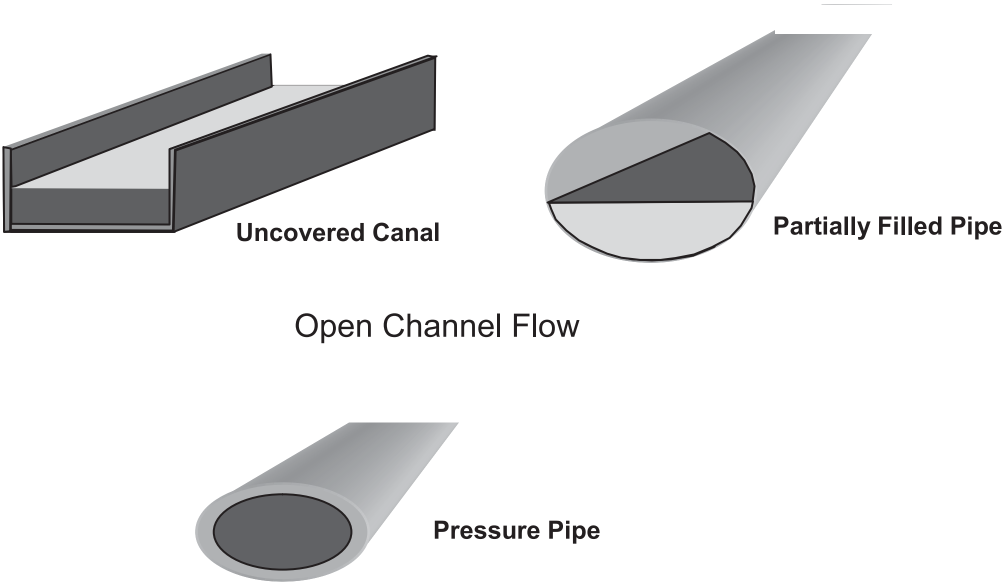

FIGURE 3.1 Closed- and open-channel flow systems (adapted from Walkowiak, 2006).

either several discrete flow measurements or flow volume measured over a long period of time (e.g., 1 day).

Wastewater flow can be either measured or estimated, depending on the degree of accuracy and precision required. *Accuracy* is the extent to which a given measurement agrees with the parameter's true value. *Precision* is the extent to which a set of measurements of one sample agree with each other. (For more information on accuracy and precision, see the "Quality Assurance/Quality Control" section of this chapter.) The following sections discuss common, practical estimation and measurement options. They are by no means exhaustive.

ESTIMATION OPTIONS. There are several methods for estimating flow in the field using little or no special equipment.

Bucket and Stop Watch. This is the simplest method of estimating flow rate; it does not require any special equipment. Field personnel record the time needed to fill a bucket (or other container with a known volume) and calculate the flow as follows:

$$\text{Flow rate} = \text{Volume}/\text{Time}$$

This method is only useful for small discharges from pipes or other conveyance devices where a bucket can intercept the entire flow. Ideally, field personnel should do it at least three times and average the results.

Float or Dye Method. Theoretically, flow in a geometrically well defined channel can be estimated via the following formula:

$$\text{Flow} = AV$$

Where

A = cross-sectional area of flow, and

V = average flow velocity in the channel.

The area of flow can easily be calculated based on the channel's geometry and the depth of water in the channel. The velocity can be estimated by dropping a floating object (e.g., ping-pong ball, stick, or specially designed floats) in the flow channel and timing how long it takes to travel a known distance. The velocity is calculated as follows:

$$\text{Velocity} = \text{Float's travel distance}/\text{Travel time}$$

In open channels, the velocity profile varies with the depth of flow. The float's velocity on the water surface may not accurately reflect the entire flow's average velocity. Correction factors can be applied to relate surface velocities to the average velocity of various stream depths (U.S. Department of the Interior, Bureau of Reclamation, 1997). Some specially designed floats have segments that extend into the water column, thus providing a more accurate velocity measurement.

Tracer dyes can also be used to visually estimate velocity. Dyes provide a better estimate than surface floats because the dye particles disperse in the water and travel at different velocities across the flow area. The dye's travel time should be the average of the total elapsed time from when the dye first appears downstream to when it is no longer visible.

Pump Cycles. Sometimes flow can be estimated based on a wet well's or process sump's pumping cycles. Typically, an event recorder (Figure 3.2) is connected to the pump's electric circuit, and the on-off signals are logged electronically or on a chart recorder. Field personnel then can calculate the flow based on pumping time and the pump's rated capacity.

FIGURE 3.2 An example of an event recorder (Model EV100) (courtesy of Dickson Company, www.DicksonData.com).

Time to Fill or Empty a Tank. Field personnel can estimate the flow in sumps, wet wells, tanks, or any other well-defined geometric structure by monitoring the time needed to fill or empty it. They also monitor the change in liquid depth and multiply that by the surface area to calculate the volume. Then, they divide the volume by the recorded time to obtain a flow estimate.

Estimating Stormwater Flows. Sometimes field personnel must estimate stormwater runoff flows without expensive flow-measuring devices or sophisticated setups. One of the most widely used methods is based on rainfall-intensity and -frequency data and the following rational equation:

$$Q = CiA$$

Where

Q = peak runoff rate (cu ft/sec),

C = runoff coefficient (the ratio of the peak runoff rate to the average rainfall rate for a period called *the time of concentration*),

i = average rainfall intensity (in./hr) for a period equal to the time of concentration, and
A = drainage area (ac).

A detailed discussion of the rational method can be found in *Water Supply and Pollution Control* (Viessman and Hammer, 2004).

MEASUREMENT OPTIONS. For a detailed discussion of flow-measurement devices in closed and open channel flow systems, see Chapter 14. Following is one measurement method not mentioned in that chapter.

In the dilution method, the flow rate is measured by determining how quickly the flowing water dilutes a tracer. Field personnel inject a predetermined concentration of the tracer into the flow stream at a constant flow rate. Then at a certain distance downstream of the injection point, they measure the diluted tracer's concentration. With data on the tracer's initial concentration, final concentration, and injection flow rate, field personnel can calculate the stream's flow as follows:

$$Q_{\mathrm{w}} \times C_{\mathrm{e}} = q_{\mathrm{t}} \times C_{\mathrm{i}}$$

Where
Q_{w} = wastewater flow rate (gpm or m^3/h),
q_{t} = tracer injection flow rate (gpm or m^3/h),
C_{i} = initial tracer concentration (mg/L), and
C_{e}= diluted tracer concentration measured downstream (mg/L).

This equation is based on the principle of mass conservation, so tracer losses should be minimized.

Field personnel have used various tracers in this method, including brine tracers, radioactive tracers, and fluorescent dyes. The latter is more commonly used today. Rhodamine WT is widely used in water and wastewater applications because it is safe and analytical instruments can detect ppb levels of it when using fluorometric techniques. Fluorescent tracers in water and wastewater samples can be analyzed in discrete samples or via a flow-through cell, which allows continuous flow measurements to be taken at second or minute intervals (Figure 3.3).

The dilution technique does not cause pressure losses or obstructions, is not dependent on channel geometry, can be used in closed or open channel flow systems of any size, and is not affected by submergence of the primary flow device. Fluorometric tracer techniques have been used to calibrate and confirm the measurements of other flow measuring devices (ISO, 1994; Turner Designs, 1990).

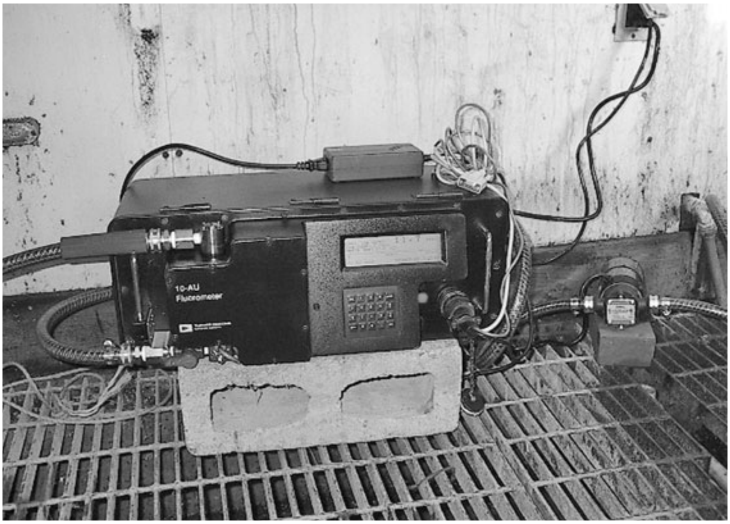

FIGURE 3.3 Turner Designs fluorometer setup for continuous rhodamine WT tracer analysis (courtesy of URS Corporation).

SAMPLING

Sampling is the act of taking a portion of a medium (gas, liquid or solid) so its characteristics and properties can be described via observations and chemical or physical testing. Sample collection plays a critical role in deriving sound, relevant data that may be used to make important decisions. In fact, the nature of the decision dictates the type of sampling required.

Basically, there are three types of sampling: intuitive, statistical, and protocol (Taylor, 1986). Intuitive sampling plans are those based on personal judgment and expertise. They are devised according to the planner's general knowledge of similar materials, past experience, and current information—ranging from guesses to good scientific data—about the medium of concern. The resulting data, therefore, are only as good as the sampler's perceived expertise and are subject to interpretation.

Statistical sampling plans typically are developed based on modeling and may involve hypothesis testing. To ensure that the resulting data are definitive, such plans typically include a statistically significant number of samples, random sampling locations, replicate sampling requirements, and error analysis. Although there is less subjectivity in using a statistically based sampling plan (as opposed to an intuitive plan), the underlying statistical model used to design the sampling program could still be challenged.

Protocol sampling plans are based on a predefined set of conditions and steps that must be followed to guarantee each sample's validity. Regulators may define such plans, for example, when the resulting data will be used to make legal decisions. The protocol may be based on statistical or intuitive considerations, but once established, the resulting data is difficult to refute. However, a sample may be discredited if any part of the protocol (e.g., chain-of-custody procedures, sample-preservation methods, or holding time limits) was not followed.

Which sampling plan is best depends on the data needed and the nature of the decision to be made. Intuitive plans are sufficient when the decision will be based on identifying large differences in sample properties. Statistical plans are better when the decision will be based on small differences because statistical methods can unequivocally determine whether there is a difference between two samples. A hybrid intuitive-statistical plan may be warranted, however, if collecting and analyzing a large number of samples is not feasible.

No matter which sampling plan is chosen, it must address the following elements:

- Sampling time(s) and place(s);
- The type of samples to be collected;
- The sampling method;
- Sampling procedures and techniques (e.g., sampling containers, related cleaning methods, sample-preservation and -storage methods, sample-acceptance criteria, analysis-related sampling requirements, recordkeeping requirements; and field and equipment blanks);
- Quality assurance and quality control issues; and
- Health and safety considerations.

TYPES OF SAMPLING. There are two major types of samples: grab and composite. Both are useful and can help characterize a particular wastewater or residual.

A grab sample is one taken at any given time to represent the wastewater at that moment. In other words, it provides a "snapshot" of the wastewater. Grab sampling is useful when:

- Wastewater characteristics vary over time;
- The wastewater is affected by batch or intermittent discharges (its true characteristics can only be obtained via a sample taken during the discharge);

- The wastewater characteristics are essentially constant over a long period of time (e.g., discharges from holding ponds, equalization basins, or any other containment structure or tank with a long hydraulic retention time);
- Specific parameters (e.g., pH, dissolved oxygen, temperature, and total residual chlorine) must be analyzed immediately after sample collection (according to regulations, grab samples are those collected in less than 15 minutes);
- Specific parameters (e.g., soluble ferrous iron) must be preserved immediately to avoid altering the sample's chemical, physical, or biological properties; and
- The concentration of a specific parameter (e.g., volatile organic compounds or oil and grease) would drop during the composite-sample collection process.

A composite sample is one collected over time. It reflects the wastewater's average characteristics. There are two main types of composite sampling methods: time-based and flow-proportional. In time-based composite sampling, equal volumes of wastewater samples (aliquots) are collected in one container at regular time intervals. The sample is representative of the wastewater only when the flow is constant or varies by less than 10%.

In flow-proportioned composite sampling, the volume of each aliquot is proportional to the wastewater flow at the time it is collected. Such sampling can be flow-paced or time-paced. In flow-paced sampling, a fixed volume of wastewater is collected at a constant flow interval [e.g., a 200-mL aliquot per 20 m^3 (5283 gal) of wastewater flow] and placed in one container.

In time-paced sampling, each aliquot is collected in one container at a fixed time interval but its volume varies in proportion to the wastewater flow. Larger samples are taken during higher flows and smaller ones during lower flows. Alternatively, each aliquot can be a fixed volume collected at a fixed time interval and deposited in its own container. Afterward, a composite can be prepared by pulling volumes from each aliquot in proportion to the wastewater flow when the aliquot was taken.

SAMPLING METHODS. Samples can be taken manually or automatically. The choice depends on such factors as:

- Costs,
- The duration of the sampling event,
- Accessibility and safety considerations, and
- The nature of the sampling event.

FIGURE 3.4 Various manual sampling devices (from left to right: sample dipper, swing sampler, and sample containers) (USA Bluebook, Waukegan, Illinois).

Manual Sampling Methods. Manual sampling is an event strictly triggered and controlled by one or more persons. The sample can only be collected at the sampler's behest. Automatic sampling, on the other hand, is controlled by a programmable or mechanical logic sequence. A person determines the logic sequence, but a machine initiates the sample collections.

Manual samples can be collected via simple field equipment (e.g., dip poles, rope and bucket, or a variety of sample bottles) (Figure 3.4). More sophisticated manual methods involve battery operated peristaltic pumps or pump heads mounted on an ordinary battery-operated drill (Figure 3.5), submersible or aboveground centrifugal pumps, or automatic sampling equipment operated in the manual mode.

FIGURE 3.5 Peristaltic pump head, which can be mounted on a battery-operated drill and used to collect manual samples (Barnant [Thermo Scientific], Barrington, Illinois).

Manual sampling is preferred when a parameter (e.g., pH, dissolved oxygen) must be analyzed immediately in the field, only grab samples are required, when the sampling event is reasonably short and can be completed during working hours, when labor costs are not excessive, and when the sampling frequency and analysis can only be determined based on direct observation of the wastewater (e.g., color, turbidity, or presence of oil sheens).

Automatic Sampling Methods. In automatic sampling, a machine collects the sample(s). This technology has advanced significantly in the past 10 to 15 years, and automatic samplers can now be used to collect both grab and composite samples. Commercial samplers are available in 1-, 4-, or 24-bottle configurations, and custom configurations are possible. They can be programmed to collect samples based on a time sequence, a flow sequence (when connected to a flow metering device), or any other event that triggers a signal.

For example, automatic samplers are widely used in stormwater sampling programs, which require both grab and composite samples. The sampler is typically connected to a flow meter and programmed to collect a grab sample during the first 30 minutes of a storm event as well as a flow-paced composite sample of the entire event's runoff. The sampler also could be connected to a rain gauge and programmed to begin collecting samples once a certain rainfall intensity is detected.

Automatic samplers work well when collecting composite samples, especially flow-proportioned ones (Figure 3.6). They also are preferred when the sampling site is difficult to access (e.g., down a ravine or surrounded by mud, dense vegetation, or floodwater) or when a person's safety could be jeopardized (e.g., stormwater sampling during events involving lightning). In addition, automatic samplers may be more cost effective than manual sampling when multiple locations must be sampled simultaneously.

When selecting automatic samplers and sample locations, readers should make sure that:

- The sampler is made of materials that are resistant to the wastes being sampled (e.g., acidic flows, high organic solvent concentrations);
- It is protected from corrosive atmospheres, especially in confined areas;
- It will not be used in explosive environments unless intrinsically safe or appropriately designed;

FIGURE 3.6 An example of a commercially available automatic sampler (courtesy of TELEDYNE ISCO, Lincoln, Nebraska).

- Its suction pump provides enough velocity to prevent heavier solids from settling in the sampling tube and include representative levels of them in the samples;
- It can keep the sample cold enough (via ice or refrigeration) during the composite sampling period;
- Its proposed location will not exceed the sampling pump's suction head capabilities;
- If intended for automatic flow-paced sampling, the sampler and flow meter have a compatible interface; and
- The purge cycle between sampling events actually cleans the sampling tube.

As with all equipment, preventive maintenance and frequent cleaning are necessary. In particular, the intake tube must be cleaned regularly and replaced periodically to avoid solids buildup and biofouling.

SAMPLING PROCEDURES AND TECHNIQUES. Because wastewater varies, sampling and analysis personnel should do the following to ensure success:

- Select sampling points carefully—in the main body of flow where the velocity is high and not influenced by previous deposits or side currents—to ensure that the collected wastewater is thoroughly mixed;

- Clearly mark sampling points so later samples can be collected from the same location;
- Make sure that proper sampling equipment is available and adequate safety precautions are observed;
- Before sample collection, rinse the sampling containers two or three times with the water to be collected (unless biological samples will be collected or the sample bottle contains a chemical preservative);
- Thoroughly flush the sample lines first to ensure that each sample is representative of the source (e.g., if a sample line holds 20 L, then at least 25 L of wastewater should be drained from the line before a sample is collected);
- Use the appropriate sampling containers;
- Use proper sample-preservation techniques;
- Collect samples large enough for both the required analysis and a confirmation analysis in case the first results are questionable;
- Label the sample containers with the date, time, exact sampling point, type of sample (grab or composite), sampler's initials, preservatives used (if any), and type of analysis required;
- Thoroughly mix the composite-sample reservoirs before collecting samples; and
- Mix all samples immediately before analysis.

RELEVANT ANALYSIS METHODS AND PROCEDURES. Analytical methods and procedures relevant to wastewater sampling are mostly published as regulations in the Code of Federal Regulations (CFR) at Title 40 Part 136. The U.S. Environmental Protection Agency (U.S. EPA) publishes these methods for use by industries and municipalities to analyze the chemical, physical, and biological components of wastewater and other environmental samples as required by the Clean Water Act (CWA). The following U.S. EPA Web site, http://www.epa.gov/waterscience/methods/, lists a number of references on this subject, including:

- Approved and promulgated test procedures to measure pollutants in various media;
- Methods submitted for approval or already in use but not promulgated;

- Approval and validation process for submitting new test methods or procedures for U.S. EPA approval;
- Procedures to confirm laboratory performance; and
- Method updates to revise the list of approved analysis and sampling procedures.

QUALITY ASSURANCE AND QUALITY CONTROL

Basically, quality assurance is equated with trained personnel, standard methods and reagents, calibrated instruments, documented laboratory results, and chain-of-custody procedures and other recordkeeping requirements. Quality control is equated with adherence to approved methods, routine analysis of standards and spikes, and records of spike results.

Checks must be conducted during sampling and analysis to ensure that the results are precise and accurate (Figure 3.7). Sample-collection techniques can be checked via the following samples:

- Trip blanks are used to check for potential contamination during the sampling process and during transportation of the sample between the sampling site and the laboratory. These are sample vials filled with deionized water at the laboratory that travel with the sample bottles and samples. Although never opened, they are exposed to the same environmental conditions as the collected samples. The blanks then are analyzed at the laboratory for the same parameters as the samples using the same analytical methods.

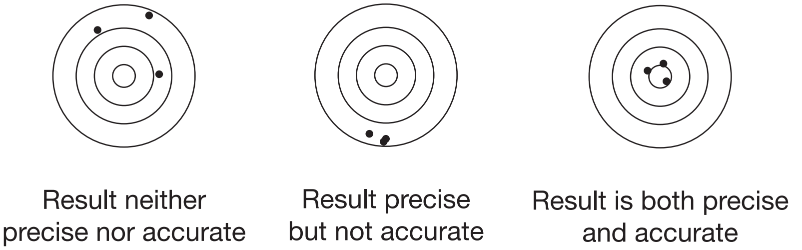

FIGURE 3.7 Demonstration of accuracy and precision (adapted from Willard et al., 1981).

- Field blanks or field reagent blanks are similar to trip blanks but are prepared in the field by filling a vial with deionized water in the same way that actual samples are taken. These blanks should detect any contaminants introduced into the sample via sampling techniques or analytical procedures.
- Equipment or rinsate blanks check the cleanliness of the equipment or sampling containers, as well as the effectiveness of decontamination procedures between sampling events. Typically, deionized water is poured onto the sampling equipment (or pumped through an automatic sampler, as appropriate) and then collected for analysis of the parameters of concern.
- Field duplicates are used to both check analytical precision and evaluate how well a sample represents its source. Duplicate samples of a source are collected simultaneously and then analyzed for constituents of concern.
- Split samples are used to check for discrepancies in two laboratories' analytical results. One sample is split into two containers and then each is sent to a different laboratory for the same analysis.

Analytical techniques can be checked via the following control measures:

- A reagent blank is a sample of the reagents used in an analytical procedure. Lab staff analyze it to determine if these constituents might bias the results in actual samples.

Matrix spikes and matrix spike duplicates are used to verify an analytical procedure's accuracy and precision and to check for matrix interferences. Analysts add a known amount of an analyte (called a "spike") to a sample and then prepare and analyze it just like any other sample. The difference between the amount of spike added and the amount found during analysis (percent recovery) indicates the effect of a particular sample matrix on the procedure's accuracy. A matrix spike duplicate sample is theoretically equal to the corresponding matrix spike sample and provides a means of measuring method precision.

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Chapter 4

Industrial Wastewater Survey and Characterization

A thorough, methodical assessment of an industrial facility and the characteristics of its wastewater sources is a prerequisite for an effective wastewater management plan. The methods and procedures for surveying and characterizing industrial wastewater typically are used by regulators and consultants to implement Clean Water Act (CWA) requirements, but they also can be used to help develop treatment facilities, identify potential savings, optimize production, determine compliance with discharge requirements, and establish a sound troubleshooting program.

DEFINITIONS

Following are several terms commonly used when characterizing wastewater:

- *Acidity* is the strength of an acidic solution, measured via a titrimetric procedure with an alkaline reagent and commonly expressed as mg/L of calcium carbonate ($CaCO_3$) equivalents.
- *Alkalinity* is the strength of an alkaline solution, measured via a titrimetric procedure with an acidic reagent and commonly expressed as mg/L of $CaCO_3$ equivalents.
- *Bioassay* is a test used to evaluate the relative potency of a chemical or mixture of chemicals by comparing its effect on a living organism to that of a standard preparation.
- *Biochemical oxygen demand* (BOD) is a measure of the amount of oxygen used by decomposing organic material in a wastewater sample over a specific period (typically 5 days); it is used to measure the readily decomposable organic content in wastewater.
- A *colony forming unit* (CFU) indicates the number of bacteria in a known volume of water by measuring the number of bacterial colonies grown on a nutrient substrate.
- *Chemical oxygen demand* (COD) is a measure of the oxygen-consuming capacity of the organic and inorganic matter in wastewater; it is expressed as mg/L of consumed oxygen. These results do not necessarily correlate to BOD because the chemical oxidant may react with substances that bacteria do not stabilize.
- *Coliform bacteria* are bacteria in the intestinal tract of warm-blooded animals; they are used to indicate fecal contamination in water.

- *Colloids* are finely divided solids that will not settle but may be removed via coagulation, membrane filtration, or biochemical action.
- *Composite sample (weighted)* is a sample composed of two or more portions collected at specific times and added together in volumes related to the flow at time of collection.
- *Conventional pollutants* are those typically found in municipal wastewater [e.g., BOD, total suspended solids (TSS), fecal coliform bacteria, oil and grease, and pH], which municipal secondary treatment plants typically are designed to treat; these pollutants are defined in 40 *CFR* 401.16.
- *Daily discharge* is the discharge of a pollutant measured during any 24-hour period that, for sampling purposes, reasonably represents a calendar day. For pollutants with limits expressed in units of mass, the daily discharge is calculated as the total mass of pollutant discharged during the day. For pollutants with limits expressed in other units (e.g., concentration), the daily discharge is calculated as the pollutant's average measurement throughout the day (40 *CFR* 122.2—Definitions).
- *Dissolved oxygen* is the amount of oxygen gas dissolved in a given quantity of water at a given temperature and atmospheric pressure. It typically is expressed as a concentration in parts per million or as a percentage of saturation.
- A *grab sample* is a sample taken from a wastestream on a one-time basis without consideration of time or flow rate.
- A *hazardous substance* is any substance other than oil that, when discharged to U.S. waters, is an imminent, substantial danger to the public health or welfare, including fish, shellfish, wildlife, shorelines, and beaches (CWA Sec. 311); identified by the U.S. EPA as the pollutants listed in 40 *CFR* 116.4—Designation of Hazardous Substances.
- *Heavy metals* are metallic elements (e.g., cadmium, chromium, copper, lead, mercury, nickel, and zinc), many of which are toxic at relatively low concentrations and are found in industrial wastewaters.
- *Inorganic material* is material derived from non-organic (non-living) sources.
- *Laboratory water* is purified water used in the laboratory as the basis of solutions or to dilute samples.

- A *mass-based standard* is a discharge limit measured in a mass unit (e.g., lb/day).
- A *method blank* is laboratory-grade water taken through the entire analytical procedure to determine whether samples are being accidentally contaminated by chemicals in the laboratory.
- A *method detection limit* (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is more than zero; it is determined via analysis of a sample in a given matrix containing the analyte.
- *Million gallons per day* (mgd) is a unit of flow typically used to measure wastewater discharges.
- *Monitoring* is the process of collecting data to systematically check a substance or process.
- *Nitrates* is the generic term for materials containing the nitrate ion (NO_3); sources include animal wastes and some fertilizers. Nitrates are linked to human health problems and also may cause overgrowth of aquatic plants in surface waters.
- *Nonconventional pollutants* (e.g., COD, TOC, nitrogen, and phosphorus) are those not included in the list of toxic and conventional pollutants in 40 *CFR* 401.15 and 401.16, respectively.
- *Nephelometric turbidity units* (NTU) is a measure of turbidity.
- *Organic material* is material derived from organic (living) things that contains carbon compounds.
- *Peak flow* is the highest instantaneous flow expected to be encountered under any operating condition.
- *pH* is a numeric value describing a solution's degree of acidity or alkalinity; it is calculated as the negative logarithm of the hydrogen ion concentration in moles per liter.
- *Phosphates* is the generic term for materials containing a phosphate (PO_4) group; sources include fertilizers and detergents. Phosphates are plant nutrients and may cause overgrowth of aquatic plants in surface waters.

- A *pollutant* is an impurity (contaminant) that changes the physical, chemical, or biological characteristics of air, water, or land in a manner that may be harmful to humans or other living organisms.
- *Parts per billion* (ppb) is a unit of concentration denoting the amount of a chemical found in 1 billion parts of a solid, liquid, or gaseous mixture; it is equivalent to micrograms per liter.
- *Parts per million* (ppm) is a unit of concentration demoting the amount of a chemical found in 1 million parts of a solid, liquid, or gaseous mixture; it is equivalent to milligrams per liter.
- A *preservative* is a chemical added to a water sample to keep it stable and prevent compounds or microorganism densities from changing before analysis.
- *Priority pollutants* are those considered most important to control under the CWA based on the Natural Resources Defense Counsel (NRDC) consent decree settlement, a list of which is provided in Appendix A to 40 *CFR* 423—126 Priority Pollutants.
- *Process wastewater* is any water that, during industrial manufacturing or processing, comes into direct contact with, or results from the production or use of any raw material, intermediate product, finished product, byproduct, or waste product.
- *Purgeable organics* are volatile organic chemicals that can be forced out of a water sample relatively easily via forced gas purging.
- *Self-monitoring* is sampling and analyses performed by a facility to determine its compliance with a permit or other regulatory requirements.
- *Settleable solids* are particulate in wastewater that will settle via gravity in a reasonable length of time (typically 1 hour) when the water is quiescent.
- *Specific conductance* is a measure of a water's ability to conduct an electrical current; it is related to the type and concentration of ions in solution and can be used to approximate the total dissolved solids (TDS) concentration in water.
- *Total dissolved solids* is the sum of all inorganic and organic particulate material in a water sample; it is an indicator test used for wastewater analysis.

- *Total organic carbon* (TOC) is a measure of the organic carbon concentration in a water sample.
- A *toxic chemical* is one that could damage or kill humans, animals, or plants.
- *Total suspended solids* is a measure of the filterable solids in a sample; it is determined via the method specified in 40 *CFR* 136.

The following terms are primarily associated with effluent toxicity:

- *Whole effluent toxicity* (WET) is the aggregate toxic effect of an effluent or receiving (ambient) water measured directly via a toxicity test using prescribed biological specimens.
- *Acute toxicity* is a measure of primarily lethal effects that occur over a short period of time (e.g., 96 hours or fewer).
- *Chronic toxicity* refers to sublethal effects (e.g., inhibition of fertilization, growth, and reproduction) that occur over a longer exposure period (e.g., 7 days).
- *Biomonitoring tests* is a generic term for the U.S. EPA's analytical methods used to determine acute and chronic toxicity in a biological system.
- A *toxicity reduction evaluation* (TRE) is a site-specific, stepwise study designed to identify the cause(s) of effluent toxicity, isolate them, evaluate the effectiveness of toxicity-control options, and then confirm the reduction in effluent toxicity.
- A *toxicity identification evaluation* (TIE) is the portion of the TRE that uses toxicity tests to track changes in the presence and magnitude of toxicity as the effluent is manipulated to isolate, remove, or render biologically unavailable specific types of constituents. Its objective is to relate toxicity to the wastewater's physical or chemical characteristics to try to determine the compound(s) causing effluent toxicity.
- *Test organisms* are the aquatic species typically used in biomonitoring tests [in freshwater biomonitoring tests, these typically include the fathead minnow (*Pimephales promelas*) and the water flea (*Ceriodaphnia dubia*)].
- The *50% lethal concentration* (LC_{50}) denotes the concentration of an effluent (or toxicant) that will kill 50% of the test organisms within a specified period (typically 24, 48, or 96 hours). It typically is the endpoint of acute toxicity tests. For example, if test results estimate that the 24-hour LC_{50} is 70%, then half of the test organisms in a sample containing 70% effluent would be expected to die within 24 hours.

- The *50% effective concentration* (EC_{50}) denotes the concentration of an effluent (or toxicant) that adversely affects half of the test organisms (based on visual observations).
- The *lowest observed effect concentration* (LOEC) is the lowest concentration of an effluent or toxicant that causes observable adverse effects on the test organism.
- The *no observed effect concentration* (NOEC) is the highest concentration of an effluent or toxicant that causes no observable adverse effects on the test organism; it is an important endpoint for both acute and chronic tests.
- The *chronic value* is the geometric mean of the LOEC and NOEC.
- A *toxicity unit* expresses the relative toxicity of an effluent; the larger the toxic unit, the more toxic the effluent is (e.g., $TU = 100/LC_{50}$).
- *Dilution water* is water used for controls and to make specified dilutions of the effluent. If laboratory water is used to prepare dilutions, the water must meet the U.S. EPA's specifications for such parameters as hardness, pH, alkalinity, and conductivity.
- A *reference toxicant* is a substance whose degree of toxicity to test organisms is known. The organisms can be tested with this toxicant to ensure that they are in their normal range of sensitivity to toxic substances.
- A *screening test* is a simple biomonitoring test to determine whether a sample containing 100% effluent is lethal to the tested species within a specified period (typically 24 hours). Screening tests are useful for rapidly evaluating the acute toxicity of a raw effluent (e.g., stormwater).

INDUSTRIAL WASTEWATER SURVEY

OBJECTIVE. An industrial wastewater survey should gather enough information so professionals can develop a wastewater management plan. Such data include identification of the wastewater sources, and corresponding chemical compositions, quantities, variations, distribution, and discharge frequencies and durations of all process wastestreams. The data are used to describe the facility's wastewater, develop or model potential management strategies, and provide a baseline for evaluating the effects of changes in production, water conservation, or regulations.

To develop an effective strategy, wastewater management professionals need to fully understand how each manufacturing process uses water and generates wastes. The best way to collect such information is to discuss and diagram facility operations with the production manager and shift supervisors. The result should be accurate facility drawings showing the locations of various processing units and their relationship with water supply and wastewater generation and associated collection systems. Then, each wastestream should be analyzed to determine its frequency, duration, flow rate, and pollutant types and concentrations. If possible, flows should be measured and samples collected via permanent monitoring stations; otherwise, temporary data-collection points should be used. The frequency, extent, and type of monitoring and sampling needed depend on each wastestream's nature and variability. To ensure that each wastestream is characterized appropriately, a sampling and analytical plan should be prepared.

Once all wastestreams have been fully characterized, they can be sorted based on pollutant types or concentrations, or applicable U.S. EPA categorical effluent standards (see Table 2.1 in Chapter 2). Surveyors also should obtain environmental reports (e.g., community right-to-know reports or discharge monitoring reports), as well as monthly and annual records of chemical and raw material use and production. This information helps wastewater management professionals correlate material use and waste generation.

IDENTIFYING CATEGORICAL WASTESTREAMS. The standard industrial classification (SIC) code is typically used to determine applicability to industrial categorical effluent standards. Any wastestreams covered by federal categorical effluent standards should further be identified as subject to concentration limits, raw materials-based standards, or production-based standards. Production-based standards, for example, directly relate the allowable mass rates of specific pollutants to the appropriate process's production rate. If categorical and noncategorical wastewater sources are combined before compliance sampling, the combined wastestream formula is used to determine compliance with the categorical limits. (For more information on this subject, see U.S. EPA, 1985.)

IDENTIFYING WASTEWATER GENERATORS. The in-plant survey should identify wastestreams from both production processes and pollution-control efforts (e.g., wet air scrubber blowdown, sludge dewatering, product change washouts, site cleanup, yard drainage, noncontact cooling water, boiler blowdown, or secondary containment spillage). Although some of these wastestreams may be small and discharged infrequently (e.g., slugs), they could seriously affect the overall wastewater's treatability. Many industrial facilities consider treating hazardous wastes onsite because of the restrictions and costs associated with offsite disposal.

Surveyors should categorize wastestreams according to pollutant types. Doing so may reveal incompatibilities that must be resolved before the wastestreams can be combined. For example, plating shops may generate both acidic and cyanide-laden wastestreams that would be dangerous to combine until after the cyanide has been removed. Categorizing wastestreams also may reveal some that only contain conventional pollutants (e.g., BOD and suspended solids) and so may simply be discharged to a publicly owned treatment works (POTW) or a biological treatment plant onsite without additional treatment.

Some wastewaters—especially high-strength, complex industrial wastewaters—exhibit inhibited results when the BOD analysis involves a minimum number of dilutions and unacclimated seed (e.g., seed from a local POTW or commercial laboratory). The COD test is not subject to the effects of inhibition and can also be used to characterize industrial wastewaters. Chemical oxygen demand may be used to approximate BOD if the compounds contributing to BOD are consistent enough for a typical COD-to-BOD ratio factor to be applied. Chemical oxygen demand analyses may be run onsite in 2 to 3 hours, while BOD analyses, because of the incubation period, take 5 days in a laboratory to complete. When using COD to characterize a wastewater's organic strength, analysts must account for any inorganic, oxidizable components (e.g., ferrous, nitrite, sulfide, and sulfite) that may contribute to the COD concentration.

IDENTIFYING WATER USERS. A comprehensive wastewater management evaluation should identify all processes that require water; their minimum, average, and maximum flow requirements; and the water quality required. Water quality can be categorized by type (e.g., city water, demineralized water, well water, or filtered river water) or by specific constituent (e.g., TDS, TOC, pH, or iron) concentrations. These data can be used to evaluate water-conservation and wastewater-minimization strategies.

Site-specific constraints may limit how much water can be supplied to the site and how much wastewater it can discharge. Also, reducing the wastewater volume via recycling, reuse, and other conservation methods may lower the pretreatment system's capital and operating costs, as well as the facility's water and sewer use charges. Water-conservation methods include reusing cooling water as product-makeup or product-cleanup water, reusing water as evaporative cooling-water system makeup, collecting stormwater for noncritical water uses, installing flow-restricting or water-saving devices, purifying and recovering selected wastewater sources, and recycling water in closed-loop systems.

PREPARING FLOW AND MASS BALANCES. Water often serves as both a raw material and a cleanup agent, so its consumption and fate (e.g., wastewater flows, product incorporation, and evaporative losses) must be accounted for in a process mass balance. The wastewater professional should use the survey data to prepare mass balances of the facility's wastewater flows and wasteloads. These mass balances confirm that the survey accounted for all wastewater flows and pollutant loads (not counting differences in water and wastewater flows that can be attributed to cooling-tower evaporation losses, boiler steam-condensate losses, landscape irrigation water, water used in the product, ambient air humidity condensation, stormwater impoundment drainage, and potential subsurface piping leaks). Mass rates may be affected by seasonal issues, so surveyors should obtain any significant time-sensitive correlations to avoid overlooking a potential worse-case scenario.

A facility-wide mass balance can be complex, especially if it involves multiple processes generating separate wastestreams that flow through one wastewater-collection system. So, the wastewater professional should first prepare a mass balance for each process that accounts—as accurately as possible—for the conversion of raw materials into products, solid wastes, wastewater loadings, etc. during a specific period. Then, each mass balance can be consolidated into an overall mass balance for the entire facility. If possible, the overall mass balance's results should be verified by measuring the facility's total effluent flow and analyzing its pollutant concentrations during a representative period.

Properly prepared mass balances provide data that can be used to prepare a treatment strategy and determine flow-equalization requirements. They also uncover opportunities for recycle or reuse of water. (Wastewater managers should focus on cost-effective recovery and reuse methods, which often reduce the cost of end-of-pipe treatment systems.)

Figure 4.1 is an example of a water flow balance for a combined cycle power-generating station. It shows four sources of inflow—recovered chiller condensate, well water, potable water, and stormwater—and six outflows—sanitary waste, chemical

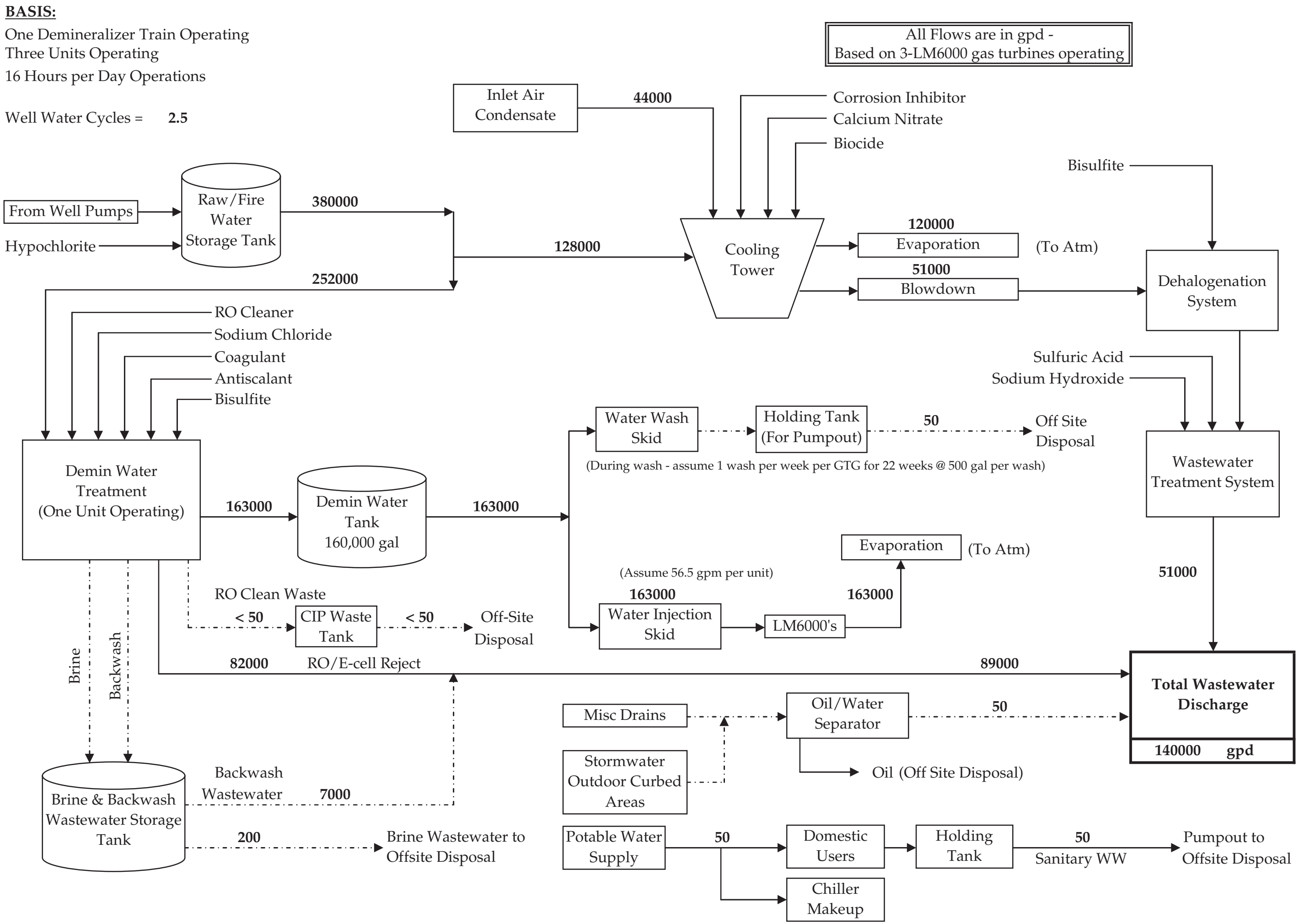

FIGURE 4.1 Mass balance for a combined cycle power-generating station (gpd × 0.003785 = m^3/d; gpm × 5.451 = m^3/d).

cleaning waste, softener regenerant wastewater, cooling tower evaporation, treated process wastewater, and untreated process wastewater. The water balance provides useful information for the design of water treatment, storage, and conveyance systems. It can also be used to furnish information required in the application for an NPDES wastewater discharge permit.

IN-PLANT CONTROL AND POLLUTION PREVENTION. Once the industrial facility's mass balance is completed and the sources and loads of various wastestreams have been determined, facility staff should consider options for reducing the concentrations and volumes of wastestreams that must be pretreated.

Staff should first focus on eliminating pollutants by substituting raw materials that generate no wastewater or only wastewater that requires no pretreatment. When such substitutions are impossible (e.g., because of product specifications) or economically infeasible, staff should consider the possibility of recycling or reusing process wastes. For example, sometimes the concentrated solutions obtained during cleanup operations can be recycled as part of a feedstock in the next production run. If treated wastewater cannot be reused in-plant, perhaps an outside party can reuse it.

If the wastes cannot be eliminated, recycled, or reclaimed via changes in production activities, staff should focus on reducing them by implementing good housekeeping measures, controlling spills (via spill-containment enclosures and drip trays around tanks), eliminating any "wet floor" areas, and using rinses that are either static or have no overspray. Proper housekeeping is especially important because it can be one of the most cost-effective methods for reducing pollutant loads and maintaining regulatory compliance.

Pollution-prevention and waste-minimization efforts should be continual, not a one-time event. Success depends on specific, measurable goals that all facility personnel are committed to achieving, and on public recognition of all milestones. Unless everyone is working to achieve these goals, "significant" achievements may be only temporary and the program's long-term success is less likely.

The facility's waste management strategy should be incorporated at the beginning of the plan and linked with all other components of the planning and implementation process. The benefits of a well-implemented plan include lower costs, better product quality, increased production, better public relations, less liability, and successful regulatory compliance. (For more information on pollution prevention, see Chapter 7).

CHARACTERIZING INDUSTRIAL WASTEWATER

OBJECTIVE. An industrial wastewater characterization should confidently estimate the volumes and properties of individual water and wastewater streams. This is a challenge because both hydraulic and constituent flow rates vary greatly in most industrial processes. So, a protocol must be developed to obtain enough data to illustrate this variability without exceeding the characterization budget, which is often limited. Costs can be minimized by judiciously limiting analyses to constituents of concern.

Those familiar with the industrial or manufacturing processes can make sound assumptions that will minimize the number of samples, measurements, and new data points needed. An economic alternative to sampling is to research applicable data from purchasing documents, chemical-use records, MSDSs, water-use records, wastewater DMRs, and manufacturing production logs. However, existing plant data should only be used if sufficient information is available when the data were collected, such as plant operating conditions, the collection procedures used, and the data's accuracy.

FLOW MEASUREMENT PLAN. The flow measurement plan should be designed to provide the specific flow data needed. For example, if the facility's effluent limit is based on maximum daily flow, then the plan should generate enough data so this flow can be estimated. Average weekly or monthly flow estimates may be needed to determine how often a tanker should deliver treatment chemicals to a bulk storage tank. Peak instantaneous flow rates (in gallons or liters per minute) may be needed to determine a new pump's capacity or a pipe's diameter.

The most reliable flow estimates are those available via existing flow meters. Industrial facilities typically use flow meters to monitor water supply to both the facility and individual processes, water used in the product(s), cooling tower makeup and blowdown, boiler feedwater, outfalls, and demineralized water makeup and production. If the facility does not have historical flow records, the flow measurement plan should have the metered flows recorded for a predetermined period.

If data records and flow meters are unavailable, flows can be estimated via several methods. For example, a constant-speed pump's flow rate can often be estimated via the pump curve if discharge pressure and motor horsepower are known. Temporary recording ammeters can be attached to the pump motors to log their run times.

Flow also can be estimated based on the time required to add a known volume to a container [e.g., a 19-L (5-gal) carboy, a 0.2-m^3 (55-gal) drum, or an existing bulk storage tank whose fill depth and diameter are known]. Other flow-estimation methods include per capita domestic water use, manufacturer's equipment specifications, production records, hose or spray nozzle size, portable strap-on ultrasonic flow meter, depth of flow in open channels formula, current meter or timed velocity of a floating object in an open pipe or channel, dimensional measurements of end of pipe free flow discharge and formula, and temporary V-notch weirs.

SAMPLING AND ANALYTICAL PLAN. The sampling and analytical plan should be designed to support the specific data needed. If the data will be used to develop a preliminary wastewater management plan or provide a rough characterization of the facility's wastewater, then relatively few samples are required. This type of sampling, called *judgmental sampling*, is cost-effective but does not precisely characterize the facility's wastestreams. If the data will be used to design a wastewater treatment system or make significant economic decisions, a more rigorous sampling program, called *systematic sampling*, should be developed. Systematic sampling designs ensure that the resulting data provide a statistically significant representation of the wastestream constituents.

Several factors should be considered when developing the sampling and analytical protocols. These include sampling-point location, type of sample, frequency of sampling, duration of each sample event, and appropriate coincidence of sampling activities with plant operations. To create a cost-effective analytical schedule, planners may first need to analyze representative effluent samples for the full spectrum of pollutants to determine which are present in the facility's wastewater. The schedule can then be established accordingly.

Sampling requirements are typically parameter-specific (see *Standard Methods for the Examination of Water and Wastewater*, Sec. 1060, et al. [APHA et al., 2005]). Some analyses require discrete (grab) samples, and others need samples that are a combination (composite) of several discrete samples to try to obtain an average. Basically, there are three types of samples (Corbitt, 1999):

- Grab samples are required for certain parameters (e.g., pH and volatile organic compound analyses), but they do not necessarily reflect wastewater characteristics accurately, especially when flow and pollutant concentration varies over time.

- Time-based composite samples consist of multiple aliquots taken at preset intervals and deposited in one container. This procedure will yield a partial representation of the wastewater's average composition. Some automatic samplers can put each aliquot in an individual container, which can help analysts evaluate the diurnal fluctuations of specific constituents (e.g., pH). Time-spaced data, for example, may help design engineers size equalization tanks.
- Flow-proportional composite samples mirror the actual wastewater quality most accurately. In this sampling method, an automatic sampler is connected to a flow meter with an electronic output signal and programmed to collect samples at equal flow intervals.

Typically, samples may be taken by a person or an automatic sampler, which can be rented or purchased. Commercial laboratories often furnish both the equipment and labor required to conduct the sampling program via automatic samplers.

Once the appropriate wastewater constituents and sampling-related variables have been determined, a sampling schedule should be prepared that lists the analytical constituents, the sampling dates and times, the types of samples to be taken, and any special instructions and comments. Cost estimates of the sampling and analysis program should be based on this schedule, which can be conveniently transmitted to a commercial laboratory for its use.

For more specific guidance on oil and grease sampling procedures, see Chapter 10. For more specific guidance on pH sampling and evaluation procedures, see Chapter 11.

REPRESENTATIVE SAMPLING. Sampling activities must be done by trained, experienced personnel because if the samples are not representative of the actual wastewater, then no matter how good the data are or which analytical methods were used, the results will be wrong.

One common challenge is ensuring that the sample contains the same suspended solids concentration that the overall wastestream does. Because solids entrainment depends on velocity, samplers should try to obtain samples isokinetically (i.e., not changing the stream's velocity as it approaches and enters the sampler intake). Isokinetic sampling is difficult but can be approximated by using automatic samplers and rigidly securing the sample tube so it faces upstream—but is not near the water surface or at the bottom of the pipe or tank being sampled. Sampling program staff also should inspect the sample tubing for cleanliness before use (to avoid introducing non-representative impurities into samples). If representative sampling of a wastestream is problematic, sampling staff may use mixed-flow equalization (see Chapter 8) to obtain accurate time-averaged results.

Facility operations should be forecast before and confirmed after each sampling event to avoid any planned variations that could skew the analytical results. Such variations include floor washing (especially if it involves cleaning chemicals), concentrated spent-solution tank dumps, tank cleanups, regeneration of ion-exchange units, clean-in-place operations, off-spec product dumps, and spills or tank overflows.

ANALYTICAL SERVICES. Wastewater analyses can range from field test kits to complex laboratory procedures. Typically, commercial field test kits are used when gross trends or approximations are acceptable, although the U.S. EPA has approved such kits for some monitoring purposes. Test kits provide quick, inexpensive results and can be completed by an operator or technician.

Many industrial facilities have onsite laboratories or direct access to a corporate laboratory. Such facilities must decide whether to analyze samples in-house or hire an independent commercial laboratory to do the work. This decision depends on such factors as cost, the plant laboratory's objectivity, laboratory-certification requirements, and the overall analytical workload. If a commercial laboratory is selected, facility staff should verify its qualifications, including any required certifications and the use of U.S. EPA-approved quality-assurance and -control procedures. Staff also should periodically "split" samples and have two laboratories analyze them to verify that the analytical results are accurate.

The analytical methods for wastewater and residuals are well established and updated periodically. Regulations sometimes specify which methods may be used. Most commercial laboratories use the latest editions of the following references:

- *Methods for Chemical Analysis of Water and Wastes* (U.S. EPA, 1983),
- *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (U.S. EPA, 2004), and
- *Standard Methods for the Examination of Water and Wastewater* (APHA et al., 2005).

Laboratory staff should inform the sampling team about special requirements for sample collection, preservation, and maximum holding times. The laboratory also should furnish labels and sample bottles, including pre-dosed preservatives (if necessary). If soluble and particulate constituents must be speciated, the laboratory will furnish bottles that contain a preservative for the overall wastewater sample and no preservative for the particulate sample, which will be filtered in the laboratory. (For more on sampling requirements, see Chapter 3.)

Once the results are made available, they must be carefully reviewed to ensure that they are reasonably consistent. The laboratory should be made aware of questionable results immediately and given the opportunity to recalculate the results or re-analyze the sample. Once the data have been accepted, a summary spreadsheet should be prepared. Various spreadsheet programs can then be used to graph the data and perform statistical analysis.

DATA INTERPRETATION. After flow and analytical data have been verified and tabulated, findings can be drawn by interpreting the data properly via graphing and statistical analysis. Typically, a data set's average and standard deviations are calculated; they provide the primary basis for developing overall wastewater management concepts (e.g., control methods, operational changes, recycle and reuse, segregation and treatment, and alternative-concept evaluations).

When designing wastewater treatment facilities, more statistical manipulations are recommended (Eckenfelder, 2000). These include a probability plot showing a specific parameter's frequency of occurrence. To do this, the data are sectioned into values that the parameter may be expected to equal (or not exceed) 10, 50, or 90% of the time. Each value is then plotted on a graph, and the resulting linear curve can be used to determine the median and high-probability values for design or decision-making purposes. If probability data are only known for individual wastestreams (not the aggregate flow), a Monte Carlo simulation can use the individual stream data to estimate aggregate stream characteristics. (For a discussion of the statistical methods used to evaluate data, see Chapter 3.)

It is often useful to display the data so pollutant loads are related to specific facility operations. Some U.S. EPA effluent guidelines (e.g., 40 *CFR* 420 and 40 *CFR* 461) relate the allowable pollutant discharges to production or raw material rates. For example, the lead battery subcategory of the battery-manufacturing effluent guidelines establishes discharge limits in pounds of lead or copper per million pounds of lead used as a raw material. The continuous casting subcategory of the iron- and steel-manufacturing effluent guidelines establishes limits in pounds of lead or zinc per million pounds of product. Comparing wastewater constituents to facility operations also helps staff predict how future production-rate increases will affect pollutant loadings.

INDUSTRIAL WASTEWATER TOXICITY CHARACTERIZATION

REGULATORY FRAMEWORK. The Clean Water Act prohibits the discharge of "toxic pollutants in toxic amounts" to U.S. waterways; it regulates discharges via the National Pollutant Discharge Elimination System (NPDES). Industrial facilities that discharge directly to a waterbody are subject to NPDES permit conditions, which include both chemical-specific and WET (whole effluent toxicity) limits to ensure that water quality standards are achieved and maintained. Whole effluent toxicity tests, which the U.S. EPA approved in 1995 (60 *FR* 53529, October 16, 1995) and updated in 2002, measure the acute and chronic toxicity of effluents to freshwater, marine, and estuarine organisms. (For more information on applicable regulations, see Chapter 2.)

APPLICABILITY. Industrial facilities that discharge directly to surface water receiving streams must have NPDES permits, which typically include a requirement to measure the toxicity of a wastewater effluent sample. Effluents from permitted facilities are monitored, and WET limits are established if the effluent could reasonably exceed numeric toxicity criteria. If a permittee discovers a toxicity problem, a toxicity reduction evaluation (TRE) may be used to identify and reduce or eliminate the sources, whether or not the NPDES permit contains WET limits. Regulators also may require the permittee to perform a TRE via special permit conditions or an enforcement action.

COMMON TOXICS. The following pollutants are typically found in wastewater treatment system effluents:

- Chlorine (at concentrations between 0.05 and 1.0 mg/L);
- Ammonia (at 5 mg/L as NH_3-N);
- Nonpolar organics (e.g., organophosphate insecticides);
- Metals (e.g., cadmium, copper, iron, lead, nickel, and zinc) at various concentrations;

- Chemical treatment additives (e.g., dechlorination chemicals and polymers);
- Surfactants; and
- Total dissolved solids (at concentrations between 1000 and 6000 μmhos/cm).

For more information on toxic pollutants, see Chapter 2.

TESTING APPROACH. Toxicity can be identified via two approaches: conventional and toxicity-based. In the conventional approach, an effluent sample is analyzed for the 126 "priority pollutants" to try to identify the substance(s) responsible for the effluent's toxicity. If any were found to be present, analysts then compare the concentration(s) in the sample to the known reference toxicity data for that pollutant. Unfortunately, this approach often fails to pinpoint sources of toxicity for two reasons:

- The 126 priority pollutants are a tiny fraction of the chemicals that could be toxic to aquatic organisms, and
- This approach does not take into account a chemical's bioavailability [the synergistic effect of other factors (e.g., TSS, pH, hardness, and alkalinity) can affect a toxicant's bioavailability and, thus, its toxicity].

In the toxicity-based approach, the effluent sample is subjected to various physical and chemical treatment methods that categorize the nature of the toxic substance(s). Each physical and chemical treatment test method that is applied to the wastewater sample narrows the field of possible toxicants. Once the screening test procedures have been applied, a list of suspect toxicants is developed and further specific chemical analysis may then pinpoint the cause of toxicity. This latter approach has proven to be more efficient and effective.

TEST METHODS. The U.S. Environmental Protection Agency has issued guidance on the TIE test program (U.S. EPA, 1999), and modified WET procedures to reduce the testing procedures' time and cost burdens. The decision to use the acute or short-term chronic tests depends on NPDES permit requirements and the effluent's toxicity. The initial TIE testing should be performed using the test organism shown to be most sensitive to the effluent. If several organisms are equally sensitive, analysts should select the one that is easiest to use.

The effluent's toxicity is initially characterized via the so-called Phase I approach, in which several treatment methods are used to indicate the types of compounds responsible. These treatment methods include:

- Filtration—removes insoluble compounds.
- Ion exchange—removes inorganic ionic species.
- C18 SPE column—the C18 SPE column's resin removes nonpolar compounds.
- Aeration—batch aeration at acid, neutral, and basic pH removes essentially all volatile organics, as well as ammonia at high pH.
- EDTA addition—this chelation test removes combined cationic metals.
- Zeolite resin—zeolite ion exchange removes ammonia.
- Sodium thiosulfate—reduces any oxidants (e.g., chlorine).
- Biodegradability—biological treatment almost completely oxidizes biodegradable organics.

After each treatment step, analysts test both treated and untreated samples for toxicity. Through this process of elimination and knowledge of the facility's manufacturing processes and operations, analysts can discover the specific chemical or chemicals responsible for the toxicity. Then, control alternatives are identified and evaluated, and the appropriate controls are selected. Finally, the toxicity control method or technology is implemented and monitored to ensure that it achieves the TRE objectives and meets permit limits.

TRE CASE STUDIES. Following are examples of TRE procedures used to identify and solve toxicity problems.

Case A. An insecticides manufacturer evaluated various treatment methods for diazinon and chlorpyrifos. Studies suggested that solids adsorption was the best mechanism for removing organophosphate insecticides. Treatability tests showed that about 30% of diazinon and 85 to 90% of chlorpyrifos in the POTW's primary influent samples adsorbed to primary solids, and about 65 to 75% of the diazinon added to the mixed liquor adsorbed to the biomass. Chloropyrifos adsorbed to the biomass so strongly that none remained after biological treatment. The results suggested that longer MCRTs may remove more organophosphate insecticides. More diazinon was adsorbed in a 30-day MCRT biomass than in a 15-day biomass.

Case B. Sometimes process chemicals may cause problems. One industrial wastewater treatment plant routinely passed effluent toxicity tests until staff obtained a dechlorination chemical from a new vendor. When the chemical was used, the facility began failing effluent toxicity tests. The facility hired consultants to conduct TREs to determine the source of this toxicity. They discovered it when the dechlorination agent was changed to a new formulation and the facility again passed effluent toxicity tests. The lesson learned is to insist that purchased chemicals come with complete information on potential contaminants, including toxicity tests on product samples to verify their suitability.

Case C. A facility's discharge caused chronic effluent toxicity to *C. dubia.* Toxicity-identification-evaluation characterization tests conducted on the effluent did not show a reduction in toxicity as a result of the Phase I manipulations. Independent analyses of the effluent indicated elevated chloride concentrations. A mock effluent was prepared by adding the same cation and anion concentrations observed in the effluent sample, but using deionized water as the diluent. The mock effluent was found to be as toxic as the actual effluent. Laboratory toxicity data for sodium chloride were used to confirm that the effluent chloride levels would impair reproduction in *C. dubia* at the effect concentration.

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Chapter 5

Wastewater Treatability Assessments

Treatability assessments are essential to any consideration of industrial wastewater treatment but present a complicated challenge to environmental engineers. This chapter provides an overview of treatability assessment options. Not all options can be covered here, but the basic approaches for conducting biological and physical-chemical tests will be used as illustrations. Because most treatability tests will be conducted by experienced personnel at commercial laboratories and engineering firms, specific test protocols will not be covered in depth, but references will be cited where appropriate.

Industrial wastewaters come from various sources and have widely varying characteristics. No two industrial wastewaters are alike; two similar plants (e.g., breweries) can produce very different wastewaters. While most are too dilute to justify recovering products for beneficial reuse, many industrial wastewaters contain much higher concentrations of organic constituents than municipal wastewaters. Most industrial wastewaters contain a mixture of constituents. Some can be toxic or nonbiodegradable to biological treatment processes, intermittent discharges are common, and treatment plant designers and operators often have no control over these characteristics. A number of industries that produce wastewaters with readily biodegradable organic constituents (e.g., breweries, dairies, and food-processing facilities) often use chemicals at the end of operating shifts or on weekends for cleaning and disinfecting storage and processing vessels and pipelines. These chemicals can cause misleading results when conducting biological treatability tests if they exist in test samples in excessively large amounts. On the other hand, the potentially negative effects of these materials can be overlooked if their presence is not known. Industries that operate on a batch basis with frequent changes in product mix present almost insurmountable obstacles to proper conduct of treatability tests. In such cases, testing wastewater from a number of sources in the production facility or at various times may be required, or wastewaters must be monitored continuously to detect events that can cause upset or failure of a treatment process.

A prerequisite to conducting treatability tests is that the analyst understand the sources of wastewater and the treatment objectives and be familiar with the operating features of the proposed treatment process. Also, the analyst should know whether the test sample is a grab or a composite. Ideally, the analyst will know the raw chemicals and manufactured products that can appear in the wastewater. Much can be learned about potential interferences by examining material safety data sheets (MSDS) for chemicals used in processing plants. However, MSDS do not always list all materials that can adversely affect treatability.

There are two basic options for conducting treatability tests: batch tests and continuous reactor tests. Batch tests indicate reaction potential and potential interferences. Operating bench-scale reactors under continuous or semi-continuous feed conditions often can provide more realistic indications of treatability. These tests typically involve setting up a number of reactors with each operated at different input or operating conditions. These reactors must be operated long enough for steady-state conditions to occur with respect to both wastewater treatment and product formation. Such tests allow for reactor maturation—which can occur slowly—and show cumulative effects of substances that may accumulate over time. For example, ammonia released during the biodegradation of high-strength protein wastes can inhibit nitrification when operating at low solids retention times; an influx of chelating agent can adversely affect chemical precipitation processes.

The decision to conduct semi-continuous or continuous bench-scale reactor tests in addition to batch tests is somewhat subjective and depends to some extent on the intended use of the data and the risk associated with design on the basis of short-term batch tests. If the data will be used to design new processes, then bench-scale reactor tests have significant value because they estimate process design and operating parameters that considerably reduce the risk of failure. If the tests are conducted to evaluate operating problems in existing processes, then batch tests may have more value because more variables can be tested in a short time. An option for fewer risks of performance failure is to conduct laboratory- or field-scale pilot tests, but at a substantial increase in time and costs.

MATERIALS, SUPPLIES, AND INSTRUMENTATION

To conduct treatability tests, analysts need standard laboratory glassware, hardware, and diagnostic instrumentation (Table 5.1). Equivalent types and sizes may be substituted as long as the test setup is unaffected.

WASTEWATER CHARACTERIZATION

Adequate wastewater characterization is a prerequisite for treatability tests (Table 5.2). Treatability assessments typically involve only one or a few samples, so the sample(s) must be representative of the wastewater. They typically are composite samples collected over a normal operations cycle and ideally should contain the expected full-scale, maximum concentrations of all constituents. Otherwise, the treatability tests could miss the adverse effects of high concentrations or loading rates. Analysts often spike a sample with a waste stream or chemical when evaluating the effect of changes in that waste stream or chemical. (For more information on wastewater characterization, see Chapter 4.)

AEROBIC BIOLOGICAL TREATABILITY TESTING

BATCH TESTS. Batch biological tests indicate the biodegradation characteristics of wastewater constituents, show the extent of biodegradation, provide a basis for estimating kinetic parameters, and indicate potential toxicity. They typically involve a series of wastewater dilutions or various concentrations of constituents expected to appear in the pretreatment system's influent. Ideally, the test sample's COD should be at or near the maximum concentration expected in practice. Respirometers often

Table 5.1 Summary of test materials, supplies, and instrumentation needed to conduct treatability tests.

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1. Laboratory glassware and hardware for sample handling, mixing, and transfer glassware (see *Standard Methods* [APHA et al., 2005], Sect. 1070)
    - a. Pipettes, syringes, beakers, etc.
    - b. pH meter and standards
    - c. Bench-top centrifuge capable of producing $G > 5000$
    - d. Dissolved oxygen meter
    - e. Filtration apparatus for TSS analysis (see *Standard Methods,* Sect. 2540)
    - f. Apparatus for measuring COD (see *Standard Methods,* Sect. 5220)
    - g. Glass vials suitable for storing samples for subsequent chemical analysis
2. Instrumentation
    - a. Bench-scale instruments for measuring pH, dissolved oxygen, turbidity, conductivity
    - b. Spectrophotometer for measuring optical absorbance and color intensity
    - c. Analytical instrumentation as required to detect and quantify organic and inorganic wastewater constituents (GC, GC/MS, ion chromatograph, AA, ICP, LC, etc.)
3. Reagent or analytical grade chemicals are required for test solutions
4. Reagent grade water source (Type IV as defined by ASTM Standard D 1193 [2003] or *Standard Methods,* Sect. 1080)
5. For biological treatability tests:
    - a. Respirometer system having sufficient oxygen uptake and/or gas production measurement capacity to meet test objectives
    - b. Water bath, incubator chamber, or constant temperature room for maintaining constant temperature in respirometer vessels (+1.0° C) and bench-scale reactors (+3° C)
    - c. Nutrient, mineral, and buffer solutions to support biological growth
    - d. Culture source suitable for meeting test objectives
    - e. Organic chemicals suitable for use as control substrates
    - f. Glass or other vessels suitable for use as bench scale reactors
6. For physical/chemical treatability tests:
    - a. Jar test apparatus
    - b. Filtration apparatus for measuring TSS
    - c. Turbidity meter

Table 5.2 A list of characterization parameters typically associated with various treatment process options.

Process options	Wastewater characterization tests
Biological processes	COD, BOD, TSS, VSS, NH_3-N, NO_2-N, NO_3-N, PO_4^{3+}, $SO_4^{=}$, pH. (Heavy metals, salts, specific cations, etc. should be included if these parameters are expected to affect biological treatability). GC/MS analysis for specific organic chemicals often is required if wastewaters include pesticides, herbicides, or other anthropogenic compounds of interest.
Inorganic chemical precipitation processes, ion exchange processes	Instrumental analysis of all cations and anions of interest or those expected to affect the proposed treatment process (ICP, ion chromatograph, etc.)
Solids concentration processes: Settling, dissolved air flotation (DAF), thickeners, belt filters, filter presses, etc.	TSS, VSS, particle size distribution of water applied sometimes after pretreatment by other physical/chemical processes.
Granular media, microfilter, or ultrafilter processes	TSS, VSS, particle size distribution of water applied to filter, sometimes after pretreatment by other physical/chemical processes.
Carbon absorption	Total soluble organic concentration as TOC or COD; GC/MS analysis to determine concentrations of individual organic chemicals of interest.

are used to measure oxygen uptake in response to various test combinations. The seed culture used for these tests should be obtained from a source acclimated to the wastewater constituents, but this option is not always available. While acclimated cultures can be developed in the laboratory, this may require considerable time. So, batch respirometer tests often are done with unacclimated cultures. This option indicates the need for acclimation and will help show unusual biodegradation characteristics. However, using unacclimated cultures may indicate less organic removal than actually will occur in a continuously operated treatment process. A number of standardized batch test protocols are available for assessing biodegradation characteristics, and the selection of a specific protocol is based on test objectives (Table 5.3).

The use of batch tests to assess biodegradation characteristics must be accompanied by good experimental design. Among other things, the experimental design must

Table 5.3 Batch biological test options.

Batch Test Type	Objective
Aerobic batch tests : a. Standard Methods, 5210.D (APHA et al., 2005) Respirometric method (for BOD). b. OECD Method 301 (1992); U.S. EPA, OPPTS 835.3110 (1998): Ready biodegradability. c. ISO 9408 (1999), 7827 (1994), 10707 (1994) Biodegradability tests. d. ASTM 5120-90 (1995), U.S. EPA, OPPTS 850.6800 (1996); OECD 209 (1994); ISO 8192 (1996). Inhibition of respiration test for sparingly soluble chemicals. e. Intrinsic and extant kinetic tests (Ellis, Barbeau, et al., 1996; Ellis, Smets, et al., 1996; Magbanua et al., 2003; Young and Cowan, 2004).	1. To assess biodegradability of specific organic compounds or the mixture of organic constituents in industrial wastewaters. 2. To provide a database for estimating intrinsic kinetic coefficients in enriched culture, single-compound environments. 3. To provide a database for assessing extant kinetic parameters for specific organic chemicals in a natural biological treatment plant environment.
Anaerobic respirometer tests: a. U.S. EPA, OPPTS Method 835.3400 (1998); ASTM 1196-7 (1987) Anaerobic Biodegradability (BMP). b. Anaerobic toxicity assays (ATA) (Owen et al., 1979). c. Anaerobic biomass activity tests (Cho et al., 2004). d. Intrinsic kinetic tests (Kim et al., 1996, Davies-Venn et al., 1989; Young and Cowan, 2004).	1. Anaerobic batch tests are used to assess biodegradation characteristics of specific chemicals or the mixture of chemicals in industrial wastewaters and to provide a database for estimating intrinsic kinetic parameters for specific chemicals. 2. Anaerobic biomass activity tests provide a measure of the maximum rate at which an anaerobic culture converts acetate to methane.

consider the proper balance between the initial substrate and biomass, an adequate number of data points throughout the substrate uptake reaction, and the influence of biomass decay if long time periods are required for substrate use. Equipment limitations often control the type of batch tests that can be run. For example, some aerobic respirometers often are limited to low rate tests because of oxygen transfer limits in the reaction vessels (Moon and Young, 2002). This limit is related to the size of the reaction vessel, the culture's oxygen demand, and the respirometer's mixing capabilities.

Figure 5.1 illustrates three possible batch test responses. In this case, the test samples' oxygen uptake is compared to that for a control substrate that is easily degraded so the terminal oxygen uptake approaches the sample's COD. Wastewaters requiring acclimation will show an extended lag with recovery when acclimation occurs. In some cases, inhibition will occur and the oxygen uptake rate will be substantially less than that for the control. A similar trend will occur when the wastewater contains organic substances that are slowly biodegradable. When extremely toxic chemicals are present, the oxygen uptake can be less than that for the seed culture.

Batch biological treatability testing often is used to determine the biodegradation coefficients for use in process design and performance models. The biodegradation of organic materials is typically expressed as follows:

$$R_S = \frac{q_m\, S\, X_a}{K_S + S} \tag{5.1}$$

and

$$R_g = Y_g\,(R_S) - K_d\, X_a \tag{5.2}$$

Where

R_S = rate of substrate conversion (typically mg COD/L·d),
R_g = rate of biomass growth (mg VSS/L·d),
S = substrate concentration (typically COD) (mg/L),
q_m = maximum specific substrate uptake rate (mg COD/mg VSS·d),
K_S = half-saturation coefficient (mg/L),
X_a = active biomass concentration (mg/L),
Y_g = biomass yield coefficient (mg VSS/mg COD_R), and
K_d = decay coefficient (d^{-1}).

Test data are modeled using various forms of Equations 1 and 2 and nonlinear numerical analysis techniques to estimate the kinetic parameters: Y_g, K_d, q_m, and K_S (Dang et al., 1989; Young and Tabak, 1993). Parameters found when testing at high S_o/X_o ratios (> 5:1) typically are labeled *intrinsic*, while tests conducted at low S_o/X_o ratios (< 1:1) typically provide extant kinetic parameters (those that characterize reactions under in-plant operating conditions) (Young and Cowan, 2004).

BENCH-SCALE REACTOR TESTS. More realistic indications of treatability can be obtained by operating bench-scale reactors under continuous or semicontinuous feed conditions. These tests typically involve setting up a number of reactors, each

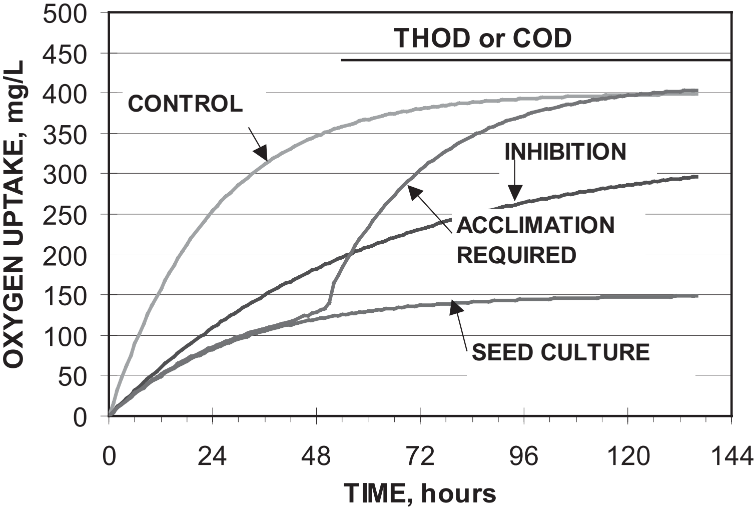

FIGURE 5.1 Examples of oxygen uptake reactions that can occur in batch treatability tests (Young and Cowan, 2004; used with permission).

operated at different hydraulic and solids retention times. The reactors must be operated for enough time for steady-state conditions to occur with respect to both effluent quality and biomass growth. This condition typically requires operating the test units for at least two solid retention times, so test durations range from 20 to 30 days for aerobic bench-scale reactor tests and 45 to 90 days for anaerobic tests. Such tests can allow for acclimation of microorganisms—which can occur slowly—and can show cumulative effects of toxic substances that may be in wastewater or accumulate as biodegradation products. A limited number of standardized protocols are available for continuous bench-scale reactor tests (Table 5.4).

Satisfactory results require precise control of the culture reactors throughout the test program, as well as accurate and precise measurement of substrate concentration, often at very low levels. Biological consistency also must be maintained among reactors throughout the test program. If a problem occurs with a given reactor (e.g., system upset or operating error), that reactor ideally should be operated until new equilibrium conditions are reestablished. If acclimation is required, longer times must be permitted for equilibrium to be reached. This type of operation can be time-consuming, labor-intensive, and costly.

TABLE 5.4 Standardized bench-scale continuous reactor test protocols.

Test Type	Objective
Bench-scale aerobic reactor tests: a. OECD Method 302 (1981); U.S. EPA, OPPTS Method 835.3210 (1998): ISO 9439 (1999) Semi-Continuous Activated Sludge (SCAS) Test. b. OECD Method 303 (2001); U.S. EPA Method 304 (1996): Assessing biodegradation and/or toxicity of specific chemicals or wastewaters. c. U.S. EPA, CFR 40,k part 63, App. C (1996). Determination of biodegradable fraction (BOX test). d. Custom-designed bench-scale reactor tests (Young and Cowan, 2004).	Bench-scale reactor tests are designed to assess the rate and extent of biodegradation of specific organic chemicals or the mixed constituents of industrial wastes. The data are used for process selection; design of full-scale treatment facilities, or to assist in the operation of full-scale facilities; and to provide estimates of treatment efficiency, waste biosolids production, and response to inputs of industrial wastes. The BOX test is specifically designed to determine biodegradability of volatile organic compounds.
Bench-scale anaerobic reactor tests: a. Anaerobic treatability (Young and Cowan, 2004).	Same as for aerobic bench-scale reactors.

Data from bench-scale reactors typically are modeled as follows:

$$Y_{\mathrm{n}} = Y_{\mathrm{g}} \frac{(1 + 0.2\, K_{\mathrm{d}}\, \mathrm{SRT})}{(1 + 1.2\, K_{\mathrm{d}}\, \mathrm{SRT})} \tag{5.3}$$

and

$$S_{\mathrm{e}} = \frac{K_{\mathrm{S}}\,(1 + K_{\mathrm{d}}\, \mathrm{SRT})}{\mathrm{SRT}\,(Y_{\mathrm{g}}\, q_{\mathrm{m}} - K_{\mathrm{d}}) - 1} + \mathrm{COD_{nd}} + \mathrm{SMP} \tag{5.4}$$

Where

Y_{n} = net yield (g VSS/g COD removed),

S_{e} = soluble COD remaining in each bench-scale reactor (mg/L),

$\mathrm{COD_{nd}}$ = non-biodegradable soluble COD in reactor effluents (mg/L), and

SMP = soluble microbial products (mg/L).

Example yield data from continuous reactor tests are shown in Figure 5.2, where three reactors were operated at 5-, 15-, and 30-day SRTs. Solids and soluble COD were measured at steady-state conditions. In this case, there was a significant source

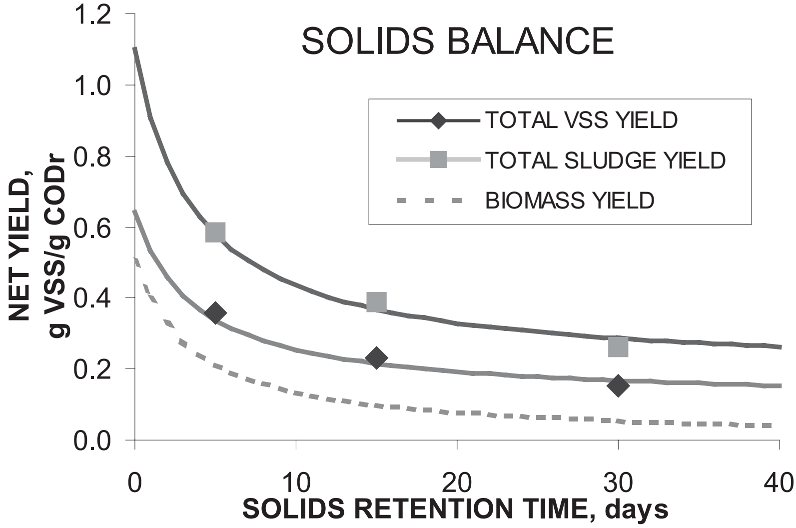

FIGURE 5.2 Solids balance for wastewater containing significant amounts of non-biological volatile suspended solids (Young and Cowan, 2004; used with permission).

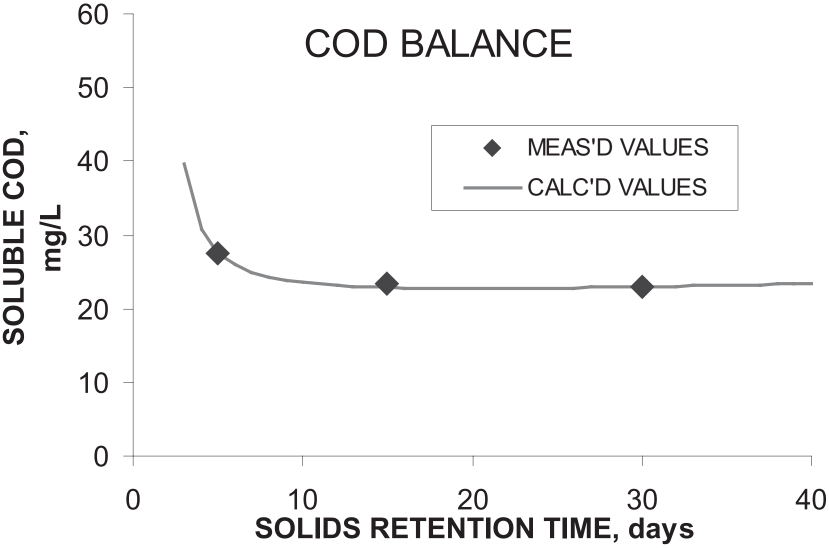

FIGURE 5.3 Example of modeling effluent chemical oxygen demand versus solids retention time using eq 5.4 (Young and Cowan, 2004; used with permission).

of non-biodegradable volatile solids, so the net VSS yield (Y_{vo} = 0.642 g VSS/g COD_r) was higher than anticipated for biomass growth alone (dashed line). The resulting total sludge (TSS + VSS) yield (Y_t = 1.1 g TSS/g COD_r) was substantially higher than the net VSS yield because the wastewater contained substantial amounts of nonvolatile suspended solids.

Corresponding soluble COD balances using Eq. 5.4 are shown in Figure 5.3. In this case, the associated q_m and K_S were 1.5/d and 8 mg/L, respectively. The tests further showed that the nonbiodegradable COD was 17 mg/L. The slight increase in soluble COD at the 30-day SRT was caused by the production of soluble microbial products.

ANAEROBIC BIOASSAYS AND TREATABILITY TESTING

Anaerobic bioassays require a slightly different approach than that used for aerobic testing. A number of methods, test reactors, test procedures, and test combinations can be used, and onsite pilot tests may be justified to verify the treatability indicated by laboratory-scale tests. Standardized protocols for batch anaerobic tests are shown in Table 5.1.

BATCH ANAEROBIC TREATABILITY TESTS. Batch anaerobic tests typically are called biochemical methane potential (BMP) and anaerobic toxicity assay (ATA) tests. The objective of BMP tests is to determine the potential amount of methane that can be produced per unit of COD added to the test reactor under nontoxic conditions. About 0.37 L of methane is produced per gram of COD removed if the wastewater constituents are 100% biodegradable and treatment occurs at 35° C. Lesser amounts of methane indicate lower conversion efficiencies. Results of an example BMP test are shown in Figure 5.4. These data represent the methane produced from three sequential doses of test wastewater to an anaerobic culture. The gas production for each dose becomes constant as the biodegradable COD was exhausted. The increase in methane production with each feed dose reflects the culture's acclimation to the test constituents and would approach the methane production for the control as the reactor matures.

The objective of ATA tests is to assess the toxicity of specific chemicals or wastewater streams to acclimated anaerobic cultures. The reduction in the methane production rate with an increasing dose reflects toxic effects. Test data are shown in Figure 5.5 for a typical ATA test where various doses of an industrial disinfecting agent were added to an acclimated culture that received acetate as a biodegradable

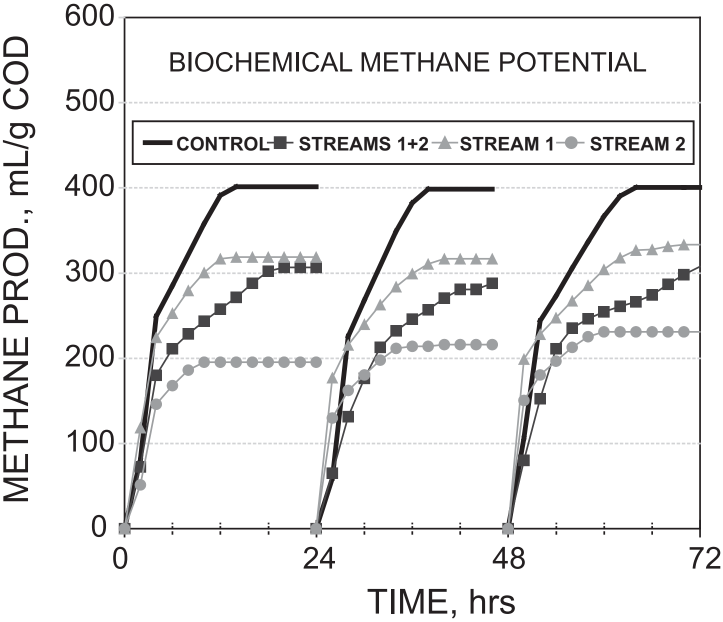

FIGURE 5.4 Anaerobic biochemical methane potential tests for three industrial wastewaters (Young and Cowan, 2004; used with permission).

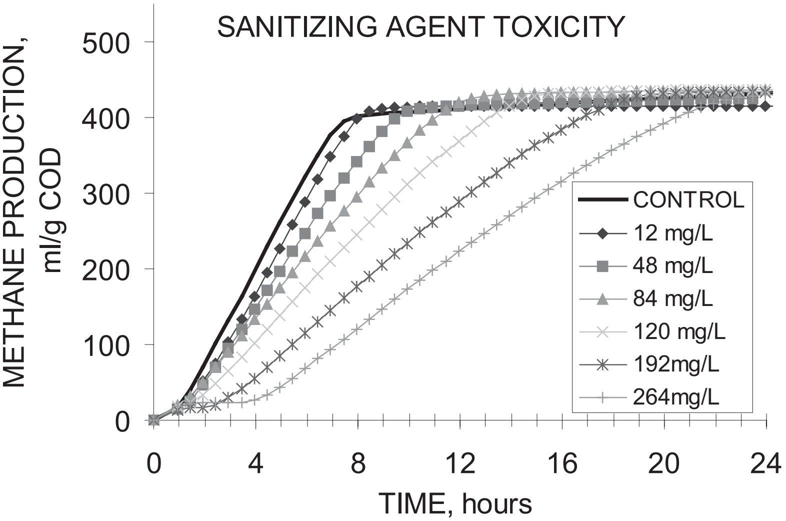

FIGURE 5.5 Anaerobic toxicity assay for a sanitizing agent (Young and Cowan, 2004; used with permission).

substrate. In this case, a concentration of 120 mg/L of disinfecting agent caused a 50% decrease in the methane production rate.

CONTINUOUS ANAEROBIC REACTORS. Continuous anaerobic tests involve adding wastewater or a test chemical to reactors that contain an active anaerobic culture on a continuous or semicontinuous basis. Methane production for each test reactor is monitored using suitable flow-measuring devices. The cumulative methane production for the control will plot as a straight line with a slope equal to the rate of daily methane production (Figure 5.6) for tests with a chemical-production wastewater. In this case, the feedstock included a control (acetic acid) plus three mixtures of control and wastewater plus one reactor receiving 100% wastewater. All reactors were operated at a 20-day SRT and at an organic loading rate of 1 g COD/L·d. Methane production initially was the same in all reactors. After about 10 days, the reactors receiving the 100% wastewater began to show a decline in methane production rate compared to the control. Batch tests on the 27th day of operation verified the substantial inhibition of methane production, with the 100% wastewater showing essentially no methane production (data not shown).

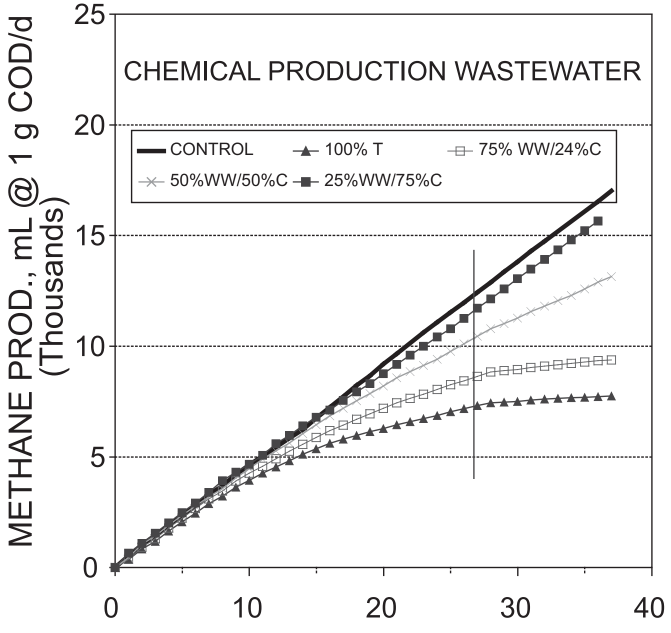

FIGURE 5.6 Cumulative methane production from anaerobic bench-scale test reactors (Young and Cowan, 2004; used with permission).

PHYSICAL AND CHEMICAL TESTS

Options for physical and chemical treatability testing vary considerably but typically include chemical precipitation followed by physical separation using clarification, filters, dissolved air flotation (DAF) or other means; ion exchange; electro-coagulation; and carbon absorption. Treatability assessment protocols for physical and chemical process combinations depend on the wastewater characterization and the treatment objectives. Treatment for removing one constituent (e.g., chromium from plating wastewaters) will require completely different approaches than removing dissolved solids from wastewaters with a mix of mineral constituents. Chemical treatment typically requires use of an acceptable solids separation device [e.g., clarifier, filter, membrane separator, centrifuge, dissolved air flotation (DAF)] and treatability tests must incorporate suitable means for assessing the suitability of these processes. Selecting a specific treatability protocol then requires carefully defined treatment objectives, accurate characterization of the wastewater constituents, assessment of the variability in composition and conditions (e.g., pH, temperature, and ORP). Often, a process combination will be selected based on the designer's experience, previous history of treatment of the subject wastewater, and economic analysis. Treatability tests then are set up to verify the selected system's performance. A list of contaminant classes and potential process options associated with physical and chemical treatment is given in Table 5.5. Other combinations of contaminant and process options can exist.

The basic approach to initial testing for chemical treatment is the jar test (ASTM, 2003b). Jar tests involve adding various amounts of test chemicals to a series of reactions vessels, which then are mixed under controlled conditions. Coagulating chemicals typically include iron or aluminum salts that neutralize anionic charges on contaminant particles and form precipitates. Organic polymers typically are added to aid flocculation. Test procedures are designed to simulate anticipated reactions in full-scale physical and chemical processes. Test configurations can be as varied as the number and types of processes being considered for the full-scale facility. Test parameters typically include chemical combination and dose, mixing intensity, and settling time. After mixing intensely for a few seconds after adding chemicals, the sample is mixed slowly to allow the chemical precipitates or wastewater solids to flocculate. The solids are then removed by settling, filtering, or other means followed by analyzing the clarified solution for residual contaminants and assessment of the solids' settling and/or filtering properties.

TABLE 5.5 Contaminant class and potential process options for physical/chemical treatment.

Contaminant class	Potential treatment process options
Suspended solids removal	Chemical precipitation using iron or alum salts as coagulants plus polymer as flocculation aid followed by solids separation.
Sodium, potassium, chloride, sulfate	Pretreatment by chemical precipitation and filtration followed by ion exchange, reverse osmosis.
Calcium, magnesium, iron, manganese	Ion exchange, chemical precipitation followed by coagulation and flocculation and solids separation.
Chromium, copper, zinc, silver, mercury, lead, other heavy metals	Co-precipitation with iron or aluminum salts plus polymer followed by settling, filtration, or membrane separation; also electrocoagulation using iron or aluminum electrodes.
Arsenic, selenium	Co-precipitation with iron salts, absorption on iron-rich solid medium or activated alumina.

The rate at which neutralized particles agglomerate is controlled by physics. The amount of mixing or power input used in a flocculation process affects the manner in which flocs are formed and the floc's size and settling properties. Typically, mixing in flocculation reactors is expressed in terms of the mean velocity gradient (Camp and Stein, 1943; Weber, 1972), as follows:

$$G = \left(\frac{P/V}{\mu}\right)^{0.5} \tag{5.5}$$

Where

G = mean velocity gradient (sec^{-1}),
P = power input (N-m/s),
V = reactor volume (m^3), and
μ = absolute viscosity of the water (N-s/m^2).

The product of G and hydraulic retention time (t) often is used to size rapid-mix and flocculation basins. G values for conventional flocculation reactors typically are limited to between 10 and 75 sec^{-1} to prevent floc breakup (Amirtharajah and Tambo,

TABLE 5.6 Typical steps used during chemical testing using jar tests.

1. Collect a sample that is representative of the wastewater being tested.
2. Measure physical/chemical parameters of interest in raw wastewater – TSS, VSS, TCOD, sCOD, BOD_5, specific cations and anions of interest, pH, conductivity, alkalinity, etc.
3. Adjust the pH of the test sample if needed to simulate operating conditions.
4. Add test chemicals singly or in various combinations ranging from zero (control) to above maximum anticipated for full-scale operation.
5. Mix sample appropriately. A short rapid mix usually is used to allow chemical reactions to occur usually at $G = 1500$ to 5000 sec^{-1}.
6. Mix samples slowly to allow flocculation of chemical precipitates or coagulated solids usually at $G = 10$ to 75 sec^{-1}.
7. Settle or filter solids as appropriate to produce a simulated treated effluent (typically for 30 to 60 minutes).
8. Analyze the clarified supernatant in test jars for analytes of interest.
9. Measure the amount of sludge produced per unit of wastewater treated.

1991). Hydraulic retention times in conventional flocculation basins typically range from 10 to 30 minutes, and $G \times t$ values range from 10^4 to 10^5. However, as with rapid mixers, the type of mixing device and basin geometry can affect the optimum combination of energy input and retention time. So, jar test apparatus used for conducting chemical treatability must allow control of mixing intensity, and, therefore, velocity gradient and mixing time. The steps in typical jar test protocols are summarized in Table 5.6.

Flocs formed in coagulation and flocculation processes typically are removed from suspension by sedimentation. For most physical and chemical applications, solids settleability is defined by settling rates (in kg $TSS/m^2 \cdot d$) and the sludge zone's concentration is expressed as sludge volume index (SVI) in milliliters of sludge volume per gram of settled solids after 30 to 60 minutes of settling. Other means for removing solids from suspension can be used (e.g., centrifugation or filtration).

Example data from a test designed to remove various heavy metals from an industrial wastewater are shown in Figure 5.7. Ferric chloride was used as a chemical coagulant and an anionic polymer was used as a flocculent aid, solids were removed by settling and filtration, and the filtrate was analyzed for residual metals. In this case, the optimum Fe^{+++} dose was around 30 mg/L.

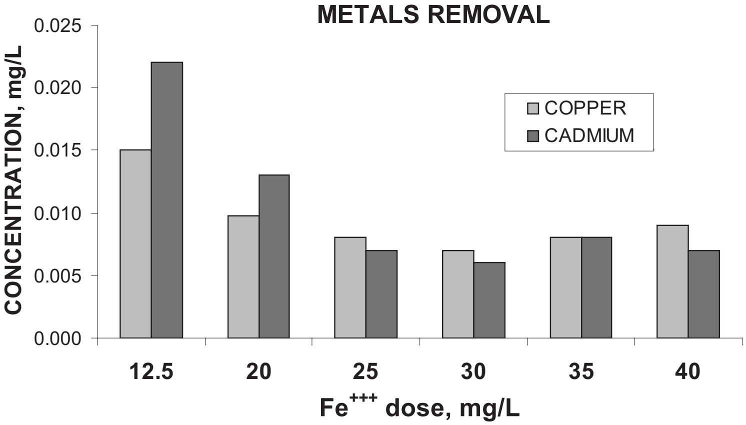

FIGURE 5.7 Data from a typical jar test used to assess the appropriate chemical dose needed to remove copper and cadmium from a wastewater via chemical precipitation and filtration.

MEMBRANE FILTRATION. Membrane systems are used to separate solids in membrane bioreactors (microfilters), to remove residual precipitates from chemically treated wastewater (microfilters, ultrafilters), to remove colloidal solids (ultrafilters, nanofilters), and to remove dissolved salts (nanofilters, reverse osmosis, electrodialysis). Membrane process equipment can consist of hollow-fiber, flat sheet or plate, or spiral-wound sheet devices. The possible combinations of pretreatment and membrane type and module configuration are quite large, so it is impossible to cover all treatability test options. Therefore, environmental engineers must first minimize the number of options based on experience, proven history of membrane application for treating similar wastewaters, and cost estimates. Treatability tests then include a series of chemical pretreatments, sometimes incorporating solids separation by DAF, settling or granular media filtration, followed by membranes. Most manufacturers of membrane systems have treatability laboratories or suggested test protocols.

ACTIVATED CARBON ABSORPTION. Soluble organic materials in industrial wastewaters can be removed from solution via absorption on granular or powdered activated carbon (see Chapter 13). Batch absorption tests are used to determine absorption isotherms (i.e., absorption capacity of a specific chemical or mixture of chemicals on a specific carbon type) (Weber, 1972). Batch isotherm tests are conducted somewhat the same as jar tests, in which various doses of substrate are added to vessels containing a known amount of GAC or PAC (Table 5.6). The vessels are mixed for enough time for equilibrium to occur between bulk solution and the carbon. The mass difference in substrate concentration after this contact time and the beginning concentration represents absorbed material. The amount of substrate absorbed per gram of GAC or PAC is plotted versus substrate concentration (Figure 5.8). Carbons producing the most absorption capacity typically are selected for use in the full-scale process.

The relationship between the mass of adsorbate (the material being absorbed) per unit of absorbent (the GAC or PAC) typically is expressed as follows:

$$q_{\mathrm{F}} = k_{\mathrm{F}}\, S^{\mathrm{n}} \qquad \text{(Freundlich isotherm)}$$

$$q_{\mathrm{L}} = k_{\mathrm{L}}\, S\, q_{\mathrm{m}}/(1 + S) \qquad \text{(Langmuir isotherm)}$$

$$q_{\mathrm{B}} = \frac{k_{\mathrm{B}}\, S\, q_{\mathrm{m}}}{(S_{\mathrm{B}} - S)\,[1 + (k_{\mathrm{B}} - 1)\, S/S_{\mathrm{B}}]} \qquad \text{(BET isotherm)}$$

Where

$q_{\mathrm{F,L,B}}$ = g substrate (S)/g GAC or PAC,
S = substrate concentration (mg/L in contact with GAC or PAC),
$k_{\mathrm{F,L,B}}$, n = absorption coefficients,
q_{m} = maximum absorption (g S/g GAC or PAC), and
S_{B} = mg/L substrate in solution when carbon is saturated.

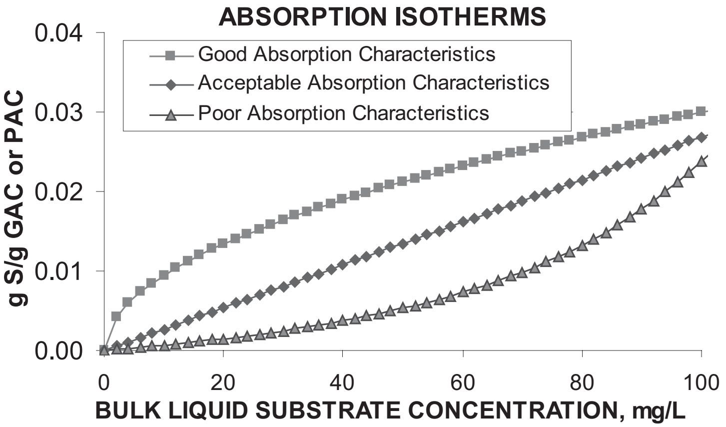

FIGURE 5.8 Illustration of three absorption characteristics of activated carbon.

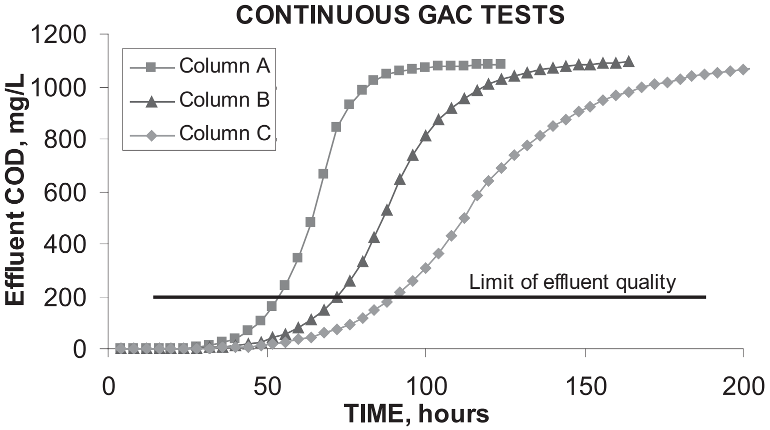

FIGURE 5.9 Illustration of breakthrough curves for granular activated carbon absorption columns.

Continuous absorption tests are used to assess the performance of GAC in situations designed to simulate the performance of carbon columns under anticipated full-scale plant operating conditions. In this case, wastewater samples are fed to laboratory-scale columns of GAC followed by monitoring of the effluent quality. The pattern of effluent concentration over time indicates the time of operation and the mass of contaminant absorbed per unit of carbon. Process variables include bed depth, carbon source and grain size, contact time, and wastewater characteristics. An illustration of effluent COD versus time for three GAC columns operated under different conditions is shown in Figure 5.9.

PILOT PLANT OPERATIONS. Pilot-scale testing often is desirable to confirm or expand the information obtained in bench-scale testing. Pilot testing can be accomplished at laboratory or field scale. Both levels involve operating units continuously using wastewater for which treatment is anticipated. Laboratory-scale pilot units range from around 10 L to 1 m^3. Wastewater samples typically are shipped to the test laboratory on a weekly or more-frequent schedule to cover a range of characteristics. One advantage of laboratory-scale pilot plants is the flexibility of unit sizing and operation, and changes can be made easily and quickly. The major disadvantage is that laboratory-scale reactors do not allow operation at full-scale operating conditions. The cost of laboratory-scale pilot tests depends on the treatment options covered and the duration of testing, but typically is about one-tenth the cost of field-scale pilot tests.

Field-scale pilot plants range in size from around 1 to 100 m^3. The major advantages of field-scale piloting are that the process units can be operated under actual wastewater flow and characteristic conditions, and field-scale units can simulate better the actual design of a full-scale reactor. The value of field-scale piloting depends on how well the pilot-scale reactor simulates functional parameters of the anticipated full-scale reactor. For example, a key parameter for some full-scale processes is upflow velocity. For true simulation, a pilot-scale reactor should have upflow velocities in the same range as the full-scale system. Without reasonable similitude between pilot and full-scale reactors, the value of a field-scale pilot test is questionable. The cost of field-scale piloting depends on the size of the equipment and duration of the testing program.

SAMPLE WITHDRAWAL, PROCESSING, AND STORAGE. Samples are withdrawn from treatability test reactors for analysis to meet various test objectives. These samples must be processed appropriately to prevent further changes in composition or loss of constituents because of volatilization or biodegradation (APHA, 2002). Specific steps involve sample transfer, preservation, and liquid-solids separation. Ideally, centrifugation should be used to remove the biomass from anaerobic test reactors because the high vacuum used in filter apparatus can cause loss of volatile organics. Preservative should be added before solids separation if more than 5 minutes will elapse before liquid-solids separation can be completed. The goal of sample preservation is to stop biochemical reactions involving the compounds of interest, including the base substrate, metabolic intermediates, and organic toxic chemicals, if any are present.

Preservation techniques for biological samples typically involve adding an organic or inorganic toxic substance, adding an acid to reduce the pH, or holding the sample at reduced temperatures. Preserving agents must not mask or interfere with the measurement of target constituents. For maximum effectiveness, the preserving agent must stop the reactions immediately. However, each method has certain disadvantages. Refrigeration is not effective as the sole preservation technique because biological reactions continue until storage temperatures are reached and resume upon thawing. Organic preservatives (e.g., formaldehyde or chloroform) are unacceptable because of potential interference with organic chemical measurement and because their addition can dilute the sample considerably. Acids cannot be used with samples containing biological solids because the reduced pH can shift the equilibrium of toxic organic chemicals between solids and liquid and may cause hydrolysis of biological solids.

The preservation method recommended for biological samples includes a combination of the above. Samples removed from test reactors are placed immediately into vials containing 1 mL of 10 g/L $AgSO_4$ per 100 mL of solution or one to two drops per 10-mL sample. This procedure provides an $AgSO_4$ concentration of about 100 mg/L. [Note: This $AgSO_4$ replaces the $HgCl_2$ recommended in older U.S. EPA (1986) documents.] In most cases, the preserved samples should be centrifuged within 30 minutes of adding the preservative to remove suspended solids and inorganic precipitates. Subsamples of each centrate are then placed in smaller vials containing one drop of concentrated sulfuric acid per 10 mL. These acidified samples may be stored for up to 30 days at 4° C without loss of nonvolatile substrates, as long as the bottles have not been opened or the septa have not been pierced. Samples containing highly volatile organic compounds should be analyzed within 24 hours after collection. Once the bottle is opened or the septum is pierced, volatile compounds are lost rapidly (U.S. EPA, 1989).

Preservation methods for chemically treated samples are less severe than for biological samples. Typically, acid or alkaline agents—depending on cation or anion being preserved—are used before further precipitation or absorption. Specific cation or anions may require unique preservation techniques. Metallic cations typically are preserved using ultra-pure nitric acid to $pH < 1$. Some chemicals (e.g., phthalates) require storage under alkaline conditions to prevent precipitation of the acid salt.

SUMMARY

Treatability test options vary widely, and specific protocols must be carefully chosen to meet test objectives. Typically, such tests should be conducted by trained professionals who understand the relationships between biological or chemical reactions and process technologies. Well-designed treatability tests provide valuable insight into the factors affecting process performance. Treatability tests also are relatively inexpensive insurance against oversights by applying conventional design approaches to wastewaters with unknown or poorly defined characteristics (e.g., toxicity and unfavorable reaction kinetics). Well-designed laboratory pilot tests often can preclude the need for costly field-scale pilot tests. However, field-scale pilot tests provide more accurate design parameters and demonstrate process performance under field conditions, and are beneficial when the risks of failure are high.

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Chapter 6

Industrial Wastewater Characteristics and Approach to Wastewater Management

(continued)

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This chapter summarizes general characteristics and treatment approaches for industrial wastewaters, and presents brief descriptions of each regulated point source category. Wastewater characteristics and treatment approaches have been organized in tables for ease of reference. Most of the information was obtained from U.S. Environmental Protection Agency (U.S. EPA) technical development documents prepared to support the effluent limitations for related point-source categories. Treatment options and wastewater flow for about 21 point-source categories were supplemented with information presented in the U.S. EPA's *Technical Support Document for the 2004 Effluent Guidelines Program Plan* (U.S. EPA, 2004). Other references used for point-source categories for which the development documents were not available online are listed under the "Suggested Readings" section.

The information in this chapter can serve as a reference for potential pollutants of interest and treatment approaches, but before selecting wastewater management procedures, each facility should properly characterize its wastewater (Chapter 4), perform the appropriate treatability and pilot testing (Chapter 5), and evaluate the cost-effectiveness of various wastewater management approaches (e.g., water use minimization, pollution prevention, recycling, reuse, and treatment and discharge) as described in this chapter and Chapter 7. The variations between facilities resulting from site-specific conditions (e.g., climate, receiving-water type and conditions, types of products, manufacturing capacity, or need to reuse water) can be significant, and should be carefully considered. Specific descriptions of treatment systems are provided in Chapters 8 through 13.

WASTEWATER CHARACTERISTICS

As of March 31, 2007, the U.S. Environmental Protection Agency had promulgated effluent limits for 56 point source categories (see Table 2.6 in Chapter 2). Table 6.1 lists the regulated constituents for these point source categories (based on a review of 40 *CFR* 405–471), but they may not be the only pollutants found in the point sources' wastewaters. Sometimes the U.S. EPA only regulates several indicator pollutants because their removal ensures that related pollutants also have been treated appropriately. For example, 5-day biochemical oxygen demand (BOD_5) and volatile organic compounds (VOCs) are not regulated in the iron and steel category because the biological treatment process required to remove benzo(a)pyrene also reduces BOD_5 to acceptable levels, and the distillation process required to remove ammonia also removes VOCs.

When reviewing Table 6.1, also keep in mind that:

- Not all pollutants may apply to all of the subcategories in a point source category,
- Some effluent pollutant limitations only apply if the facility discharges to a publicly owned treatment works (POTW),
- Not all pollutants of concern may be listed for subcategories in which "no discharge" is the promulgated effluent limitation, and
- Not all of the "no discharge" effluent limitations are listed.

When characterizing wastewaters for a specific facility, wastewater professionals should be aware that some pollutants must be analyzed via a specific method. For example, pollutants in pharmaceutical wastewaters must be analyzed via Methods 1666, 1667, and 1671, which were specifically developed for this type of wastewater.

TABLE 6.1 Pollutants regulated in wastewaters from point-source categories.

Point source category	40 CFR Part Number	Pollutant regulated[1,2]
Aluminum Forming	467	O&G, pH, TSS; Al, CN, Cr, Zn ; TTO (sum of 39 toxic organic compounds listed at 40 *CFR* 467.02[q])
Asbestos Manufacturing	427	pH, TSS; COD
Battery Manufacturing	461	O&G, pH, TSS; Ag, Cd, CN, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Z*n*; COD
Canned and Preserved Fruits and Vegetables Processing	407	BOD5, O&G, pH, TSS
Canned and Preserved Seafood Processing	408	BOD5, O&G, pH, TSS
Carbon Black Manufacturing	458	O&G, pH, TSS; TDS
Cement Manufacturing	411	pH, *T*, TSS
Centralized Waste Treatment	437	BOD5, O&G, pH, TSS; Ag, As, Ba, Cd, CN, Co, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se, Sn, Ti, V, Zn; acetone, acetophenone, aniline, 2-butanone, butylbenzyl phthalate, carbazole, *o*-cresol, *p*-cresol, *n*-decane, 2,3-dichloroaniline, bis(2-ethylhexyl) phthalate, fluoranthene, *n*-octadecane, phenol, pyridine, 2,4,6-trichlorophenol
Coal Mining	434	pH, TSS; acidity, alkalinity, Fe, Mn, settleable solids
Coil Coating	465	O&G (petroleum based), pH, TSS; Al, CN, Cr, Cu, Fe, fluoride, Mn, phosphorus, Zn; TTO [sum of butyl benzyl phthalate, di-n-butyl phthalate, bis(2-chloroethyl)ether, chloroform, 1,1-dichloroethane, 1,1-dichloroethylene, bis(2-ethylhexyl)phthalate, methylene chloride, pentachlorophenol, phenanthrene, 1,1,2,2-tetrachloroethane, tetrachlorethylene, toluene, 1,1,1-trichloroethane]
Concentrated Animal Feeding Operations	412	BOD_5, fecal coliforms (nitrogen and phosphorus regulated via requirements for land application of manure)
Concentrated Aquatic Animal Production[1]	451	None. Instead, best management practices and monitoring are required to control discharge of pollutants.
Copper Forming	468	O&G, pH, TSS; Cr, Cu, Ni, Pb, Zn; TTO (sum of anthracene, benzene, chloroform, 2,6-dinitrotoluene, ethylbenzene, methylene chloride, naphthalene, *n*-nitrosodiphenylamine, phenanthrene, toluene, 1,1,1-trichloroethane, trichloroethylene)
Dairy Products Processing	405	BOD_5, pH, TSS

(continued on next page)

Table 6.1 *(Continued)*

Point-source category	40 *CFR* Part Number	Pollutant regulated[1,2]
Electrical and Electronic Components	469	pH, TSS; As, Cd, Cr, fluoride, Pb, Sb, Zn; TTO (sum of limited lists of organic priority pollutants specified at 40 *CFR* 469.12, 469.22, and 469.31)
Electroplating	413	pH, TSS; Ag, Cd, CN, CN(A), Cr, Cu, Ni, Pb, Zn, total metals (sum of Cr, Cr, Ni, and Zn); TTO (sum of all 111 organic priority pollutants)
Explosives Manufacturing	457	BOD_5, O&G, pH, TSS; COD
Ferroalloy Manufacturing	424	pH, TSS; CN, Cr, Cr(VI), Mn, NH_3; phenols
Fertilizer Manufacturing	418	BOD_5, pH, TSS; fluoride, NH_3, NO_3, organic nitrogen, total phosphorus
Glass Manufacturing	426	BOD5, oil (animal and vegetable), oil (mineral), pH, TSS; fluoride, NH_3, Pb, phosphorus; COD, phenol
Grain Mills	406	BOD_5, pH, TSS
Gum and Wood Chemicals Manufacturing	454	BOD_5, pH, TSS
Hospital	460	BOD_5, pH, TSS
Ink Formulating	447	No discharge, specific pollutants not provided.
Inorganic Chemicals Manufacturing	415	O&G, pH, TSS; As, Ag, Ba, Cd, CN, CN(A), Co, Cr, Cr(VI), Cu, Fe, fluoride, Hg, NH_3, Ni, Pb, Sb, Se, sulfide, total residual chlorine, Zn; COD, TOC
Iron and Steel Manufacturing	420	O&G, pH, TSS; CN, Cr, Cr(VI), NH3, Ni, Pb, total residual chlorine, Zn; benzo(a)pyrene, naphthalene, phenols, tetrachloroethylene, TCDF
Landfills	445	BOD_5, pH, TSS; As, Cr, NH_3, Zn; α-terpineol, aniline, benzoic acid, naphthalene, *p*-cresol, phenol, pyridine
Leather Tanning and Finishing	425	BOD_5, O&G, pH, TSS; Cr, sulfide
Meat and Poultry Products[2]	432	BOD_5, O&G, fecal coliforms, TSS; NH_3, total nitrogen
Metal Finishing	433	O&G, pH, TSS; Cd, CN, CN(A), Cr, Cu, Pb, Ni, Ag, Zn; TTO (sum of all 111 organic priority pollutants)
Metal Molding and Casting	464	O&G, pH, TSS; Cu, Pb, Zn; total phenols, TTOs (sum of limited lists of organic priority pollutants specified at 40 *CFR* 464.11, 464.21, and 464.31)
Metal Products and Machinery	438	O&G, pH, TSS
Mineral Mining and Processing	436	pH, TSS; Fe, total fluoride
Nonferrous Metals Forming and Metal Powders	471	O&G, pH, TSS; Ag, Cd, CN, Cr, Cu, fluoride, Mo, NH_3, Ni, Pb, Sb, Zn; *n*-nitrosodimethylamine, *n*-nitrosodiphenylamine, *n*-nitrosodi-*n*-propylamine

Point source category	40 *CFR* Part Number	Pollutant regulated[1,2]
Nonferrous Metals Manufacturing	421	O&G, pH, TSS; Ag, Al, As, Au, Be, Cd, CN, Co, Cr, Cu, Fe, fluoride, Hg, In, Mo, NH_3, Ni, Pd, Pb, Pt, Sb, Se, Sn, Ta, Ti, W, Zn, combined metals (sum of Au, Pd, and Pt); COD, total phenolics, benzo(a)pyrene, hexachlorobenzene
Oil and Gas Extraction	435	O&G; Cd, Hg, total residual chlorine; base fluid retained on cuttings, base fluid sediment toxicity (10-day LC50 ratio), biodegradation rate, diesel oil, drilling fluid sediment toxicity (4-day LC50 ratio), floating solids, foam (domestic waste), formation oil, free oil, garbage, PAHs, SPP toxicity (96-hr LC50)
Ore Mining and Dressing	440	pH, TSS; As, Al, Cd, Cu, Fe (total and dissolved), Hg, NH_3, Ni, Pb, Ra226 (total and dissolved), settleable solids, U, Zn; COD
Organic Chemicals, Plastics, and Synthetic Fibers	414	BOD_5, pH, TSS; CN, Cr, Cu, Ni, Pb, Zn; and organic pollutants listed at 40 *CFR* 414.91, 414.101, or 414.111
Paint Formulating	446	Cr, Cu, Hg, Ni, Pb, Zn; benzene, di-n-butyl phthalate, carbon tetrachloride, ethyl benzene, di(2-ethylhexyl) phthalate, naphthalene, tetrachloroethylene, toluene
Paving and Roofing Materials (Tars and Asphalt)	443	BOD_5, O&G, pH, TSS
Pesticide Chemicals	455	BOD_5, pH, TSS; CN, Pb; COD, 49 organic pesticide chemicals listed in 455.20(d), 93 pesticide active ingredients in Tables 2 and/or 3 of 40 *CFR* 455, 26 organic priority pollutants listed in Tables 4, 5, and 6 of 40 CFR 455
Petroleum Refining	419	BOD_5, O&G, pH, TSS; Cr, Cr(VI), NH_3, sulfide; COD, phenolic compounds, TOC
Pharmaceutical Manufacturing	439	BOD_5, pH, TSS; CN, NH_3; COD; acetone, acetonitrile, n-amyl acetate, amyl alcohol, benzene, n-butyl acetate, chlorobenzene, chloroform, o-dichlorobenzene, 1,2-dichloroethane, diethyl amine, dimethyl sulfoxide, ethanol, ethyl acetate, *n*-heptane, *n*-hexane, isobutyraldehyde, isopropanol, isopropyl acetate, isopropyl ether, methanol, methyl cellosolve, methyl formate, methyl-2-pentanone, methylene chloride, phenol, tetrahydrofuran, toluene, triethyl amine, xylenes
Phosphate Manufacturing	422	pH, TSS; total phosphorus, fluoride
Photographic	459	pH, Ag, CN
Plastics Molding and Forming	463	BOD_5, O&G, pH, TSS
Porcelain Enameling	466	O&G, pH, TSS; Al, Cr, Fe, Ni, Pb, Zn

(continued on next page)

TABLE 6.1 *(Continued)*

Point source category	40 *CFR* Part Number	Pollutant regulated[1,2]
Pulp, Paper, and Paperboard	430	BOD_5, pH, TSS; settleable solids, Zn; AOX, COD, TCDD, TCDF, chloroform, pentachlorophenol, tetrachlorocatechol, tetrachloroguaiacol, 2,3,4,6-tetrachlorophenol, 3,4,5-trichlorocatechol, 3,4,6-trichlorocatechol, 3,4,5-trichloroguaiacol, 3,4,6-trichloroguaiacol, 4,5,6-trichloroguaiacol, trichlorosyringol, 2,4,5-trichlorophenol, 2,4,6-trichlorophenol
Rubber Manufacturing	428	BOD_5, O&G, pH, TSS; Cr, Pb, Zn; COD
Soap and Detergent Manufacturing	417	BOD_5, O&G, pH, TSS; COD, surfactants
Steam Electric Power Generating	423	O&G, pH, TSS; Cu, Fe, free available chlorine, and total residual chlorine; and the 126 priority pollutants (of which only Cr and Zn have numerical limits; the rest are required to be nondetect)
Sugar Processing	409	BOD_5, pH, temperature, TSS
Textile Mills	410	BOD_5, pH, TSS; Cr, sulfide; COD, phenols
Timber Products Processing	429	BOD_5, O&G, pH, TSS; As, Cr, Cu, settleable solids; COD, phenols
Transportation Equipment Cleaning	442	BOD_5, O&G, pH, TSS; Cd, Cr, Cu, Hg, Ni, Pb, Zn; non-polar material, fluoranthene, phenanthrene
Waste Combustors	444	pH, TSS; Ag, As, Cd, Cr, Cu, Hg, Pb, Ti, Zn

Key:

Ag = Silver
Al = Aluminum
AOX = Adsorbable organic halides
As = Arsenic
Au = Gold
Be = Beryllium
BOD_5 = Five-day biochemical oxygen demand
BPT = Best practicable control technology currently available
Cd = Cadmium
CN = Total cyanide
CN(A) = Cyanide amenable to chlorination
Co = Cobalt
COD = Chemical oxygen demand
Cr = Total chromium
Cr(VI) = Hexavalent chromium
Cu = Copper
Fe = Iron
Hg = Mercury
In = Indium
LC50 = Concentration lethal to 50% of tested organisms
Mn = Manganese
Mo = Molybdenum
NH^3 = Ammonia
NO_3 = Nitrate
Ni = Nickel
O&G = Oil and grease
PAH = Polynuclear aromatic hydrocarbons
Pb = Lead
Pd = Palladium
Pt = Platinum
Ra226 = Radium 226
Sb = Antimony
Se = Selenium
Sn = Tin
SPP = Suspended particulate phase
T = Temperature
Ta = Tantalum
TCDD = 2,3,7,8-Tetrachlorodibenzo-p-dioxin
TCDF = 2,3,7,8-Tetrachlorodibenzofuran
TDS = Total dissolved solids
Ti = Titanium
TOC = Total organic carbon
TSS = Total suspended solids
TTO = Total toxic organics (check specific lists in 40 *CFR* 405 to 471)
U = Uranium
V = Vanadium
Zn = Zinc
W = Tungsten

Source:
Title 40 of the Code of Federal Regulations, Parts 405 to 471, as of March 31, 2007.

Notes:

[1] Pollutants are listed in the following order: conventional, inorganic, and organic pollutants.

[2] In some cases, the pollutants shown are the BPT pollutants, and the higher-tier limitations require no discharge of wastewaters. The appropriate regulation for the point source should be consulted.

Tables 6.2 through 6.6 list ranges of minimum, maximum, and mean concentrations of various pollutants for several industries, as follows:

- Table 6.2: Conventional and classic nonconventional pollutants,
- Table 6.3: Toxic VOCs,
- Table 6.4: Toxic semivolatile organic compounds (SVOCs),
- Table 6.5: Toxic inorganic pollutants, and
- Table 6.6: Other pollutants.

Conventional pollutants include BOD_5 (actually listed as “biochemical oxygen demanding” in the Clean Water Act, but, as BOD_5 in the effluent discharge regulations), total suspended solids (TSS); oil and grease (O&G); and pH. “Classic” nonconventional pollutants include chemical oxygen demand (COD), total organic carbon (TOC), total Kjeldahl nitrogen (TKN), and phosphorus. The word *toxic* refers to the list of 126 priority pollutants included in 40 *CFR* 401.15, as updated in Appendix A of 40 *CFR* 423 (see Table 2.1). Although some of the pollutants in Table 6.6 are not priority pollutants, they and others not listed may be regulated for a particular point source category if the U.S. EPA or local regulator determines that they can be problematic in the receiving waters.

The concentrations detected at each facility can vary widely. Each facility has its own set of raw materials, process equipment, types of processes, products, production schedule, water recycling and conservation measures, wastewater segregation and at-the-source treatment practices, and even intake water type, which collectively determine the type and concentration of pollutants in raw wastewater. So, it is important to properly characterize the wastewater at a particular facility before designing or improving its wastewater treatment system (see Chapter 4).

TABLE 6.2 Typical ranges of mean concentrations of conventional and several classic nonconventional pollutants in wastewaters from selected point source categories.[1]

Point source category	BOD_5	TSS	O&G	COD	TOC	TKN	P
Battery[2]		210	14				
Carbon Black		38–1 800					
Coil Coating		84–180	52–340				5.5–43
Food Processing							
Beverages	1 000–10 000	ND–200	50–100			50–150	
Dairies	1 000–2 500	1 000–2 000	300–1 000			50–100	
Fruit and Vegetable Processing	300–1 000	200–800					
Grain Processing	225–4 450	81–3 500		473–4 900			0.5–98
Meat Processing							
First Processing	2 200–7 200	1 200–3 300	150–670			230–310	35–72
Further Processing	1 500–5 000	360–2 400	160–1 800			24–72	44–82
Poultry Processing							
First Processing	1 600–2 200	760–980	160–670			54–90	12–21
Further Processing	3 300	1 660	790			80	72
Rendering	2 000	3 200	1 600			180	38
Electrical and Electronic Components	5–7.4	185–1 440	3–7				
Electroplating[3]		0.1–10 000					0.02–140
Explosives	ND–1 300	60–520		50–7 200	2–980	3–490	
Iron and Steel Manufacturing[4]		31–5 000	13–4 100	72–9 900		83 8	
Landfills[3]	1–7 600	4–16 500	5–65	35–16 700	2–4 800		0.01–23
Leather Tanning and Finishing	400–5 900	710–8 600	86–1 600	1 800–13 600	ND–2 900	46–890	
Metal Finishing							
Metal Cutting and Forming	3 000–4 000	2 000–3 000	10 000–20 000	20 000–30 000	7 500–10 000	100–200	
Metal Plating			100–500				
Printed Wire Board			100–500				
Metal Products and Machinery[5]	2 000	1 000	2 300	11 300	3 400	600	170
Nonferrous Metals[3]		4.6–4 390					
Organic Chemicals, Plastics, and Synthetic Fibers[3]	7–2 500	15–6 100	Present	270–31 000	68–5 600		
Organic Chemicals, Plastics, and Synthetic Fibers[3]	7–2 500	15–6 100	Present	270–31 000	68–5 600		
Paint Formulating[3]	280–65 500	280–148 000	42–3 400	1 200–350 000	1 500–46 000		
Paving and Roofing Materials (Tars and Asphalt)	8–12	11–13 900	ND–50				

Pharmaceutical	220–4 500	16–1 400		718–10 000			
Porcelain Enameling		110–32 500	ND–96				0.08–9.3
Pulp and Paper				0–12 000			
Rubber Processing[6]							
Tire & Inner Tube	0.2–30	8–1 100	0.8–96	0.01–300			
Synthetic Rubber	9–420	15–770	1–200	50–2 800			
Textile							
Cotton	200–1 000	200–2 000					
Wool	150–300	150–300		300–500			
Timber Products	56–4 000	400–1 100	300	2 600–19 300		0.17–4	0.3–3
Waste Combustors[3]	1–10 000	1–420		13–19 000	1.7–4 500		0.01–1 200

Key:

BOD_5 = Five-day biochemical oxygen demand
COD = Chemical oxygen demand
O&G = Oil and grease
ND = Not detected
P = Total phosphorus
TKN = Total Kjeldahl nitrogen
TOC = Total organic carbon
TSS = Total suspended solids

Notes:

[1] Concentrations in mg/L, values are rounded. Range of mean concentrations for different subcategories or for the entire point source category. From U.S. EPA's effluent limitations development document for each point source category and personal database compiled by Terrence Driscoll.

[2] Average concentrations for the lead subcategory.

[3] Range of detected concentrations.

[4] Range of mean concentrations for all subcategories except the by-product recovery segment of the cokemaking subcategory. TKN value is for the ironmaking subcategory.

[5] Mean concentrations.

[6] Based on raw waste loads.

Table 6.3 Typical range of mean concentrations of toxic volatile organic pollutants in wastewaters from selected point source categories.[1]

Pollutant	Coil coating[2]	Landfills[3]	Metal products and machinery[4]	OCPSF
Acrolein			0.31	2.5–35
Acrylonitrile				0.29–890
Benzene		ND–0.23		0.01–714
Bromoform				0.02–0.07
Carbon tetrachloride				0.02–44
Chlorobenzene			0.28	0.01–50
Chlorodibromomethane				
Chloroethane			4.2	0.06–1
Chloroform	ND–0.01 5		0.05	0.01–5.3
Chloromethane				0.05–0.13
1,2-Dichlorobenzene				0.01–23
1,3-Dichlorobenzene				0.01–4.6
1,4-Dichlorobenzene				0.01–0.07
Dichlorobromomethane				
1,1-Dichloroethane	ND–0.02 5	ND–0.25	0.09	0.01–0.64
1,2-Dichloroethane				0.01–1 270
1,1-Dichloroethylene	ND–0.09		0.42	0.23–18
1,2-trans-Dichloroethylene	0.009	ND–6.2		0.01–0.52
1,2-Dichloropropane				0.03–11
1,3-Dichloropropylene				0.02–4.9
Ethyl benzene		ND–1.1	0.17	0.02–80
Hexachlorobenzene				0.01–0.92
Hexachlorobutadiene				0.08–9.1
Hexachloroethane				0.04–3.4
Methylene chloride	ND–0.02	ND–19	0.4	0.01–13
1,1,2,2-Tetrachloroethane	ND–0.06			0.03–0.19
Tetrachloroethylene	ND–0.02 5		0.21	0.01–32
Toluene	ND–0.14	0.03–2.5	0.23	0.01–160
Tribromomethane				
1,2,4-Trichlorobenzene				0.02–1.9
1,1,1-Trichloroethane	ND–0.56		0.33	0.01–7.2
1,1,2-Trichloroethane				0.01–1.2
Trichloroethylene		ND–27	0.09	0.01–0.48
Vinyl chloride		ND–1.4		

Key:

OCPSF = Organic Chemicals, Plastics, and Synthetic Fibers

Notes:

[1] Concentrations in mg/L, values are rounded. Range of mean concentrations for different subcategories or for the entire point source category. From U.S. EPA's effluent limitations development document for each point source category.

[2] Range of median concentrations.

[3] Range of detected concentrations, for the pulp and paper category, only compounds detected in more than two mills are shown.

[4] Mean concentrations.

[5] Found in treated effluent samples from the canmaking subcategory.

Table 6.3 *(Continued)*

Pollutant	Paint formulating	Pesticide	Pharmaceutical	Pulp and paper[3]	Transportation equipment
Acrolein		ND–5.6			
Acrylonitrile					ND–41
Benzene	0.02–9.9	ND–31	0.01–0.3		ND–11
Bromoform					
Carbon tetrachloride	ND–30	0.0005–44.3			
Chlorobenzene	ND–5.5	0.04–0.11			ND–0.02
Chlorodibromomethane		ND–39			
Chloroethane					
Chloroform	0.02–0.9	ND–110	1.1–1 200	ND–57	ND–0.09
Chloromethane		ND–0.11	2.9–10	ND–30	
1,2-Dichlorobenzene		0.07–14			ND–9.4
1,3-Dichlorobenzene					
1,4-Dichlorobenzene		0.08–0.55			
Dichlorobromomethane	0.03	ND–29			
1,1-Dichloroethane	ND–0.01	ND–2.9			ND–0.01
1,2-Dichloroethane	ND–0.42	ND–3 260	2.7–13		ND–0.45
1,1-Dichloroethylene	ND–0.62	ND–813			ND–0.01
1,2-trans-Dichloroethylene	ND–0.26	0.016–0.018			
1,2-Dichloropropane	ND–0.97	ND–1.2			ND–0.01
1,3-Dichloropropylene	0.1	ND–11			
Ethyl benzene	0.08–113	ND–9.6			ND–4.5
Hexachlorobenzene	0.09				ND–0.07
Hexachlorobutadiene					
Hexachloroethane		0.03–5.3			ND–0.07
Methylene chloride	ND–210	ND–11 300	1.9–11 500	ND–9.2	ND–12
1,1,2,2-Tetrachloroethane	ND–0.03				
Tetrachloroethylene	ND–4.9	ND–403			ND–1.1
Toluene	0.07–260	ND–400	0.13–46 700		ND–13
Tribromomethane		ND–43			ND–0.01
1,2,4-Trichlorobenzene		ND–4.5			ND–0.08
1,1,1-Trichloroethane	ND–0.93	ND–15 500			ND–0.71
1,1,2-Trichloroethane	ND–2.8				
Trichloroethylene	ND–0.25	ND–0.04		ND–0.02	ND–0.03
Vinyl chloride					ND–0.01

Key:

OCPSF = Organic Chemicals, Plastics, and Synthetic Fibers

Notes:

[1] Concentrations in mg/L, values are rounded. Range of mean concentrations for different subcategories or for the entire point source category. From U.S. EPA's effluent limitations development document for each point source category

[2] Range of median concentrations.

[3] Range of detected concentrations, for the pulp and paper category, only compounds detected in more than two mills are shown.

[4] Mean concentrations.

[5] Found in treated effluent samples from the canmaking subcategory.

TABLE 6.4 Typical range of mean concentrations of toxic semivolatile organic pollutants in wastewaters from selected point source categories.[1]

Pollutant	Leather	Metals products and machinery[2]	OCPSF	Paint formulating	Pesticide[3]	Transportation equipment cleaning
Acenaphthene	ND–0.03	0.33	0.01–7			ND–0.66
Acenaphthylene	ND–0.02		0.01–19			ND–0.61
Anthracene		0.12	0.02–2.9			ND –0.39
Benzidine	ND–0.03					
Benzo(a)anthracene			0.01–2.4			ND–0.02
Benzo(a)pyrene			0.01–0.43			
Benzo(b)fluoranthene			0.01–0.37			
Benzo(ghi)perylene			0.02			
Benzo(k)fluoranthene			0.01–0.35			
Butyl benzyl phthalate		1.1		ND–1.8	ND–2.1	
di-n-Butyl phthalate	ND–0.01	0.35	0.02–5.9	ND–69	ND–0.45	
bis(2-Chloroethyl) ether			0.03–1.7			
bis(2-Chloroisopropyl) ether			0.19–20	3.2		ND–0.03
4-Chloro-3-methylphenol	ND–0.003	260				
2-Chloronaphthalene	ND–0.001					
2-Chlorophenol			0.01–247		ND–24	ND–0.07
4-Chlorophenyl phenyl ether				0.27		
Chrysene			0.02–2.2			ND–0.03
Dibenzo(a,h)anthracene			0.02–0.03			
3,3-Dichlorobenzidine			0.37–38			
2,4-Dichlorophenol	ND–0.02		0.06–73		ND–361	ND–0.31
Diethyl phthalate	ND–0.005		0.01–15	ND–0.68	ND–10	
2,4-Dimethylphenol	ND–0.1	0.08	0.01–74		ND–2.6	ND–0.1
Dimethyl phthalate	ND–0.12	0.74	0.01–0.63		ND–0.01	

4,6-Dinitro-o-cresol			7.1–15			
2,4-Dinitrophenol		84	0.07–360	0.11–0.25		
2,4-Dinitrotoluene			0.04–18			ND–3.4
2,6-Dinitrotoluene		2.7	0.03–4.7		ND–0.02	ND–0.94
1,2-Diphenylhydrazine					ND–0.52	
bis(2-Ethylhexyl) phthalate	ND–0.1	4.2	0.01–19	ND–2.8	ND–18	ND–0.9
Fluoranthene	ND–0.003	0.13	0.02–7.2		ND–0.01	ND–0.07
Fluorene	ND–0.002	0.96	0.01–1.9			ND–0.97
Indeno (1,2,3-cd) pyrene)			0.02			
Isophorone		0.06	0.25		ND–0.04	ND–0.14
Naphthalene	ND–1.5	0.64	0.01–37	ND–18	ND–1.2	ND–74
Nitrobenzene	ND–0.43		0.14–330	ND–0.18	ND–0.04	
2-Nitrophenol	ND–0.005	0.39	0.03–30			
4-Nitrophenol	ND–14	3	0.08–10			
n-Nitrosodiphenylamine	ND–0.25	1.1				
di-n-Octyl phthalate		1.6	0.01–0.06		ND–0.42	ND–0.79
Pentachlorophenol	ND–3.6		0.05–0.49	ND–27		
Phenanthrene		0.5	0.02–11			ND–1.5
Phenol	ND–6.6	10	0.01–980	ND–3.8	ND–98	ND–2
Pyrene	ND–0.003	0.22	0.01–5.5		ND–0.01	ND–0.52
2,4,6-Trichlorophenol	ND–3.2		0.01–17	ND–4.9	ND–16	ND–0.18

Key:

OCPSF = Organic Chemicals, Plastics, and Synthetic Fibers

Notes:

[1] Concentrations in mg/L, values are rounded. Range of mean concentrations for all subcategories or for the entire point source category. From U.S. EPA's effluent limitations development document for each point source category.

[2] Mean concentrations.

[3] Range of detected concentrations.

TABLE 6.5 Typical range of mean concentrations of toxic inorganic pollutants in wastewaters from selected point source categories.[1]

Pollutant	Battery[2]	Coil coating[3]	Copper forming	Electrical and electronic components	Electroplating[5]	Iron & steel	Landfills[5]
Antimony	0.1			0.1–2.7		0.009–0.13	
Arsenic	0.01	ND–0.02		0.01–0.2		0.05	ND–18
Beryllium				0.003–0.005		0.07	
Cadmium	0.006	0.001–0.05		0.4–4.1	0.007–22	0.08–0.12	
Chromium	0.3	6.9–58	174	0.2–1.3	0.005–526	0.04–221	0.002–0.72
Copper	0.33	0.009–0.05	24 000	0.04–0.05	0.03–540	0.02–2	ND–0.61
Cyanide, total		0.01–0.57			0.005–150	0.0003	ND–13
Lead	21.9	0.03–0.42	167	0.06–9.4	0.67–25	0.01–8.6	
Mercury	0.007	ND–0.001		0.002–0.003		0.0008	
Nickel	0.22	0.003–0.4	385	0.07–0.3	0.02–2950	0.1–11	ND–2.9
Selenium				0.004–0.005		0.035	ND–0.17
Silver	0.007			0.001–0.03	0.04–176		
Thallium				0.001–0.04			
Zinc	0.94	0.03–26	45 000	12–121	0.11–252	0.38–355	0.002–32

Key:
OCPSF = Organic Chemicals, Plastics, and Synthetic Fibers

Notes:

[1] Concentrations in mg/L, values are rounded. Range of mean concentrations for all subcategories or for the entire point source category. From U.S. EPA's effluent limitations development document for each point source category.

[2] Mean concentrations, only the lead subcategory concentrations are listed under the battery category.

[3] Range of median concentrations.

[4] Maximum concentrations detected.

[5] Range of detected concentrations.

[6] Range of mean concentrations for all subcategories except the by-product recovery segment of the cokemaking subcategory. Concentrations of some pollutants for other subcategories are also excluded for confidential business reasons. Not all parameters are detected in all subcategories.

Table 6.5 *(Continued)*[1]

Pollutant	Leather	Metal products and machinery[2]	Metal finishing	Nonferrous metals manufacturing[5]	OCPSF	Paint formulating	Porcelain enameling	Waste combustors[5]
Antimony		6.12	0.009		0.005–0.63		0.21–6	
Arsenic		0.178	0.008		0.005–0.71		ND–2.4	0.001–1.4
Beryllium	ND–0.0003	0.147	0.001			0.002–4	ND–0.05	
Cadmium	ND–0.03	244	0.28	ND–3.8	0.006–0.01	0.008–15.6	0.07–2.7	0.001–1.6
Chromium	ND–295	1 029	27.5	ND–120	0.06–5.3	ND–40	0.006–210	0.004–1.7
Copper	0.05–0.5	495	12.6	ND–110	0.024–4.8	0.05–40	0.05–2.6	0.01–4.6
Cyanide, total	ND–0.36		1.9		0.13–5.1	ND–0.31	ND–0.07	
Lead	ND–2.4	30	0.33	ND–29	0.1–430	0.02–80	0.32–173	0.05–12
Mercury	ND–0.21	0.0014	0.001		0.0005–0.9	ND–62		0.0001–0.22
Nickel	0.006–0.18	356	15.5	ND–28	0.05–37.5	ND–40	ND–33	
Selenium		0.14	0.001		0.003–0.25		0.23–29	0.0005–0.29
Silver		0.53						
Thallium		0.065	0.009		0.002–0.005			
Zinc	0.15–0.82	188	12.5	ND–340	0.014–450	0.6–900	0.3–130	0.05–29

Key:

OCPSF = Organic Chemicals, Plastics, and Synthetic Fibers

Notes:

[1] Concentrations in mg/L, values are rounded. Range of mean concentrations for all subcategories or for the entire point source category. From U.S. EPA's effluent limitations development document for each point source category.

[2] Mean concentrations, only the lead subcategory concentrations are listed under the battery category.

[5] Range of detected concentrations.

Table 6.6 Typical range of other pollutant concentrations in wastewaters from selected point source categories.[1]

Pollutant	Coil coating[2]	Electroplating	Iron & steel	Landfills	Paint formulating	Porcelain enameling[4]	Waste combustors
Aluminum	0.6–112		0.7–8.2	ND–712	8–3 000	3.8–340	0.02–35
Barium			0.11	ND–3.6	0.05–100		
Chromium, hexavalent	4.3–13	0.004–340	0.18–9	0.002–0.25			
Cobalt			0.15–0.25		ND–12	0.006–29	
Cyanide, amenable	0.02–0.17	0.004–130	0.24	ND–30		ND–0.07	
Fluorides	2.1–21	0.02–680	1.2–190			0.9–41	0.12–7 500
Gold		0.007–25					
Iron	0.3–10	0.4–1480	14–2500	0.6–1 700	3–6 000		0.24–51
Magnesium			25–210	8.1–440	4–2 100		
Manganese	0.12–0.57		0.09–60	0.08–79	0.04–40	0.05–33	0.01–1.5
Molybdenum			0.06–4	ND–19	ND–11		0.004–0.51
Nitrite/nitrate			2–4.3	0.02–193		0.24–270	0.21–33
Palladium		0.008–2.2					
Platinum		0.11–6.5					
Rhodium		0.03					
Tin		0.06–103	0.3–0.4	ND–1.1	ND–20		
Titanium			0.007–2.8	0.003–1.7	0.08–210	2.6–150	0.002–3.8
Total dissolved solids	430–1670			752–33 900	500–145 000		89–185 000
Vanadium			0.3–0.7		0.03–11		
Total phenols	0.008–0.03		0.2–1.5	0.05–2 100	1–1 900		0.006–146

Notes:

[1] Concentrations in mg/L, values are rounded. Range of detected concentrations for all subcategories or for the entire category. From U.S. EPA's effluent limitations development document for each point source category.

[2] Range of median concentrations for all subcategories.

[3] Range of mean concentrations for all subcategories except the by-product recovery segment of the cokemaking subcategory. Concentrations of some pollutants for other subcategories are also excluded for confidential business reasons. Not all parameters are detected in all subcategories.

[4] Range of means for all subcategories.

WASTEWATER MANAGEMENT APPROACH

Following are issues to consider when selecting a wastewater management program, and the U.S. EPA's treatment options used as the basis for the effluent limitations.

SELECTION OF A WASTEWATER MANAGEMENT PROGRAM. Chapter 7 presents the options for wastewater recycling or reuse, pollution prevention, and water use minimization considered by the U.S. EPA in selecting effluent limitations. Besides wastewater characteristics, a facility's wastewater management approach must take into account the indirect- and direct-discharge requirements and the facility's site-specific conditions.

Discharge Requirements. The degree of treatment needed is based on indirect or direct discharge requirements (see Chapter 2). In the case of indirect discharge, local fees or surcharges should also be considered (see Chapter 2). Direct-discharge requirements may be limiting if, for example, the potential receiving water is used for recreation or a water supply, is protected for fish reproduction, or is protected via interstate or international agreements (e.g., the Great Lakes). A combined approach of water use minimization, pollution prevention, and wastewater treatment, reuse, and recycle (Chapter 7) is required to meet effluent limitations for several point source categories, including those whose limitation is "no discharge of process wastewater." The pretreatment standards discussed in Chapter 2 are also important in determining the wastewater treatment approach, because they vary by city, depending on the existing POTW facilities and the POTW's National Pollutant Discharge Elimination System (NPDES) discharge permit.

Facility's Site-Specific Conditions. A facility's site-specific conditions may restrict wastewater management options. Such conditions may include climate, receiving water type and conditions, manufacturing capacity, process equipment, processes, products, production schedule, availability of water for processing or cooling, availability of discharge points, reuse and recycle capabilities, or feasibility of wastewater segregation at the source. Typically, the less wastewater produced, the lower the total cost of wastewater (and its treatment residuals) handling. Following are some examples of how site-specific conditions affect the wastewater management approach:

- Climate determines whether evaporation ponds or wastewater treatment lagoons are feasible.

- If the nearest receiving water has stringent restrictions on the type and concentration of pollutants that can be discharged, pollution prevention measures or product change may be necessary.
- Manufacturing capacity, processes, and products determine the facility's effluent limitations and the wastewater's treatability.
- The process equipment and products may limit the options for product change or wastewater reuse or recycle.
- If the water available for processing or cooling is limited, wastewater reuse is important.
- Batch treatment systems may be more adequate than continuous treatment systems if manufacturing is performed on a batch basis.
- An old facility with interconnected sewers that handle process, laboratory, sanitary, and utilities water together may not be able to afford segregation of sewers or reuse and recycling.

Options for Wastewater Management. Sometimes it is cost efficient to upgrade the wastewater treatment facility or increase its capacity, and sometimes pollution prevention, water conservation, recycling, or reuse may be better (Chapter 7). Some facilities find that a combination of these options works best. For example, a facility with limited space that meets federal pretreatment standards but whose discharges are still problematic for the local POTW may find it less expensive to upgrade the POTW's equipment (e.g., better pH-control or skimming equipment) than its own, even after taking into account the POTW's surcharge fees. (For more details on the options and how to evaluate them, see Chapter 7.)

SUMMARY OF TREATMENT APPROACHES PER POINT SOURCE CATEGORY. Table 6.7 presents the wastewater/pollutant treatment technologies used by the U.S. EPA to establish the effluent limitations for each of the 56 currently-regulated point source categories (as of March 31, 2007). Some of the regulations are old (from the mid-1970s) and so rely on older processes (e.g., activated sludge or granular filtration). Any other individual or combination of technologies may be used at any facility, as long as the facility meets its discharge limits. Note that some treatment approaches in the table summarize processes that apply to different subcategories, and may not be applicable to all of the subcategories. In general, the treatment processes selected by the U.S. EPA for establishing effluent limits are:

- Biological treatment (activated sludge, aerated lagoons, sequential batch reactors) to remove BOD_5 and some toxic organic compounds;

- Gravity settling or filtration to remove suspended solids;
- Precipitation and settling to remove metals;
- Steam stripping or biological nitrification to remove ammonia;
- Chemical reduction followed by precipitation and settling to remove hexavalent chromium; and
- Alkaline chlorination or precipitation with iron sulfate to remove cyanide.

These technologies typically were chosen because existing facilities were using them when the rules were established rather than because of their cost-effectiveness, especially if the existing systems already met the limits. As indicated in Chapter 2, this is a requirement of the regulations for best practicable technology (BPT) for currently available effluent limitations. However, newer technologies (e.g., ultrafiltration, combined hydrogen peroxide and ultraviolet light oxidation, fixed-film biological reactors, membrane biological reactors, and other membrane technologies) can be as efficient or even more efficient in removing regulated pollutants.

For some categorical point sources (e.g., the iron and steel category), the regulations require that a treatment process be applied to a specific wastestream before it is combined with the rest of the industry wastewaters, to be able to monitor the adequacy of the removal efficiency achieved by the system. The justification is that once the wastewaters are combined, the pollutant of concern will no longer be detectable, which would prevent confirmation of its removal before discharge to a receiving waterbody. This approach is typically considered for pollutants that are a concern for ecological receptors because they accumulate in the environment (e.g., dioxins and furans).

In most cases, the best available technology (BAT), best conventional technology (BCT), and/or new source performance standards (NSPS) regulations require that a facility apply water reuse, recycling, and water use minimization measures to minimize the production of wastewater and the introduction of pollutants to the wastewater. For some point source categories, even the BPT requires some type of water reuse, recycling, and/or water use minimization measures. In other cases, a change in raw material is required or recommended, like eliminating defoamers that are precursors to dioxins and furans in the pulp and paper category or using barite with less mercury and cadmium for drilling fluids in the oil and gas category. Chapter 7 presents information on specific measures used by U.S. EPA when selecting the effluent limitations and on how to select these types of measures as part of an overall wastewater management approach. Chapter 2 presents a description of how BPT, BAT, BCT, and NSPS effluent limitations are selected.

Table 6.7 Wastewater treatment options used by the U.S. EPA to establish effluent limitations for selected point source categories.

Point source category	40 *CFR* Part Number	Treatment option^{1,2}
Aluminum Forming	467	Oil skimming and lime precipitation and settling and (when necessary) preliminary treatment with chemical emulsion-breaking to remove oil, chemical reduction to remove hexavalent chromium, and precipitation to remove cyanide.
Asbestos Manufacturing	427	Neutralization with sulfuric acid and settling in ponds.
Battery Manufacturing	461	*Lead Subcategory:* Oil skimming (when needed); chemical precipitation (using hydroxides, carbonates, or sulfides) and settling to remove metals; filtration; reverse osmosis; and combination of these technologies. *Other Six Subcategories:* Treatment via oil skimming (when required), chemical precipitation and settling, and filtration (if necessary).
Canned and Preserved Fruits and Vegetables Processing	407	Screening, chemical precipitation, biological treatment in lagoons, and spray irrigation. Sodium nitrate and surface sprays may be used to reduce odors and flies and other insects. Chlorine disinfection may be used in direct-discharging facilities.
Canned and Preserved Seafood Processing	408	Screens, grease traps, dissolved air flotation with or without chemical addition, and biological treatment via aerated lagoons or extended aeration systems.
Carbon Black Manufacturing	458	Evaporation and settling ponds or granular filters before recycling, and skimming before discharge to POTWs.
Cement Manufacturing	411	Treatment before recycling and reusing via cooling towers or ponds to reduce the temperature of water used in cooling process equipment, and segregation of dust-contact streams and neutralization and settling ponds or clarifiers to remove TSS.
Centralized Waste Treatment	437	*Metals Subcategory*: Primary chemical precipitation, liquid-solids separation, secondary chemical precipitation (at different pH values and using different treatment chemicals), and sand filtration. Wastewaters with concentrated metal cyanide complexes require a two-step alkaline chlorination before metals treatment: the first step is oxidation of cyanide to cyanate at a pH between 9 and 11, and the second step is oxidation of cyanate to carbon dioxide and nitrogen at a pH of 8.5. *Oils Subcategory:* Emulsion breaking/gravity separation, secondary gravity separation, and dissolved air flotation. *Organics Subcategory:* Equalization and biological treatment with sequential batch reactors. *Multiple Wastestreams Subcategory:* Combination of technologies based on types of wastestreams managed.

Coal Mining	434	Treatment of process water via pH neutralization and settling to remove suspended solids and metals. Acid discharges may be treated via chemical precipitation, pH adjustment, aeration to oxidize metals (e.g., iron and magnesium), and settling. Best Management Practices are recommended to minimize sediment production, including such measures as revegetation, rerouting of runoff, removal of acid-forming material from the area around the coal pillars, removal or reprocessing of coal refuse, surface water diversion ditches, spoil capping, stream sealing, addition of alkalinity to acid-forming materials, and capping and revegetation.
Coil Coating	465	*Steel, Galvanized, and Aluminum Subcategories:* Cyanide precipitation, hexavalent chromium reduction, oil skimming, chemical precipitation of metals using hydroxides, and removal of precipitated metals and other materials via settling. *Canmaking Subcategory:* Oil removal via skimming, dissolved air flotation, emulsion breaking, or a combination of these technologies; chromium reduction (when necessary); lime precipitation of other pollutants; and settling for removal of precipitated solids.
Concentrated Animal Feeding Operations	412	*Horse, Sheep, Duck, Beef, and Dairy:* Surface impoundments, with structures to store excess manure. *Swine, Veal, and Poultry:* Solids separation and covered storage for the wastewater and solids (if needed), covered anaerobic digestion for swine operations, and dry manure handling for new facilities. *Both:* Land application of manure at a minimum of 100 feet from streams or structures that carry water to streams; and appropriate management of dead animals, separately from liquid waste.
Concentrated Aquatic Animal Production	451	Primary settling with quiescent zones and settling basins. The development and implementation of BMPs for feed management, health management, and mortality removal are recommended to minimize potential problems associated with excess solids production, aquatic animal pathogens, the escape of nonnative species, and the use of drugs and chemicals.
Copper Forming	468	Chemical emulsion breaking, oil skimming, hexavalent chromium reduction, chemical precipitation with lime and settling, and final filtration.
Dairy Products Processing	405	Equalization; biological treatment in aerated lagoons, trickling filters, activated sludge systems, lagoons, or anaerobic digestors; and irrigation.
Electrical and Electronic Components	469	Neutralization; chromium reduction with sulfuric acid and sodium bisulfite; in-plant or end-of-pipe chemical precipitation and clarification using lime, sodium carbonate, coagulants, or polyelectrolytes; and multimedia filtration. Solvent management techniques were used to establish effluent limitations for the semiconductor, electronic crystals, and cathode ray tube subcategories.

(continued on next page)

Table 6.7 (*Continued*)

Point source category	40 *CFR* Part Number	Treatment option[1,2]
Electroplating	413	Recovery of plating solutions or etchants through reverse osmosis, ion exchange, or evaporation. Treatment of metals by precipitation and settling, with segregation and treatment of cyanide and iron or nickel wastes and wastes with chelating agents.
Explosives Manufacturing	457	At-the-source pretreatment via calcination to remove sulfate, activated carbon to remove trinitrotoluene, centrifugation to remove nitrocellulose fines, coagulation and precipitation to remove heavy metals, and oil skimming. *Manufacture of Explosives:* End-of-pipe treatment via neutralization, equalization, primary settling, activated sludge, filtration, and activated carbon. Addition of phosphorus may be necessary. *Explosives Load, Assemble, and Pack Plants:* End-of-pipe treatment via packaged extended aeration systems (biological treatment, clarification with skimming, and chlorination) followed by chemical coagulation and filtration.
Ferroalloy Manufacturing	424	*Calcium Carbide:* Wet air pollution control scrubber wastewater treatment: (1) covered furnace plants—chlorine oxidation to reduce total cyanide, clarification to remove TSS, neutralization, filtration (if needed), and partial recirculation for covered furnace plants; (2) other types of furnaces—settling in ponds and wastewater recycling to achieve no discharge. Plants using dry or no dust collection have no process wastewater discharge. *Electrolytic Ferroalloys:* Treatment via pH adjustment, flocculation-clarification, breakpoint chlorination for ammonia removal (as applicable), and neutralization.
Fertilizer Manufacturing	418	Neutralization with lime and sedimentation in retention ponds to remove TSS, phosphorus, and fluoride; and air stripping, biological nitrification-denitrification, ion exchange, or breakpoint chlorination to remove ammonia.
Glass Manufacturing	426	Precipitation with calcium chloride.
Grain Mills	406	Flow and quality equalization, neutralization, biological treatment, and solids separation (either gravity separation or deep bed filtration, if needed).
Gum and Wood Chemicals Manufacturing	454	Oil-water separation, equalization, dissolved air flotation (wood rosin and tall oil subcategories only), activated sludge or aerated lagoons treatment, and polishing ponds to remove toxic organics.
Hospital	460	At-the-source treatment may include silver recovery via either metallic replacement (a form of ion exchange) or electrolytic plating and solvent (mostly xylene and ethanol) recycling and reclamation through distillation. End-of-pipe treatment consists of biological treatment via trickling filters, activated sludge systems, or aerated lagoons.

Ink Formulating	447	Contract hauling of wastewater with water-reuse and wastewater-reduction measures. Treatment processes, if used, may include neutralization, oil skimming, coagulation, and settling.
Inorganic Chemicals Manufacturing	415	Pretreatment via hexavalent chromium reduction and cyanide or chlorine destruction, depending on the subcategory. Treatment via alkaline precipitation, clarification, granular media filtration, and final pH adjustment (if needed).
Iron and Steel Manufacturing	420	*Cokemaking:* Oil and tar removal, flow equalization, free and fixed ammonia distillation (stripping), indirect cooling, flow equalization before biological treatment, and biological treatment via nitrification, secondary clarification, and sludge dewatering. Ammonia distillation performed in two steps: free ammonia removal first, followed by addition of lime, sodium hydroxide, or soda ash to increase the pH and remove the fixed ammonia. Activated sludge systems are typically used for biological treatment. *Ironmaking and Sintering:* Solids removal with high-rate recycle and metals precipitation (using lime, caustic soda, magnesium hydroxide, or soda ash), cooling tower, breakpoint chlorination (sodium hypochlorite or chlorine gas under controlled pH), and multimedia filtration of blowdown wastewater for removal of dioxins and furans. *Steelmaking:* Recycling after treatment in a high-volume classifier for primary solids removal followed by a high-efficiency clarifier for solids removal with sludge dewatering, carbon dioxide injection before clarification in wet-open combustion and wet-suppressed combustion basic oxygen furnace recycle systems to remove scale-forming ions, and a cooling tower; and further blowdown treatment via metals precipitation. *Vacuum Degassing:* Recycling after treatment in a high-efficiency clarifier for solids removal with sludge dewatering and a cooling tower, and further blowdown treatment via metals precipitation.
Landfills	445	Aerated equalization, chemical precipitation (for Subtitle C landfills only), extended aeration activated sludge and clarification, and multimedia filtration.
Leather Tanning and Finishing	425	Equalization, primary coagulation and sedimentation, and extended aeration activated sludge.
Meat and Poultry Products	432	Pretreatment via screening, dissolved air flotation, equalization, and/or chemical addition. Treatment via secondary biological treatment and chlorination-dechlorination; partial or more complete nitrification and partial or more complete denitrification may also be required.

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Table 6.7 (*Continued*)

Point source category	40 *CFR* Part Number	Treatment option[1,2]
Metal Finishing	433	Segregate wastes for treatment to remove (as necessary): oil and grease via gravity separation and skimming of free oils followed by emulsified oils removal via chemical emulsion breaking and skimming; cyanide via oxidation; hexavalent chromium via chemical reduction; metals via chemical precipitation and clarification at pH values of 8.5 to 9.0, including separate treatment for streams with complexed metals via chemical precipitation at pH values of 11.6 to 12.5; and cadmium via evaporative recovery or ion exchange. Precious metals are typically recovered.
Metal Molding and Casting	464	Oil skimming; lime precipitation and settling (with emulsion breaking to remove emulsified lubricant oils and/or chemical oxidation with potassium permanganate to oxidize phenolics and other organic compounds, if required); neutralization as needed; and multimedia filtration.
Metal Products and Machinery	438	Chemical emulsion breaking followed by gravity flotation in a coalescing plate oil/water separator to remove oil.
Mineral Mining and Processing	436	If wastewater is produced, treatment via thickening, settling ponds, clarifiers, or drum filters to remove suspended solids, neutralization, and/or aeration to eliminate sulfides.
Nonferrous Metals Forming and Metal Powders	471	Pretreatment via oil skimming, hexavalent chromium reduction, emulsion breaking with chemicals, cyanide removal, ammonia steam stripping, and/or iron coprecipitation to remove molybdenum. Treatment via lime precipitation, settling, and (if necessary) multimedia filtration for further removal of metals; and ion exchange to remove gold.
Nonferrous Metals Manufacturing	421	Chemical precipitation and sedimentation to remove most metals, chemical reduction with sulfur dioxide or sodium bisulfite followed by chemical precipitation and sedimentation to remove hexavalent chromium, air stripping or steam stripping to remove ammonia, skimming to remove oil and grease, precipitation with ferrous sulfate or zinc sulfate to remove cyanide, ion exchange to remove precious metals, and iron co-precipitation to remove molybdenum. Precipitation via sulfide or final filtration should be used if necessary to meet the effluent limitations.
Oil and Gas Extraction	435	Solids removal (via shale shakers, high-G-force shale shakers, centrifuges, and squeeze presses) and recycling of drilling wastes. Landfarming or injection of drilling fluids and drilling cuttings into Class II wells. Grinding may be necessary to reduce the size of the drilling cuttings. Injection of produced and treatment, workover, and completion fluids; where discharge of these wastes is allowed, oil and grease removal via gas flotation. Conventional primary and secondary treatment processes for sanitary wastewater.

Ore Mining and Dressing	440	Lime precipitation and settling followed by impoundment and recycle or evaporation to achieve zero discharge (except in cases of unusual rainfall events), if required by the regulations.
Organic Chemicals, Plastics, and Synthetic Fibers	414	In-plant controls and technologies for segregated streams: steam stripping to remove volatile organics, activated carbon to remove nonvolatile organics, chemical precipitation to remove metals (via hydroxide precipitation using caustic soda or lime), alkaline chlorination to remove cyanide, and biological treatment to remove organics. *Plants with Biological Treatment Systems:* Activated sludge and aerated lagoons, preceded by any necessary pretreatment to enhance the performance of the biological system (e.g., oil-water separation, dissolved air flotation, neutralization, or equalization). *Plants with Nonbiological Treatment Systems:* Neutralization, oil-water separation with API separators, dissolved air flotation, filtration, chemical precipitation, steam stripping, equalization, coagulation, carbon adsorption, distillation, air stripping, chemical oxidation (alkaline chlorination to destroy cyanide), solvent extraction, chromium reduction, and/or ion exchange.
Paint Formulating	446	*Treatment prior to recycle:* Coagulation/flocculation and sedimentation plus biological treatment with aerated lagoons.
Paving and Roofing Materials (Tars and Asphalt)	443	Gravity oil skimmers to treat runoff and/or wet air scrubber water; sumps, tanks, or settling ponds for solids separation with recycle to the wet air scrubber system, reuse in the process, or discharge.
Pesticide Chemicals	455	*Pesticide Manufacturing:* Zero discharge for several pesticide active ingredients (PAIs). For the rest of the PAIs and other pollutants, in-plant or end-of-pipe treatment by hydrolysis, activated carbon, chemical oxidation, resin adsorption, biological treatment, solvent extraction, and/or incineration. *Pesticide Formulating, Packaging, and Repackaging:* Treatment prior to recycle or disposal may include emulsion breaking via temperature control and acid addition to remove surfactants, emulsifiers, and petroleum hydrocarbons; activated carbon adsorption; chemical oxidation via alkaline chlorination, possibly followed by air stripping, steam stripping, or activated carbon adsorption to remove chlorinated compounds, if formed during the process; chemical precipitation with sulfides (hydrogen or sodium sulfide) to remove metals (e.g., mercury, lead, and silver); and hydrolysis at high or low pH, and possibly high temperatures, to remove organics.

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Table 6.7 *(Continued)*

Point source category	40 *CFR* Part Number	Treatment option[1,2]
Petroleum Refining	419	Segregation and treatment of sour water (containing dissolved hydrogen sulfide, other organic sulfur compounds, and ammonia) via gas or steam stripping before discharge to the wastewater treatment plant. End-of-pipe treatment for separation of oil and solids in two stages, followed by neutralization and equalization as needed, biological treatment and, in some cases, a polishing step. Oil and solids removal via gravity separators (e.g., API separators, corrugated plate interceptors, or other gravity separators) followed by treatment to remove emulsified oil via settling ponds or dissolved air flotation units, with or without addition of coagulants. Biological treatment via activated sludge systems, stabilization ponds, trickling filters, or rotating biological contactors. Polishing, if needed, through activated carbon, anthracite coal, or sand filters.
Pharmaceutical Manufacturing	439	In-plant treatment systems for segregated streams: Steam stripping with or without rectification columns for solvent recovery; alkaline chlorination, hydrogen peroxide oxidation, or hydrolysis to remove cyanide; and granular activated carbon adsorption to remove organics. *End-of-pipe treatment:* Advanced biological treatment (single- or two-stage) with or without nitrification, effluent multimedia filtration, and polishing pond. Advanced biological treatment usually includes equalization with or without pH adjustment, primary clarification, biological treatment unit (aeration tanks, aerated lagoons, trickling filters, rotating biological contactors, or anaerobic tanks), and secondary clarification. The wastewater from chemical synthesis may be too concentrated or toxic from the use of solvents to be handled by biological treatment, thus requiring physico/chemical treatment processes as indicated for in-plant treatment.
Phosphate Manufacturing	422	*Phosphate rock wastewaters:* Settling of slime in ponds or removal of sand tailings in mechanical clarifiers before reuse. *Overflow from containment and cooling ponds:* Lime neutralization. *Sodium phosphates manufacturing wastewaters:* Double lime neutralization to remove fluoride, phosphate, radium 226, and TSS.
Photographic	459	Silver recovery via metallic replacement or electrolytic recovery. Other processes include ion exchange, reverse osmosis, ferricyanide bleach regeneration, ferric EDTA bleach regeneration, and ferrous sulfate precipitation. Removal of chromium includes at-the-source segregation and treatment via chromium reduction, pH adjustment for chromium precipitation, and diatomaceous earth filtration. Ferricyanide precipitation may also be used, as well as water evaporation to minimize or eliminate discharges.

Plastics Molding and Forming	463	Sedimentation, biological treatment, and/or activated carbon.
Porcelain Enameling	466	*Coating Wastewaters:* Settling, chemical precipitation with lime and settling. *Aluminum Subcategory:* Hexavalent chromium reduction. *Metal Preparation Wastewaters:* Settling and polishing filtration.
Pulp, Paper, and Paperboard	430	Equalization, neutralization, precooling, primary sedimentation, nutrient addition, aerobic biological treatment, and/or addition of flocculants to secondary clarifiers to improve settling. Multi-basin systems, some of them used as polishing ponds, may also be used. Multimedia filtration is recommended for the mechanical pulp subcategory. If necessary in bleached papergrade kraft and soda mills, extended cooking or oxygen delignification during the processing of the wood chips or after brown stock washing, respectively, to dissolve as much of the lignin that holds the cellulose fibers together.
Rubber Manufacturing	428	*Tire and Inner Tube:* Segregation of oily wastewaters and treatment in an API-type gravity separator, with a storage tank to handle large spills or leakage of a water supply line. *Synthetic Rubber:* Treatment by equalization, neutralization, solids separation, and biological treatment, followed by dual-media filtration and activated carbon adsorption. Solids separation can be achieved with chemical coagulation and primary clarification or air flotation clarification of primary and secondary solids. Biological treatment systems may include activated sludge, aerated lagoons, and stabilization pond systems. *Fabricated and Reclaimed Rubber:* Segregation of process wastewaters is encouraged. Treatment may include gravity separation and/or a filter coalescer to remove oil, coagulation and clarification to remove latex or holding ponds to remove other TSS, aerated lagoons and settling ponds to remove BOD, and chemical precipitation to remove metals.
Soap and Detergent Manufacturing	417	Flotation with skimming and precipitation with calcium chloride.
Steam Electric Power Generating	423	Ash settling ponds, lime precipitation, or evaporation. Oil skimming, equalization, filtration, aerobic biological treatment, and reverse osmosis may also be used if needed. Dechlorination can also be used to remove total residual chlorine, or ozone and ultraviolet light may be used for disinfection instead of chlorine.

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Table 6.7 (*Continued*)

Point source category	40 *CFR* Part Number	Treatment option[1,2]
Sugar Processing	409	*Cane Sugar:* Settling ponds with or without polymer addition followed by biological treatment, or containment of all wastewaters in evaporation ponds to achieve zero discharge except in cases of unusual rainfall events. *Beet Sugar:* Lagooning and land spraying, coagulation, sedimentation, and/or biological filtration.
Textile Mills	410	*Direct Dischargers:* Preliminary screening, equalization, neutralization, biological treatment with extended aeration or aerated lagoons, chemical coagulation, post chlorination, and multi-media filtration or dissolver air flotation, as needed. *Indirect Dischargers:* Sulfide oxidation and oil-water separation are optional pretreatment processes.
Timber Products Processing	429	Most subcategories recycle or reuse as much of the wastewaters as possible, or evaporate them in cooling towers or in the process. *Wood Preserving Plants:* In-plant evaporation; or oil separation in two or more stages, chemical flocculation to break oil-water emulsions, slow sand filtration, neutralization and biological treatment, and (if necessary) hexavalent chromium reduction with sulfur dioxide followed by precipitation of metal hydroxides after pH adjustment with lime or caustic soda and possibly carbon adsorption. *Barking, Veneer, Plywood, Dry Process Hardboard, Wet Process Hardboard, Log Washing, Insulation Board:* Neutralization and settling prior to recycle or reuse; neutralization, primary clarification, biological treatment via extended aeration, secondary clarification, and recycle and reuse of a portion of the treated wastewater; aerated lagoons followed by settling lagoons with very long detention times; in-plant evaporation or evaporation through ponds; and/or spray irrigation. *Wood Furniture and Fixture Production with Water Wash Spray Booth(s) or with Laundry Facilities:* Evaporation ponds, spray irrigation, burning with boiler fuel, or hauling to a landfill.

Transportation Equipment Cleaning	442	*Truck-Chemical & Petroleum:* Equalization, oil-water separation, chemical oxidation, neutralization, coagulation, clarification, biological treatment, and activated carbon adsorption. *Rail-Chemical & Petroleum and Barge-Chemical & Petroleum:* Oil-water separation, equalization, dissolved air flotation with flocculation and pH adjustment, and biological treatment. *Food:* Treatment through oil-water separation, equalization, and biological treatment. *All:* Biological treatment may not be necessary before discharge to POTWs.
Waste Combustors	444	Chromium reduction (if needed), primary precipitation and solids removal, secondary precipitation and solids removal, and sand filtration (if needed).

Key:

API = American Petroleum Institute
BOD = Biochemical oxygen demand
BMPs = Best management practices
EDTA = Ethylenediaminetetraacetic acid
PAIs = Pesticide active ingredients
POTWs = Publicly owned treatment works
TSS = Total suspended solids

Notes:

[1] From the U.S. EPA effluent limitations development document for each point source category. See Table 7.2 for wastewater minimization and pollution prevention approaches.

[2] The treatment systems used in developing the effluent limitations include one or more of the options shown, depending on the subcategory, types of processes, raw materials, and products.

In summary, a thorough review of the facility's wastewater characteristics, site-specific conditions, discharge options, treatability testing, water minimization, reuse and recycle options, and applicable federal and local regulations is necessary to select a wastewater management approach or a method to upgrade the existing system.

INDIVIDUAL POINT SOURCE CATEGORIES

Following are brief descriptions of the 56 point source categories that the U.S. EPA regulates (as of March 31, 2007), the subcategories defined by the U.S. EPA and the regulation subparts where their effluent limits are located, water use (when available in the development document), wastewater sources or types of streams, wastewater constituents, and treatment processes.

ALUMINUM FORMING (40 *CFR* 467). The facilities in this category shape aluminum or aluminum alloys into semi-finished or mill products by hot and cold working. The U.S. Environmental Protection Agency has divided the industry, based on manufacturing processes and wastewater characteristics, into the following six subcategories (40 *CFR* 467, Subparts A through F): rolling with neat oils, rolling with emulsions, extrusion, forging, drawing with neat oils, and drawing with emulsions or soaps. The industry discharges little or no water from its manufacturing processes, but may discharge large volumes of wastewater from ancillary operations (e.g., solution heat treatment, cleaning or etching, and casting).

The regulated wastewater constituents are the conventional pollutants O&G and TSS; the inorganic pollutants aluminum, cadmium, chromium, copper, cyanide, lead, nickel, selenium, and zinc; and 39 toxic organic compounds listed at 40 *CFR* 467.02(q). Treatment typically involves oil skimming, lime precipitation and settling, and (when necessary) preliminary treatment with chemical emulsion-breaking to remove oil, chemical reduction to remove hexavalent chromium, and precipitation to remove cyanide.

ASBESTOS MANUFACTURING (40 *CFR* 427). This category consists of facilities that manufacture asbestos products from asbestos ore and other materials (e.g., cement, organic fibers, heat-resisting binders, and inorganic ingredients) (Pearl Cork and Asbestos, 2004). The U.S. Environmental Protection Agency divided the industry, based on type of product and process, into the following 10 subcategories (40 *CFR* 427, Subparts A through J): asbestos-cement pipe, asbestos-cement sheet, asbestos paper (starch binder), asbestos paper (elastomeric binder), asbestos millboard, asbestos roofing, asbestos floor tile, coating or finishing of asbestos textiles, solvent recovery, and vapor absorption. Wastewater is produced via wet processing and cleaning of asbestos. The regulated wastewater constituents are the conventional pollutants pH and TSS and the nonconventional pollutant COD. Treatment consists of neutralization with sulfuric acid and settling in ponds.

BATTERY MANUFACTURING (40 *CFR* 461). The facilities in this category produce modular electric power sources based on a chemical reaction. The U.S. Environmental Protection Agency has subdivided the industry, based on the type of anode material and electrolyte, into the following seven subcategories (40 *CFR* Subcategories A through G): cadmium, calcium, lead, Leclanche, lithium, magnesium, and zinc. A Leclanche-type battery consists of zinc anode batteries with acid electrolyte.

The volume of water used depends on the plant and process. Water is used to prepare reactive materials and electrolytes; deposit reactive materials on supporting electrode structures; charge electrodes and remove impurities; and wash finished cells, production equipment, and manufacturing areas. The regulated wastewater constituents are toxic metals (e.g., arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, and zinc); nonconventional pollutants (e.g., aluminum, cobalt, COD, iron, and manganese); and conventional pollutants (e.g., O&G, pH, and TSS). Treatment options depend on the subcategory. For lead subcategory wastewaters, treatment may include oil skimming (when needed); chemical precipitation (using hydroxides, carbonates, or sulfides) and settling to remove metals; filtration; and reverse osmosis. For the other six subcategories, treatment typically consists of oil skimming (when required), chemical precipitation and settling, and filtration (if necessary).

CANNED AND PRESERVED FRUITS AND VEGETABLES PROCESSING (40 *CFR* 407). This category consists of facilities that process raw fruits and vegetables into canned and preserved products. The U.S. Environmental Protection Agency has divided the industry, based on the type of product, into the following eight subcategories (40 *CFR* 407 Subparts A through H): apple juice, apple products, citrus products, frozen potato products, dehydrated potato products, canned and preserved fruits, canned and preserved vegetables, and canned and miscellaneous specialties.

The industry's water use is highly seasonal, ranging from 90 to 15 700 m^3/d (0.025 to 4.1 mgd). Wastewater is produced via trimming, culling, juicing, and blanching fruits and vegetables; it includes washwaters, cooling waters, pulp-press liquors, and floor washings. The regulated wastewater constituents are the conventional pollutants BOD_5 (both dissolved and colloidal organic matter), O&G, pH, and TSS. Concentrations and pH values are highly variable. Other potential constituents include pesticide and disinfectant residuals. General treatment approaches include screening, O&G removal, chemical precipitation, neutralization, biological treatment in lagoons, and spray irrigation. Sodium nitrate and surface sprays may be used in the lagoons to reduce odors and flies and other insects. Chlorine disinfection may be used in direct-discharging facilities.

CANNED AND PRESERVED SEAFOOD PROCESSING (40 *CFR* 408). The facilities in this category cook, can, cure, freeze, and package (fresh or frozen) seafood—both fish and shellfish. They also process fish to produce fish meal, oils, and soups. The U.S. Environmental Protection Agency divided the industry into 33 subcategories (Table 6.8) based on the raw product, degree of pre-processing, manufacturing processes and subprocesses, form and quality of the finished product, location of the plant, and nature of the operation (intermittent or continuous).

The industry uses large volumes of water for transporting seafood into the processing plant; washing the seafood and packed cans before, during, and after processing (thawing, butchering, washing, peeling, and picking); cooking; plant washing; and removing pollutants from vapors produced during seafood processing. Another source of wastewater is "stickwater", the liquid that remains after processing fish in presses. Wastewater flows range from 320 to 17 400 m^3/d (0.08 to 4.6 mgd). The main wastewater constituents are BOD_5, O&G, pH, and TSS, with lesser quantities of ammonia, organic nitrogen, and sulfides. Treatment typically includes screens, grease traps, dissolved air flotation with or without chemical addition, and biological treatment in aerated lagoons or extended aeration systems.

CARBON BLACK MANUFACTURING (40 *CFR* 458). This category consists of facilities that produce carbon black via furnace, thermal, channel, and black lamp processes. Each of these processes is regulated separately (40 *CFR* Subparts A through D). The industry produces wastewater intermittently (as equipment washwater, process area washwater, and dehumidifier blowdown) if at all, and is expected to recycle any wastewater within the process. The regulated wastewater constituents are O&G, pH, total dissolved solids (TDS), and TSS. General treatment approaches include ponds for evaporation and settling or granular filters before recycling, and oil skimming before discharge to POTWs.

Table 6.8 Point source categories with more than 16 subcategories.

Subpart and subcategory description	Subpart and subcategory description
Canned and Preserved Seafood Processing (40 *CFR* 408)	
Subpart A: Farm-raised catfish processing subcategory	Subpart Q: Alaskan mechanized salmon processing subcategory
Subpart B: Conventional blue crab processing subcategory	Subpart R: West Coast hand-butchered salmon processing subcategory
Subpart C: Mechanized blue crab processing subcategory	Subpart S: West Coast mechanized salmon processing subcategory
Subpart D: Non-remote Alaskan crab meat processing subcategory	Subpart T: Alaskan bottom fish processing subcategory
Subpart E: Remote Alaskan crab meat processing subcategory	Subpart U: Non-Alaskan conventional bottom fish processing subcategory
Subpart F: Non-remote Alaskan whole crab and crab section processing subcategory	Subpart V: Non-Alaskan mechanized bottom fish processing subcategory
Subpart G: Remote Alaskan whole crab and crab section processing subcategory	Subpart W: Hand-shucked clam processing subcategory
Subpart H: Dungeness and tanner crab processing in the contiguous states subcategory	Subpart X: Mechanized clam processing subcategory
Subpart I: Non-remote Alaskan shrimp processing subcategory	Subpart Y: Pacific Coast hand-shucked oyster processing subcategory
Subpart J: Remote Alaskan shrimp processing subcategory	Subpart Z: Atlantic and Gulf Coast hand-shucked oyster processing subcategory
Subpart K: Northern shrimp processing in the contiguous states subcategory	Subpart AA: Steamed and canned oyster processing subcategory
Subpart L: Southern non-breaded shrimp processing in the contiguous states subcategory	Subpart AB: Sardine processing subcategory
Subpart M: Breaded shrimp processing in the contiguous states subcategory	Subpart AC: Alaskan scallop processing subcategory
Subpart N: Tuna processing subcategory	Subpart AD: Non-Alaskan scallop processing subcategory
Subpart O: Fish meal processing subcategory	Subpart AE: Alaskan herring fillet processing subcategory
Subpart P: Alaskan hand-butchered salmon processing subcategory	Subpart AF: Non-Alaskan herring fillet processing subcategory

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Table 6.8 (*Continued*)

Subpart and subcategory description		Subpart and subcategory description	
Inorganic Chemicals Manufacturing (40 *CFR* 415)			
Subpart A:	Aluminum chloride production subcategory	Subpart P:	Sodium chloride production subcategory
Subpart B:	Aluminum sulfate production subcategory	Subpart Q:	Sodium dichromate and sodium sulfate production subcategory
Subpart C:	Calcium carbide production subcategory	Subpart R:	Sodium metal production subcategory—[reserved]
Subpart D:	Calcium chloride production subcategory	Subpart S:	Sodium silicate production subcategory—[reserved]
Subpart E:	Calcium oxide production subcategory	Subpart T:	Sodium sulfite production subcategory
Subpart F:	Chlor-alkali subcategory (chlorine and sodium or potassium hydroxide production)	Subpart U:	Sulfuric acid production subcategory—[reserved]
Subpart G:	Hydrochloric acid production subcategory—[reserved]	Subpart V:	Titanium dioxide production subcategory
Subpart H:	Hydrofluoric acid production subcategory	Subpart W:	Aluminum fluoride production subcategory
Subpart I:	Hydrogen peroxide production subcategory	Subpart X:	Ammonium chloride production subcategory
Subpart J:	Nitric acid production subcategory—[reserved]	Subpart Y:	Ammonium hydroxide production subcategory—[reserved]
Subpart K:	Potassium metal production subcategory	Subpart Z:	Barium carbonate production subcategory—[reserved]
Subpart L:	Potassium dichromate production subcategory	Subpart AA:	Borax production subcategory
Subpart M:	Potassium sulfate production subcategory	Subpart AB:	Boric acid production subcategory
Subpart N:	Sodium bicarbonate production subcategory	Subpart AC:	Bromine production subcategory
Subpart O:	Sodium carbonate production subcategory—[reserved]	Subpart AD:	Calcium carbonate production subcategory
		Subpart AE:	Calcium hydroxide production subcategory
		Subpart AF:	Carbon dioxide production subcategory—[reserved]

Table 6.8 (*Continued*)

Subpart and subcategory description	
Inorganic Chemicals Manufacturing (40 *CFR* 415)	
Subpart AG:	Carbon monoxide and by-product hydrogen production subcategory
Subpart AH:	Chrome pigments production subcategory
Subpart AI:	Chromic acid production subcategory
Subpart AJ:	Copper salts production subcategory
Subpart AK:	Cuprous oxide production subcategory—[reserved]
Subpart AL:	Ferric chloride production subcategory
Subpart AM:	Ferrous sulfate production subcategory—[reserved]
Subpart AN:	Fluorine production subcategory
Subpart AO:	Hydrogen production subcategory
Subpart AP:	Hydrogen cyanide production subcategory
Subpart AQ:	Iodine production subcategory
Subpart AR:	Lead monoxide production subcategory
Subpart AS:	Lithium carbonate production subcategory
Subpart AT:	Manganese sulfate production subcategory—[reserved]
Subpart AU:	Nickel salts production subcategory
Subpart AV:	Strong nitric acid production subcategory—[reserved]
Subpart AW:	Oxygen and nitrogen production subcategory
Subpart AX:	Potassium chloride production subcategory
Subpart AY:	Potassium Iodide production subcategory
Subpart AZ:	Potassium permanganate production subcategory—[reserved]
Subpart BA:	Silver nitrate production subcategory
Subpart BB:	Sodium bisulfite production subcategory
Subpart BC:	Sodium fluoride production subcategory
Subpart BD:	Sodium hydrosulfide production subcategory—[reserved]
Subpart BE:	Sodium hydrosulfite production subcategory—[reserved]
Subpart BF:	Sodium silicofluoride production subcategory—[reserved]
Subpart BG:	Sodium thiosulfate production subcategory—[reserved]
Subpart BH:	Stannic oxide production subcategory
Subpart BI:	Sulfur dioxide production subcategory—[reserved]
Subpart BJ:	Zinc oxide production subcategory—[reserved]
Subpart BK:	Zinc sulfate production subcategory
Subpart BL:	Cadmium pigments and salts production subcategory
Subpart BM:	Cobalt salts production subcategory
Subpart BN:	Sodium chlorate production subcategory
Subpart BO:	Zinc chloride production subcategory

(continued on next page)

Table 6.8 (*Continued*)

Subpart and subcategory description	
Mineral Mining and Processing (40 *CFR* 436)	
Subpart A:	Dimension stone subcategory—[reserved]
Subpart B:	Crushed stone subcategory
Subpart C:	Construction sand and gravel subcategory
Subpart D:	Industrial sand subcategory
Subpart E:	Gypsum subcategory
Subpart F:	Asphaltic mineral subcategory
Subpart G:	Asbestos and wollastonite subcategory
Subpart H:	Lightweight aggregates subcategory—[reserved]
Subpart I:	Mica and sericite subcategory—[reserved]
Subpart J:	Barite subcategory
Subpart K:	Fluorspar subcategory
Subpart L:	Salines from brine lakes subcategory
Subpart M:	Borax subcategory
Subpart N:	Potash subcategory
Subpart O:	Sodium sulfate subcategory
Subpart P:	Trona subcategory—[reserved]
Subpart Q:	Rock salt subcategory—[reserved]
Subpart R:	Phosphate rock subcategory
Subpart S:	Frasch sulfur subcategory
Subpart T:	Mineral pigments subcategory—[reserved]
Subpart U:	Lithium subcategory—[reserved]
Subpart V:	Bentonite subcategory
Subpart W:	Magnesite subcategory
Subpart X:	Diatomite subcategory
Subpart Y:	Jade subcategory
Subpart Z:	Novaculite subcategory
Subpart AA:	Fire clay subcategory—[reserved]
Subpart AB:	Attapulgite and montmorillonite subcategory—[reserved]
Subpart AC:	Kyanite subcategory—[reserved]
Subpart AD:	Shale and common clay subcategory—[reserved]
Subpart AE:	Aplite subcategory—[reserved]
Subpart AF:	Tripoli subcategory
Subpart AG:	Kaolin subcategory—[reserved]
Subpart AH:	Ball clay subcategory—[reserved]
Subpart AI:	Feldspar subcategory—[reserved]
Subpart AJ:	Talc, steatite, soapstone and Pyrophyllite subcategory—[reserved]
Subpart AK:	Garnet subcategory—[reserved]
Subpart AL:	Graphite subcategory

Table 6.8 (*Continued*)

Subpart and subcategory description	
Nonferrous Metals Manufacturing (40 *CFR* 421)	
Subpart A:	Bauxite refining subcategory
Subpart B:	Primary aluminum smelting subcategory
Subpart C:	Secondary aluminum smelting subcategory
Subpart D:	Primary copper smelting subcategory
Subpart E:	Primary electrolytic copper refining subcategory
Subpart F:	Secondary copper subcategory
Subpart G:	Primary lead subcategory
Subpart H:	Primary zinc subcategory
Subpart I:	Metallurgical acid plants subcategory
Subpart J:	Primary tungsten subcategory
Subpart K:	Primary columbium-tantalum subcategory
Subpart L:	Secondary silver subcategory
Subpart M:	Secondary lead subcategory
Subpart N:	Primary antimony subcategory
Subpart O:	Primary beryllium subcategory
Subpart P:	Primary and secondary germanium and gallium subcategory
Subpart Q:	Secondary indium subcategory
Subpart R:	Secondary mercury subcategory
Subpart S:	Primary molybdenum and rhenium subcategory
Subpart T:	Secondary molybdenum and vanadium subcategory
Subpart U:	Primary nickel and cobalt subcategory
Subpart V:	Secondary nickel subcategory
Subpart W:	Primary precious metals and mercury subcategory
Subpart X:	Secondary precious metals subcategory
Subpart Y:	Primary rare earth metals subcategory
Subpart Z:	Secondary tantalum subcategory
Subpart AA:	Secondary tin subcategory
Subpart AB:	Primary and secondary titanium subcategory
Subpart AC:	Secondary tungsten and cobalt subcategory
Subpart AD:	Secondary uranium subcategory
Subpart AE:	Primary zirconium and hafnium subcategory

(continued on next page)

TABLE 6.8 (*Continued*)

Subpart and subcategory description		Subpart and subcategory description	
Soap and Detergent Manufacturing (40 *CFR* 417)			
Subpart A:	Soap manufacturing by batch kettle subcategory	Subpart K:	SO_3 solvent and vacuum sulfonation subcategory
Subpart B:	Fatty acid manufacturing by fat splitting subcategory	Subpart L:	Sulfamic acid sulfation subcategory
Subpart C:	Soap manufacturing by fatty acid neutralization subcategory	Subpart M:	Chlorosulfonic acid sulfation subcategory
Subpart D:	Glycerine concentration subcategory	Subpart N:	Neutralization of sulfuric acid esters and sulfonic acids subcategory
Subpart E:	Glycerine distillation subcategory	Subpart O:	Manufacture of spray dried detergents subcategory
Subpart F:	Manufacture of soap flakes and powders subcategory	Subpart P:	Manufacture of liquid detergents subcategory
Subpart G:	Manufacture of bar soaps subcategory	Subpart Q:	Manufacture of detergents by dry blending subcategory
Subpart H:	Manufacture of liquid soaps subcategory	Subpart R:	Manufacture of drum dried detergents subcategory
Subpart I:	Oleum sulfonation and sulfation subcategory	Subpart S:	Manufacture of detergent bars and cakes subcategory
Subpart J:	Air—SO_3 sulfation and sulfonation subcategory		

Key:
CFR = Code of Federal Regulations

Source:
U.S. Code of Federal Regulations, Title 40.

CEMENT MANUFACTURING (40 *CFR* 411). Facilities in this category process materials (e.g., aluminum, silica, limestone, clay, chalk, and iron oxides) to produce cement. Cement is used as a binding agent, most often as a component of mortar or concrete. Among the most common types are Portland cement, white cement, and masonry cement. About 97% of the cement used in the manufacture of concrete products is Portland cement, which is a crystalline compound formed primarily of metallic oxides (e.g., calcium carbonate and aluminum, iron, and silicon oxides). White cement, which is made from iron-free materials of exceptional purity—typically limestone, china clay or kaolin, and silica—is primarily used to manufacture decorative concrete. Masonry cement, produced by adding limestone to Portland cement, is a hydraulic cement used as a component of mortar for masonry construction. The U.S. Environmental Protection Agency divided the industry into three subcategories (40 *CFR* 411 Subparts A through C): nonleaching, leaching, and materials storage piles runoff.

Wastewater is generated through process-equipment cooling, cement-kiln-dust recovery via wet scrubbing of kiln-stack emissions, and from materials-storage-pile runoff. The main pollutants are TDS (potassium and sodium hydroxide, chlorides, and sulfates), TSS (calcium carbonate), and waste heat. The main control and treatment methods for wastewater involve (1) recycling and reusing wastewater after treatment with cooling towers or ponds to reduce the temperature of water used in cooling process equipment, and (2) segregation of dust-contact streams and neutralization and settling ponds or clarifiers to remove TSS.

CENTRALIZED WASTE TREATMENT (40 *CFR* 437). This category consists of commercial facilities that treat or recover hazardous or nonhazardous industrial wastes, wastewaters, or used materials received from offsite customers. The U.S. Environmental Protection Agency has divided the industry, based on the type of waste treated, into the following four subcategories (40 *CFR* Subparts A through D): metals treatment and recovery, oils treatment and recovery, organics treatment and recovery, and multiple wastestreams.

On average, facilities in this category discharge 0.1 to 2300 m^3/d (less than 4 gal/d to 0.6 mgd) of wastewater. The wastestreams consist of wastewater from treatment of liquid wastes, water added to solubilize solid wastes, used oil-emulsion-breaking wastewater, tanker truck/drum/roll-off box washes, equipment washes, air-pollution-control scrubber blowdown, laboratory-derived wastewater, industrial-waste-combustor or landfill wastewater from onsite landfills, and contaminated stormwater. The regulated wastewater constituents are the conventional pollutants BOD_5, O&G, pH, and TSS; the inorganic pollutants antimony, arsenic, barium, cadmium, chromium, cobalt, copper, lead, mercury, molybdenum, nickel, selenium, silver, tin, titanium, total cyanide, vanadium, and zinc; and the organic pollutants acetophenone, 2-butanone, o-cresol, p-cresol, phenol, 2-propanone, pyridine, 2,4,6-trichlorophenol, and indicator compounds from the anilines, n-paraffins, phthalates, and polyaromatic hydrocarbons groups.

The effluent limitations for each subcategory were based on different treatment approaches. For the metals subcategory, the technologies are primary chemical precipitation, liquid-solids separation, secondary chemical precipitation (at different pH values and using different treatment chemicals), and sand filtration. Wastewaters with concentrated metal cyanide complexes under the metals subcategory require a two-step alkaline chlorination before metals treatment: the first step is oxidation of cyanide to cyanate at a pH between 9 and 11, and the second step is oxidation of cyanate to carbon dioxide and nitrogen at a pH of 8.5. For the oils subcategory, the processes are emulsion breaking/gravity separation, secondary gravity separation, and dissolved air flotation. Equalization and biological treatment with a sequential batch reactor are recommended for the organics subcategory. Facilities in the multiple wastestreams subcategory are expected to combine the above technologies based on the types of wastestreams managed.

COAL MINING (40 *CFR* 434). The U.S. Environmental Protection Agency divided this category, based on the type of process and the type of discharge, into the following six subcategories (40 *CFR* 434 Subparts B through H): coal preparation plants and associated areas, acid or ferruginous mine drainage, alkaline mine drainage, post-mining areas, coal remining, and western alkaline coal mining. Subparts A and F contain general and miscellaneous provisions, respectively. Coal remining consists of mining of surface mine lands, underground mine lands, and coal refuse piles that were abandoned before the Surface Mining Control and Reclamation Act was enacted.

Wastewater mainly comes from the coal-preparation-plant water circuit; drainage from coal storage, refuse storage, and ancillary areas related to the cleaning or beneficiation of coal; and mine drainage. Wastewater discharges in 2000 ranged from 650 to 71 700 m^3/d (0.17 to 19 mgd). The main pollutants include alkalinity or acidity, iron, manganese, pH, sulfate, settleable solids, and TSS. The agency recommended treatment of process water via pH neutralization and settling to remove suspended solids and metals. Acid discharges may be treated via chemical precipitation, pH adjustment, aeration to oxidize metals (e.g., iron and magnesium), and settling. Best management practices (BMPs) are also recommended to minimize sediment production, including such measures as revegetation, rerouting of runoff, removal of acid-forming material from the area around the coal pillars, removal or reprocessing of coal refuse, surface water diversion ditches, spoil capping, stream sealing, addition of alkalinity to acid-forming materials, and capping and revegetation.

COIL COATING (40 *CFR* 465). The facilities in this category clean, chemically treat, and paint continuous, long strips of metal called coils. Based on the product and type of material coated, U.S. EPA divided the industry into four subcategories

(40 *CFR* 465 Subparts A through D): steel (plain and chrome, nickel, and tin coated steel), galvanized (zinc coated steel, zinc-aluminum alloy, and copper-zinc alloy and other copper forms), aluminum (including aluminum-coated steel), and canmaking. The canmaking subcategory covers the manufacturing of various shaped metal containers used to store foods, beverages, and other products.

The industry uses large volumes of water for its cleaning, conversion coating, and painting (quenching water) operations. The regulated wastewater constituents are the conventional pollutants O&G, pH, and TSS; the inorganic pollutants aluminum, cadmium, chromium, copper, cyanide, fluoride, iron, lead, manganese, nickel, phosphorus, and zinc; and the organic constituents butyl benzyl phthalate, di-n-butyl phthalate, bis(2-chloroethyl)ether, chloroform, 1,1-dichloroethane, 1,1-dichloroethylene, bis(2-ethylhexyl)phthalate, methylene chloride, pentachlorophenol, phenanthrene, 1,1,2,2-tetrachloroethane, tetrachloroethylene, toluene, and 1,1,1-trichloroethane.

General treatment approaches for the steel, galvanized, and aluminum subcategories include cyanide precipitation, hexavalent chromium reduction, oil skimming, chemical precipitation of metals using hydroxides, and removal of precipitated metals and other materials via settling. For the canmaking subcategory, the recommended treatment technologies include oil removal via skimming, dissolved air flotation, emulsion breaking, or a combination of these technologies; chromium reduction (when necessary); lime precipitation of other pollutants; and settling to remove precipitated solids.

CONCENTRATED ANIMAL FEEDING OPERATIONS (40 *CFR* 412). This category applies only to operations that meet certain requirements (e.g., time of animal confinement and number of animals handled). The U.S. Environmental Protection Agency divided the industry—based on the type of animal raised, the animal housing characteristics (covered versus uncovered), and the waste handling and manure management practices—into four subcategories (40 *CFR* 412 Subparts A through D): horses and sheep; ducks; dairy cows and cattle other than veal calves; and swine, poultry, and veal calves.

The wastestreams consist of liquid or semisolid manure plus other materials (e.g. hair, bedding, soil, or wasted feed), and water that is wasted or used for sanitary and flushing purposes. The main wastewater constituents are nitrogen, phosphorus, potassium, and pathogens (e.g., enterococcus, fecal coliform, salmonella, and streptococcus) for all subcategories; and BOD_5 and COD for beef, horse, and veal operations. Lesser amounts of other elements and pharmaceuticals may also be present.

These elements may include arsenic, cadmium, calcium, chlorine, copper, iron, lead, manganese, magnesium, molybdenum, nickel, selenium, sodium, sulfur, and zinc. Pharmaceuticals may include androgens and estrogens, erythromycin, penicillin, sulfonamides, streptomycin, and tetracycline.

General treatment approaches include (1) surface impoundments (with structures to store excess manure) for horse, sheep, duck, beef, and dairy wastewater; (2) solids separation and covered storage for the solids (if necessary), covered anaerobic digestion (for swine operations only), and dry manure handling for new facilities for the swine, veal, and poultry wastewaters; and (3) land application of manure at a minimum distance of 30 m (100 ft) from streams or structures that carry water to streams; and appropriate management of dead animals (separately from liquid waste) for all subcategories.

CONCENTRATED AQUATIC ANIMAL PRODUCTION (40 *CFR* 451). A concentrated aquatic animal production facility is a hatchery, fish farm, or other facility that contains, grows, or holds coldwater or warmwater aquatic animals (e.g., trout, salmon, catfish, sunfish, and minnows). The aquatic animals may be produced as food, pets, bait, and sportfish; for ornamental and display purposes; as research and test organisms; or to enhance natural populations. The U.S. Environmental Protection Agency divided the industry, based on the type of system, into two subcategories (40 *CFR* 451 Subparts A and B): (1) flow-through and recirculating systems, and (2) net pens.

Some flow-through systems discharge one combined high-volume, dilute-concentration effluent stream. Others discharge two streams: high-volume, dilute-concentration process water (the water in which the aquatic animals are raised); and low-volume, high-concentration secondary discharges from off-line settling basins or other solids removal devices.

Recirculating systems may also have two wastestreams: overtopping wastewater, a continuous low-volume, high-concentration blowdown from the production system to avoid TDS buildup; and (2) filter backwash, an intermittent low-volume, high-concentration wastewater generated by cleaning the filter used to treat process water before it is recirculated back to the system.

Net pens are in open waters and do not produce wastewater, but raw materials added to the pens (e.g., feed, drugs, and the animals' excretions) result in a continuous release of nutrients, reductions in dissolved oxygen concentrations, and accumulation of sediments under the pens. These conditions may affect the local environment via eutrophication and degradation of benthic communities.

The main wastewater constituents are BOD_5, nitrogen, phosphorus, and TSS. In addition, metals from feed additives, sanitation products, or deteriorating machinery and equipment may be present, mostly in particulate form, as well as drugs and chemicals used to restore the animals' health. Although numerical limits were not issued, the recommended treatment processes include primary settling with quiescent zones and settling basins. The development and implementation of BMPs for feed management, health management, and mortality removal are also recommended to minimize potential problems associated with excess solids production, aquatic animal pathogens, the escape of nonnative species, and the use of drugs and chemicals.

COPPER FORMING (40 *CFR* 468). This category includes facilities that roll, draw, extrude, and forge copper and copper alloys into plate, sheet, strip, wire, rod, tube, and forging products. The U.S. Environmental Protection Agency divided the industry, based on the type of materials used, into two subcategories: (a) copper forming and (b) beryllium copper forming.

Major wastewater sources include lubrication and cooling, alkaline cleaning, quenching during annealing, heat treatment, and pickling operations. The regulated wastewater constituents are the conventional pollutants O&G, pH, and TSS: the inorganic pollutants chromium, copper, lead, nickel, and zinc; and the organic constituents anthracene, benzene, chloroform, 2,6-dinitrotoluene, ethyl benzene, methylene chloride, naphthalene, n-nitrosodiphenylamine, phenanthrene, toluene, 1,1,1-trichloroethane, and trichloroethylene. Recommended wastewater treatment processes include (as needed) chemical emulsion breaking, oil skimming, hexavalent chromium reduction, chemical precipitation with lime and settling, and filtration.

DAIRY PRODUCTS PROCESSING (40 *CFR* 405). Based on the activities and products manufactured, the U.S. EPA divided this category into the following 12 subcategories (40 *CFR* 405 Subparts A through L): receiving stations; fluid products; cultured products; butter; cottage cheese and cultured cream cheese; natural and processed cheese; fluid mix for ice cream and other frozen desserts; ice cream, frozen desserts, novelties, and other dairy desserts; condensed milk; dry milk; condensed whey; and dry whey.

Wastewater flow rates in 2000 ranged between 740 and 3500 m^3/d (0.2 and 0.9 mgd). Wastewater is produced from processing losses (e.g., startup, product changeover, and shutdown of pasteurizers); accidental spills; drippings from process equipment; washing and sterilizing of containers, equipment, and floors; and process washes of butter, cheese, casein, and other products. The main wastewater constituents are BOD_5, pH, and TSS, with lesser concentrations of ammonia, O&G, and nitrate. Treatment processes may include equalization; biological treatment in aerated lagoons, trickling filters, activated sludge systems, lagoons, or anaerobic digestors; and irrigation.

ELECTRICAL AND ELECTRONIC COMPONENTS (40 *CFR* 469). The U.S. Environmental Protection Agency divided this category, based on product type, into the following four subcategories (40 *CFR* 469 Subparts A through D): semiconductor, electronic crystals, cathode ray tube, and luminescent materials. Another 17 products were determined not to produce wastewaters, so they were not regulated. Water is used to formulate acids and bases; rinse products; collect exhaust gases from diffusion furnaces, solvents, and acid baths; clean equipment and materials; cool and lubricate saws and grinding machines; rinse the product during crystal fabrication; wash raw materials and products; and remove pollutants from gases via wet scrubbers. The wastewater flow rate in 2000 ranged from 610 to 161 000 m^3/d (0.2 to 42 mgd).

The main wastewater constituents, depending on subcategory, may include the conventional pollutants pH and TSS; the inorganic pollutants antimony, arsenic, cadmium, chromium, fluoride, lead, and zinc; and the lists of toxic organics specified at 40 *CFR* 469.12, 469.22, and 469.31. Recommended treatment processes include neutralization; chromium reduction (if applicable) with sulfuric acid and sodium bisulfite; in-plant or end-of-pipe chemical precipitation and clarification using lime, sodium carbonate, coagulants, and polyelectrolyte (as needed); and multimedia filtration (if needed). In addition, the effluent limits for the semiconductor, electronic crystals, and cathode ray tube subcategories were established based on the use of solvent-management techniques.

ELECTROPLATING (40 *CFR* 413). This category consists of facilities that apply a surface coating to metals to provide corrosion protection, wear or erosion resistance, anti-frictional characteristics, or decoration. The U.S. Environmental Protection Agency divided the industry, based mainly on the production processes, into eight subcategories (40 *CFR* 413 Subparts A through H): common metal electroplating, precious metal electroplating, electroless plating, anodizing, coating, chemical milling, etching, and printed board manufacturing.

Plating activities can be continuous or in batches. Wastewater is mainly produced as spent process solutions and plating tank rinses. The main wastewater constituents may include the conventional pollutant TSS; the inorganic pollutants amenable and total cyanide, cadmium, copper, fluoride, gold, iron, lead, nickel, palladium, phosphorus, platinum, rhodium, silver, tin, total and hexavalent chromium, and zinc; and the organic constituents citric acid, ethylenediaminetetraacetic acid (EDTA), gluconic acid, glutaric acid, lactic acid, nitrilotriacetate (NTA), tartrates, and thiourea.

Plating solutions or etchants are recovered via reverse osmosis, ion exchange, or evaporation. For other wastewaters, the recommended treatment technologies are precipitation and settling for metals, with segregation and treatment of cyanide and iron or nickel wastes and wastes with chelating agents.

EXPLOSIVES MANUFACTURING (40 *CFR* 457). This category encompasses commercial and military facilities that manufacture explosives. Commercial plants produce such explosives as ammonium-nitrate based explosives, dynamite, and nitroglycerin. Military plants produce such explosives as trinitrotoluene, cyclotetramethylene tetranitramine (HMX), and cyclotrimethylene trinitramine (RDX). Based on the production processes, the U.S. EPA divided the industry into two subcategories (40 *CFR* Subparts A and C): manufacture of explosives; and explosives load, assemble, and pack plants. Subpart B was reserved.

Processes may be batch or continuous. Wastewater is generated via washing operations in the production of explosives; and via spills, mixing equipment, and bulk-transport truck washing in the loading, assembling, and packing operations. The main wastewater constituents are the conventional pollutants BOD_5, O&G, TSS; and ammonia, COD, nitrates, sulfate, TKN, TOC, and trace quantities of explosives.

The U.S. Environmental Protection Agency recommended at-the-source pretreatment and end-of-pipe treatment for this category. At-the-source pretreatment may include calcination to remove sulfate, activated carbon to remove trinitrotoluene, centrifugation to remove nitrocellulose fines, coagulation and precipitation to remove heavy metals, and oil skimming. End-of-pipe treatment for Subcategory A may include neutralization, equalization, primary settling, activated sludge, filtration, and activated carbon, with addition of phosphorus (if necessary). For Subcategory C, end-of-pipe treatment involves packaged extended aeration systems (biological treatment, clarification with skimming, and chlorination), followed by chemical coagulation and filtration.

FERROALLOY MANUFACTURING (40 *CFR* 424). Based on the products, type of processes, and air-pollution-control equipment, the U.S. EPA divided this category into seven subcategories, which can be grouped as follows:

- Smelting [open electric furnaces with wet air pollution control devices, covered electric furnaces and other smelting operations with wet air pollution control devices, and slag processing] (40 *CFR* Subparts A through C);
- Calcium carbide [covered calcium carbide furnaces with wet air pollution control devices and other calcium carbide furnaces] (40 *CFR* Subparts D and E); and
- Electrolytic [electrolytic manganese and electrolytic chromium] (40 *CFR* Subparts F and G).

The discussion on wastewater constituents and treatment only addresses the calcium carbide and electrolytic groups.

Water use varies by subcategory. The smelting segment only uses water for gas cleaning and noncontact cooling. The electrolytic segment uses water in the process to prepare electrolytes and transport filter residues, as well as for non-process uses (e.g., washdowns and noncontact cooling). The calcium carbide segment may use water in wet air-pollution-control scrubbers and as noncontact cooling water. Other calcium carbide wastewaters may include cooling tower blowdown and regeneration water produced during water treatment. Plants using dry or no dust collection have no process wastewater discharge. The main constituents in calcium carbide wastewaters are calcium, cyanide, iron, silica, TDS, and TSS. In the electrolytic segment, wastewater constituents include ammonia, chromium, iron, manganese, pH, sulfate, and TSS.

Treatment options for calcium carbide's scrubber wastewater are chlorine oxidation to reduce total cyanide, clarification to remove TSS, neutralization, filtration (if needed), and partial recirculation for covered furnace plants. For other types of furnaces, settling ponds and wastewater recycling is recommended to achieve no discharge. Electrolytic wastewater treatment options include pH adjustment, flocculation-clarification, breakpoint chlorination for ammonia removal (if necessary), and neutralization.

FERTILIZER MANUFACTURING (40 *CFR* 418). Facilities in this category use phosphate rock, natural gas, sulfuric acid, and carbon dioxide to produce a variety of fertilizers. Other raw materials may include sanitary wastewater treatment plant residues and certain industrial wastes. The U.S. Environmental Protection Agency divided this category, based on the type of fertilizer produced, into seven subcategories (40 *CFR* Subparts A through G): phosphate, ammonia, urea, ammonium nitrate, nitric acid, ammonium sulfate production, and mixed and blend fertilizer production.

Wastestreams consist of spills and leakages, cooling waters, product washing water, condensate stripping, vacuum condenser water, scrubbing water, boiler blowdowns, and phosphoric acid production pond water discharges (U.S. EPA, 2000). Stormwater runoff is also regulated. Depending on the subcategory, the wastewater constituents may include the conventional pollutants BOD_5, pH, and TSS; and ammonia, fluoride, nitrate, organic nitrogen, and total phosphorus. In some cases, aluminum, potassium, and sulfur may be present. Treatment processes may include neutralization with lime and sedimentation in retention ponds to remove TSS, phosphorus, and fluoride; and air stripping, biological nitrification-denitrification, ion exchange, or breakpoint chlorination to remove ammonia.

GLASS MANUFACTURING (40 *CFR* 426). This category consists of facilities that process silica sand, soda ash (e.g., sodium carbonate or nitrate), limestone, dolomite, cullet (scrap glass), and small amounts of other materials into molted glass that is then shaped into a variety of forms. Once finished, the glass products are cleaned using several agents, including aqueous solvents (e.g., chromic and sulfuric acid mixtures, detergent solutions, and hydrogen fluoride), organic solvents (used alone or mixed with commercial cleansers), and hydrocarbon or halocarbon solvents (to remove nonpolar organic compounds). Additional processing often involves coating the glass with thin layers of metal or chemical compounds (lead, aluminum, boron, and magnesium oxides) that absorb infrared light or improve the glass's reflecting qualities (U.S. EPA, 1995a).

The U.S. Environmental Protection Agency divided the industry, based on the type of product and process, into 13 subcategories (40 *CFR* 426 Subparts A through M): insulation fiberglass, sheet glass manufacturing, rolled glass manufacturing, plate glass manufacturing, float glass manufacturing, automotive glass tempering, automotive glass laminating, glass container manufacturing, machine-pressed and blown glass manufacturing, glass tubing (Danner) manufacturing, television picture tube envelope manufacturing, incandescent lamp envelope manufacturing, and hand-pressed and blown glass manufacturing. The machine-pressed and blown glass manufacturing subcategory (40 *CFR* Subpart I) does not have effluent limitations.

Process wastewater is generated via glass polishing, cleaning, and scrubbing. The main wastewater constituents are the conventional pollutants BOD_5, oil (animal and vegetable), oil (mineral), pH, and TSS; the inorganic pollutants ammonia, fluoride, lead, and phosphorus; and the organic pollutants COD and phenol. Other heavy metals (in addition to lead) may also be present. Precipitation with calcium chloride can be used to remove these compounds.

GRAIN MILLS (40 *CFR* 406). The U.S. Environmental Protection Agency divided this industry (based on the type of grain, product, and processes) into the following 10 subcategories (40 *CFR* Subparts A through J): corn wet milling, corn dry milling, normal wheat flour milling, bulgur wheat flour milling, normal rice milling, parboiled rice processing, animal feed, hot cereal, ready-to-eat cereal, and wheat starch and gluten.

The volume of wastewater generated varies depending on the process, from low to very high. Process wastewater includes water added as part of the process or used for grain washing, condensate from steepwater evaporation, wastewaters from cooling or ion exchange regeneration, and wastewaters from steaming and cooking processes. Other sources may include car washing and wet scrubbing. The main wastewater constituents are BOD_5, COD, and pH, with lower concentrations of nitrogen and phosphorus. Some wastewaters may also have high TDS and TSS. Depending on the subcategory, recommended treatment approaches may include flow and quality equalization, neutralization, biological treatment, and solids separation (either gravity separation or deep bed filtration, if needed).

GUM AND WOOD CHEMICALS MANUFACTURING (40 *CFR* 454). This category consists of facilities that produce hardwood and softwood distillation products, wood and gum naval stores, charcoal, natural dyestuffs, and natural tanning materials. The U.S. Environmental Protection Agency divided the industry (based on the manufacturing process, type of raw materials, and type of product) into the following six subcategories (40 *CFR* Subparts A through F): char and charcoal briquets; gum rosin and turpentine; wood rosin, turpentine and pine oil; tall oil rosin, pitch and fatty acids; essential oils; and rosin-based derivatives.

The industry produces 9 to 7600 m^3/d (0.0023 to 2 mgd) of wastewater, including raw gum wash tank wastewater, the water fraction from the turpentine-water separator, turpentine-dewatering brine waste, wastewater condensed from steam used to remove solvents from wood chips, distillation-tower condensed water, wastewater, acid washwater, retort wastewater, rosin-derivatives chemical reaction, wastewater from equipment washing, and scrubber water. The main wastewater constituents are BOD_5, COD, O&G (floating and emulsified), phenols, TOC, and TSS. Other organic components include turpenes, natural components of the wood, and solvents (e.g., toluene). Recommended treatment processes include oil-water separation, equalization, dissolved air flotation (wood rosin and tall oil subcategories only), activated sludge or aerated lagoons treatment, and polishing ponds to remove toxic organics.

HOSPITAL (40 *CFR* 460). This category consists of facilities that provide health care to people in a community (community hospitals) or to specific groups of people (e.g., military personnel, psychiatric patients, long-term patients, or people with tuberculosis and other respiratory diseases). Most hospitals are open year-round, and have diverse facilities (e.g., operating rooms, patient rooms, laboratories, cafeterias, laundries, restrooms, heating and air conditioning units, and other support systems). The industry was not divided into subcategories.

Hospitals use about 0.92 m^3 (242 gal) of water per day per bed. The main wastestreams are sanitary wastewater and discharges from surgical rooms, laboratories, laundries, X-ray departments, cafeterias, and glassware washing (U.S. EPA, 1989). Hospital wastewater is similar to residential wastewater; its main constituents include BOD_5, COD, TOC, and TSS, with lesser concentrations of acetone, barium, mercury, phenol, and silver. At-the-source treatment may include silver recovery via either metallic replacement (a form of ion exchange) or electrolytic plating and solvent (mostly xylene and ethanol) recycling and reclamation through distillation. End-of-pipe treatment is typically biological treatment via trickling filters, activated sludge systems, or aerated lagoons.

INK FORMULATING (40 *CFR* 447). The facilities in this category produce a wide range of inks (from ordinary writing ink to specialized magnetic inks) and serve many customers (from the public to the printing industry). Only the oil-base solvent wash ink subcategory is regulated. Such facilities typically work one shift per day, five days per week, and produce ink via batch processes. The industry uses relatively low volumes of water, from zero to 38 m^3/d (0.01 mgd). Wastewater is produced mainly via ink tub cleaning (spent caustic washwater and rinsewater). Other sources of wastewater could include bad or spoiled ink batches, spill residues, contaminated stormwater runoff, tank truck cleaning, steam condensate, contact water from air-pollution-control devices, and rag laundering.

Wastewater constituents include the conventional and nonconventional pollutants BOD_5, COD, O&G, pH, and TSS; the inorganic pollutants chromium, copper, lead, and zinc; and the organic compounds 1,2-diphenylhydrazine, ethyl benzene, di(2-ethylhexyl)phthalate, isophorone, methylene chloride, di-n-octyl phthalate, pentachlorophenol, tetrachloroethylene, toluene, 1,1,1-trichloroethane, and trichloroethylene. Treatment processes, if used, may include neutralization, oil skimming, coagulation, and settling. The U.S. Environmental Protection Agency recommended contract hauling the small quantity of wastewater produced (after appropriate implementation of water-reuse and wastewater-reduction measures) as the cost-effective option to meet effluent limits.

INORGANIC CHEMICALS MANUFACTURING (40 *CFR* 415). The U.S. Environmental Protection Agency divided this category (based on the products and manufacturing processes) into 67 subcategories; only 47 currently have effluent limitations (Table 6.8). Most of the rest either discharge insignificant amounts of pollutants, or only one plant produces the particular inorganic chemical involved. Wastewater sources may include decanted, filtered, or purified reaction media; washdown of equipment and area; scrubber water; decanting or filtering of slurries; washing, quenching, rinsing of pigments; filter washing; pump seal leaks and spills; condensate from evaporators; and barometric condenser blowdown.

Depending on the subcategory, the wastewater constituents are the conventional pollutants O&G, pH, and TSS; the inorganic constituents ammonia, antimony, arsenic, barium, cadmium, chromium (total and hexavalent), cobalt, copper, cyanide (total and amenable), fluoride, iron, lead, mercury, nickel, selenium, silver, sulfide, total residual chlorine, and zinc; and the organic pollutants COD and TOC. In general, the recommended treatment approaches include alkaline precipitation, clarification, granular media filtration, and pH adjustment, if necessary. Potential pretreatment processes, depending on subcategory, may include hexavalent chromium reduction, and chlorine and cyanide destruction.

IRON AND STEEL MANUFACTURING (40 *CFR* 420). The facilities in this category produce carbon steels, alloy steels, and stainless steels. Iron may be produced in blast furnaces using coke, limestone, beneficiated iron ore, and preheated air; or in electric arc furnaces by melting steel scrap. Other operations in this industry include molten-steel refining, casting, hot forming, and finishing operations; carbon-steel acid pickling, cold forming and annealing, acid and alkaline cleaning, electroplating, and hot coating. The U.S. Environmental Protection Agency divided the industry (based on manufacturing operations or products) into 13 subcategories (40 *CFR* Subparts A through M): cokemaking, sintering, ironmaking, steelmaking, vacuum degassing, continuous casting, hot forming, salt bath descaling, acid pickling, cold forming, alkaline cleaning, hot coating, and other operations.

Water is used for cooling and cleaning of process offgases, direct cooling of coke and slag, direct cooling and cleaning of steel, product rinsing, process solution makeup, and direct cooling of process equipment. Other sources of wastewater include slag quenching, equipment cleaning, air pollution control devices, rinse water, and contaminated cooling water. The main wastewater constituents are the conventional pollutants O&G and TSS; the inorganic pollutants ammonia, cyanide (amenable and total), fluoride, nitrate/nitrate, and several priority and nonconventional metals; and the organic pollutants COD, dioxins and furans, phenols, TKN, TOC, total petroleum hydrocarbons, and several other priority and nonconventional organic compounds. Cokemaking wastewaters also have BOD_5.

The recommended treatment for cokemaking wastewater includes oil and tar removal, flow equalization, free and fixed ammonia distillation (stripping), indirect cooling, flow equalization before biological treatment, and biological treatment via nitrification, secondary clarification, and sludge dewatering. Ammonia distillation should be performed in two steps: free ammonia removal first, followed by the addition of lime, sodium hydroxide, or soda ash to increase the pH and remove the fixed ammonia. Activated sludge systems are the most common type of biological treatment system.

For the ironmaking and sintering subcategories, the recommended treatment technologies are solids removal with high-rate recycle and metals precipitation (using lime, caustic soda, magnesium hydroxide, or soda ash), cooling tower, breakpoint chlorination (sodium hypochlorite or chlorine gas under controlled pH), and multimedia filtration of blowdown wastewater for removal of dioxins and furans. Steelmaking wastewater can be treated for recycling via a high-volume classifier for primary solids removal followed by a high-efficiency clarifier for solids removal with solids dewatering, carbon dioxide injection before clarification in wet-open combustion and wet-suppressed combustion basic oxygen furnace recycle systems to remove scale-forming ions, and a cooling tower; and further blowdown treatment via metals precipitation. For vacuum degassing systems, the recommended treatment for recycling includes a high-efficiency clarifier for solids removal with sludge dewatering and a cooling tower, and further blowdown treatment via metals precipitation.

LANDFILLS (40 *CFR* 445). The landfills category covers facilities that operate and maintain landfills regulated under Subtitles C and D of the Resource Conservation and Recovery Act (RCRA). The rule applies to wastewater generated at both active and closed landfills. The U.S. Environmental Protection Agency divided the industry into two subcategories, based on the regulations that apply to them (which, in turn, are based on the type of wastes managed) (40 *CFR* Subparts A and B): RCRA Subtitle C hazardous waste landfills and RCRA Subtitle D non-hazardous waste landfills.

The main wastewater streams are landfill leachate, landfill gas condensate, drained free liquids, truck/equipment contact washwater, laboratory-derived wastewater, and contaminated storm water. Wastewaters from Subtitle C and Subtitle D landfills contain 54 and 16 constituents subject to regulation, respectively, including BOD_5, pH, TSS, and other organic and inorganic pollutants. Treatment consists of aerated equalization, chemical precipitation (for Subtitle C landfills only), extended aeration activated sludge and clarification, and multimedia filtration.

LEATHER TANNING AND FINISHING (40 *CFR* 425). The U.S. Environmental Protection Agency divided this category into nine subcategories (40 *CFR* 425 Subparts A through I): (1) hair pulp, chrome tan, retan-wet finish; (2) hair save, chrome tan, retan-wet finish; (3) hair save or pulp, non-chrome tan, retan-wet finish; (4) retan-wet finish-sides; (5) no beamhouse; (6) through-the-blue; (7) shearling; (8) pigskin; and (9) retan-wet finish-splits. The subcategories were based on the nature of the raw materials and on the subprocesses required in the manufacturing process.

The industry uses different amounts of water depending on the subcategory, with a range of 2.6 to 5380 m^3/d (0.0007 to 1.42 mgd). Water is used for: soaking, washing, and unhairing of unprocessed hides; tanning and retanning with chromium, vegetable, alum, or other agents; preparing bleach, dye, or pigment solutions to produce specific colors in the final product; and cleaning and washdown of process equipment and areas.

The main wastewater constituents are ammonia, BOD_5, O&G, sulfide, total chromium, and TSS. Other pollutants may include syntans based on naphthalene and phenol; 4-nitrophenol; pentachlorophenol; hexachloroethane, ethylbenzene, and toluene solvents; 2,4,6-trichlorophenol; cresol-based biocides; and heavy metals. These pollutants are either major constituents or components of biocides, waterproofing agents, preservatives, solvents, and organo-metallic dyes. General treatment approaches include equalization, primary coagulation and sedimentation, and extended aeration activated sludge.

MEAT AND POULTRY PRODUCTS (40 *CFR* 432). Meat and poultry facilities slaughter livestock and/or poultry or process meat and/or poultry into products for further processing or sale to consumers. The industry is often divided into three categories: meat slaughtering and processing; poultry slaughtering and processing; and rendering. Meat products include all animal products from cattle, calves, hogs, sheep and lambs, and any meat that is not listed under the definition of poultry. Poultry includes broilers, other young chickens, hens, fowl, mature chickens, turkeys, capons, geese, ducks, exotic poultry (e.g., ostriches), and small game such as quail, pheasants, and rabbits. Based on size, types of meat products, and manufacturing processes, the U.S. EPA subdivided the industry into 12 subcategories, as follows (40 *CFR* Subparts A through L): simple slaughterhouse, complex slaughterhouse, low-processing packinghouse, high-processing packinghouse, small processor, meat cutter, sausage and luncheon meats processor, ham processor, canned meats processor, renderer, poultry first processing, and poultry further processing.

Wastewater production is related to live animal holding, killing, hide or hair removal, eviscerating, carcass washing, trimming, cleanup, further processing, and rendering operations. The main wastewater constituents are BOD_5, COD, TSS, O&G as hexane or Freon extractables, TKN, total phosphorus, and fecal coliform bacteria. Wastewater treatment to meet the effluent limitations includes pretreatment and treatment technologies. Pretreatment may include screening, dissolved air flotation, equalization, and/or chemical addition. Treatment options include secondary biological treatment and chlorination/dechlorination; depending on the subcategory, treatment through partial or more complete nitrification and partial or more complete denitrification may be required to meet the effluent limitations.

METAL FINISHING (40 *CFR* 433). The metal finishing category consists of facilities that perform any of the following six metal finishing operations on any basis material: electroplating, electroless plating, anodizing, coating (chromating, phosphating, and coloring), chemical etching and milling, and printed circuit board manufacture. If any of these six operations are present, discharges from any of 40 other metal-finishing process listed at 40 *CFR* 433.10 are also covered by the regulation. In general, such facilities fall under SIC Codes 34 to 39, which include: fabricated metal products (34), except machinery and transportation equipment; machinery, except electrical (35); electrical and electronic machinery, equipment, and supplies (36); transportation equipment (37); measuring, analyzing, and controlling instruments: photographic, medical, and optical goods and watches and clocks (38); and miscellaneous manufacturing industries (39).

However, facilities performing the metal finishing processes listed above that are included in the following categories are not subject to 40 *CFR* 433: nonferrous metal smelting and refining (40 *CFR* 421), coil coating (40 *CFR* 465), porcelain enameling (40 *CFR* 466), battery manufacturing (40 *CFR* 461), iron and steel (40 *CFR* 420), metal casting foundries (40 *CFR* 464), aluminum forming (40 *CFR* 467), copper forming (40 *CFR* 468), plastic molding and forming (40 *CFR* 463), nonferrous forming (40 *CFR* 471), and electrical and electronic components (40 *CFR* 469). In addition, the processes regulated under the metal products and machinery effluent limitations (40 *CFR* 438) are not covered by this regulation. The metal-finishing category was not divided into subcategories.

Depending on the type of processes, facilities may discharge from zero to 380 m^3/d (0.1 mgd) of wastewater, as a result of one or more of the following operations: workpiece rinsing, spill washing, air scrubbing, process fluid replenishment, cooling and lubrication, equipment and workpiece washing, quenching, painting in spray booths, and assembly and testing. The category has seven waste types, identified on the basis of the constituents they contain:

- Common metals wastes (cadmium, chromium, copper, cyanide, lead, nickel, zinc, and tin);
- Precious metals wastes (silver and gold, with lower concentrations of palladium and rhodium);
- Complexed metals wastes (copper, nickel, and tin);
- Cyanide wastes (cyanide);
- Hexavalent chromium waste (hexavalent chromium);
- Oily wastes (O&G as free oils, emulsified or water soluble oils, and greases);
- Toxic organics wastes (depending on the solvents used, may include mainly acetone, benzene, butyl alcohol, cyclohexane, ethers, heavy aromatics, kerosenes, naphthas, methylene chloride, methyl ethyl ketone, tetrachloroethylene, 1,1,1-trichloroethane, trichloroethylene, trichlorotrifluoroethane, toluene, and/or xylenes).

Recommended wastewater treatment processes include segregating wastes for treatment to remove (as necessary): O&G via gravity separation and skimming of free oils followed by chemical emulsion breaking and skimming for emulsified oils; cyanide via oxidation; hexavalent chromium via chemical reduction; metals via chemical precipitation and clarification at pH values of 8.5 to 9.0, including separate treatment for streams with complexed metals via chemical precipitation at pH values of 11.6 to 12.5; and cadmium via evaporative recovery or ion exchange. Precious metals are typically recovered.

METAL MOLDING AND CASTING (40 *CFR* 464). The metal molding and casting category covers facilities that pour or inject molten metal into a mold whose cavity has the dimensions of the finished product. This category consists of the following four subcategories, based on the type of metal cast (40 *CFR* Subparts A through D): aluminum, copper, ferrous, and zinc casting.

Wastewater generated in 2000 ranged from 590 to 72 700 m^3/d (0.2 to 19 mgd). In general, wastewater is produced during the following processes or from the indicated equipment: casting cleaning, casting quench, die casting, dust collection scrubber, grinding scrubber, investment casting, melting furnace scrubber, mold cooling, direct chill casting, slag quench, and wet sand reclamation. The main wastewater constituents are the conventional pollutants O&G, pH, and TSS; the inorganic pollutants copper, lead, and zinc; and phenols, and a number of toxic organic pollutants [e.g., benzidine, p-chloro-m-cresol, 4,6-dinitro-o-cresol, 2,4-dinitrophenol, bis(2-ethylhexyl)phthalate, fluoranthene, 2-nitrophenol, pentachlorophenol, pyrene, and tetrachloroethylene]. Recommended treatment processes include oil skimming; lime precipitation and settling with emulsion breaking to remove emulsified lubricant oils and/or chemical oxidation with potassium permanganate to oxidize phenolics and other organic compounds, if required; neutralization as needed; and multimedia filtration.

METAL PRODUCTS AND MACHINERY (40 *CFR* 438). This category encompasses manufacturing, rebuilding, or maintenance of metal parts, products, or machines for use in the following industrial sectors: aerospace, aircraft, bus and truck, electronic equipment, hardware, household equipment, instruments, mobile industrial equipment, motor vehicle, office machine, ordnance, precious metals and jewelry, railroad, ships and boats, stationary industrial equipment, and miscellaneous metal products. Only one subcategory was regulated, the oily wastes subcategory, which is defined as facilities that perform one of more of 28 oily operations listed at 40 *CFR* 438.2(f). The category does not include metal-bearing operations or process wastewaters subject to the limitations and standards of other effluent limitations guidelines. This regulation complements the metal finishing point source category effluent limitations established at 40 *CFR* 433, via coverage of processes not included under the metal finishing regulation.

Effluent limitations were issued only for direct dischargers and only for process wastewater, including (1) wastewater discharges from oily operations for the manufacturing, rebuilding, or maintenance of metal parts, products, or machinery for use in any of the 16 industrial sectors covered; and (2) wastewater from air pollution control devices. The main wastewater constituents are the conventional pollutants BOD_5, O&G, pH, and TSS; and a number of VOCs and SVOCs and of nonconventional pollutants. However, the U.S. EPA regulated only pH, O&G, and TSS because it was determined that treatment to remove oil by chemical emulsion breaking followed by gravity flotation in a coalescing plate oil/water separator would also remove the other pollutants of concern.

MINERAL MINING AND PROCESSING (40 *CFR* 436). The mineral mining and processing category consists of facilities that mine and process different minerals (e.g., sand, gravel, phosphate rock, attapulgite, stone, and gypsum), with 38 subcategories defined based on the type of mineral. Only 21 of them have effluent limitations (Table 6.8). The industry uses volumes of water ranging from 0 to 100 000 m^3/d (26 mgd). Wastewater originates from non-contact cooling water; process-generated water, including washwater, transport water, scrubber water (80% of the regulated wastewater), process and product-consumed water, and miscellaneous water; auxiliary process water; and stormwater and groundwater, including mine dewatering, mine runoff, and plant runoff (U.S. EPA, 1995b).

The main wastewater constituents are TSS, but dissolved substances (e.g., fluorides, acids, alkalies, and chemical additives from ore processing) may also be present. If wastewater is produced, treatment options include thickening, settling ponds, clarifiers, or drum filters to remove suspended solids; neutralization; and/or aeration to eliminate sulfides.

NONFERROUS METALS FORMING AND METAL POWDERS (40 *CFR* 471). This category is comprised of facilities that (1) form nonferrous metals and their alloys (with the exceptions indicated at 40 *CFR* 471.01) into specific shapes by hot or cold working and (2) produce mechanical metal powder mechanically or form parts from metal powders. The U.S. Environmental Protection Agency has divided the industry, based on the operations, into the following 10 subcategories (40 *CFR* Subparts A through J): lead-tin-bismuth forming, magnesium forming, nickel-cobalt forming, precious metals forming, refractory metals forming, titanium forming, uranium forming, zinc forming, zirconium-hafnium forming, and metal powders.

Wastewater streams may include spent neat oils, emulsions, soap solutions, lubricants, and synthetic coolants; contact cooling water; hydraulic fluid leakage; equipment and/or production floor cleaning wash waters; wet air pollution control blowdown; steam condensate; spent baths; rinsewaters; and others. The main wastewater constituents are O&G, TSS, COD, metals, and other toxic and nonconventional pollutants. Depending on the subcategory, nonconventional pollutants may include ammonia, cyanide, and/or fluoride; inorganic pollutants may include aluminum, antimony, chromium, lead, magnesium, nickel, silver, tin, and zinc; and toxic organic compounds may include benzo(a)pyrene, hexachlorobenzene, n-nitrosodiphenylamine, total phenolics, and 1,1,1 trichloroethane.

Pretreatment processes may include, as needed, oil skimming, hexavalent chromium reduction, emulsion breaking with chemicals, cyanide removal, ammonia steam stripping, and/or iron coprecipitation for removal of molybdenum. Wastewater treatment can then be accomplished through lime precipitation, settling, and, if necessary, multimedia filtration for further removal of metals; and ion exchange to remove gold.

NONFERROUS METALS MANUFACTURING (40 *CFR* 421). The nonferrous metals manufacturing category includes facilities that recover and increase the purity of metals in ore concentrates and scrap metals. The industry has been subdivided into 36 subcategories, based on the raw material and products (e.g., aluminum, copper, beryllium, nickel, rare metals) and the manufacturing process (e.g., metallurgical acid plants, primary copper smelting, primary electrolytic copper refining). Only 31 of the subcategories are regulated (Table 6.8); the five unregulated subcategories are primary boron, primary cesium and rubidium, primary lithium, secondary zinc, and primary magnesium. Effluent limitations were established only for process wastewaters; non-process wastewaters are to be regulated through the permitting authority, because they depend on the plant layout and water-handling practices.

Wastewater streams may include wet air pollution control wastewater, cooling and quenching water, spent electrolyte, washwaters, leaching water, acid wash, rinsewater, and other streams. The main wastewater constituents are subcategory-dependent, and include toxic metals (e.g., antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and/or zinc) or other metals (e.g., gallium, gold, palladium, vanadium, zirconium) produced by the facility. In addition, wastewaters from this category may contain ammonia, COD, cyanide, O&G, pH, TSS, and some toxic organics (e.g., polynuclear aromatic hydrocarbons and phenols).

Recommended treatment approaches are (as appropriate) chemical precipitation and sedimentation to remove most metals, chemical reduction with sulfur dioxide or sodium bisulfite followed by chemical precipitation and sedimentation to remove hexavalent chromium, air stripping or steam stripping to remove ammonia, skimming to remove O&G, precipitation with ferrous sulfate or zinc sulfate to remove cyanide, ion exchange to remove precious metals, and iron coprecipitation to remove molybdenum. Precipitation via sulfide or final filtration should be added if necessary to meet the effluent limitations.

OIL AND GAS EXTRACTION (40 *CFR* 435). The oil- and gas-extraction category encompasses facilities involved in exploration, development, and production operations. The U.S. Environmental Protection Agency has divided the industry, based on the geographic location of the operations and the type of production wells, into the following five subcategories (40 *CFR* 435 Subparts A and C through F): offshore, onshore, coastal, agricultural and wildlife water use, and stripper. Subpart B is reserved, and subpart G contains general provisions. Stripper wells are those that produce less than 10 barrels of oil per day, after a period of higher production.

The industry generates large volumes of wastewater, mostly produced water. Other wastewaters include organic acids, alkalis, and acidic stimulation fluids during well development; completion fluid, wastewater containing well-cleaning solvents (detergents and degreasers), paint, and stimulation agents during maintenance work; escaping oil and brine from abandoned wells, spills and blowouts; and deck drainage and sanitary waste.

The main constituents in produced water are chloride, sodium, calcium, magnesium and potassium. Other constituents that may be found at elevated concentrations in produced water include the organic compounds benzene, bromodichloromethane, naphthalene, phenanthrene, pentachlorophenol, and toluene; the inorganic pollutants antimony, arsenic, barium, lead, sulfur, and zinc; and the radionuclides radon, uranium, and radium in certain areas of the country. In addition, amines, biocides, corrosion inhibitors, glycol, lubricants, and untreatable emulsions may be present. Constituents of concern in drilling fluids are O&G, total residual chlorine, cadmium, mercury, polynuclear aromatic hydrocarbons, free oil, diesel oil, base fluid sediment toxicity [10-day LC_{50} (concentration lethal to 50% of tested organisms) ratio], drilling fluid sediment toxicity (4-day LC_{50} ratio), suspended particulate phase toxicity (96-hour LC_{50}), biodegradation rate, formation oil, and base fluid retained on cuttings. Drainage deck waters may contain oils and drilling fluids, and sanitary wastes contain BOD_5 and TSS.

General disposal approaches include injection for enhanced recovery, injection for disposal, beneficial use, evaporation and percolation ponds, treat and discharge, and road spreading. In areas west of the 98th meridian, treated produced water from onshore wells in the agricultural and wildlife beneficial use subcategory that meets water quality standards may be released directly to agricultural canals for use in irrigation or livestock watering. Treatment of drilling wastes may include solids removal (via shale shakers, high-G-force shale shakers, centrifuges, and squeeze presses), landfarming, or injection into Class II wells. Grinding may be necessary to reduce the size of drilling cuttings. If produced water and treatment, workover, and completion fluids can be discharged into surface waterbodies, the recommended treatment is gas flotation technology to remove O&G. Contamination of drainage deck water should be controlled via stormwater pollution prevention plans, and sanitary waste is treated via any combination of primary and secondary wastewater treatment processes.

ORE MINING AND DRESSING (40 *CFR* 440). This category's facilities mine and process ore to separate valuable metals from less valuable rock. The U.S. Environmental Protection Agency divided the industry, based on the type of metal ore, into 12 subcategories (40 *CFR* 440 Subparts A through K and M), including iron ore; aluminum ore; uranium, radium, and vanadium ores; mercury ore; titanium ore; tungsten ore; nickel ore; vanadium ore (mined alone and not as a byproduct); antimony ore; copper, lead, zinc, gold, silver, and molybdenum ores; platinum ore; and gold placer mine. Subpart L contains general provisions and definitions. Placer mining consists of excavating gold bearing gravel and sands that are later separated by physical means. All subcategories have effluent limitations, except for the antimony ore subcategory, because there is only one facility in the subcategory, and it does not discharge wastewater.

Wastewater flows in 2000 ranged from zero to 505 000 m^3/d (130 mgd). The wastewater generated by this category includes mine drainage, mill wastewater, water used in ancillary operations used for beneficiating the ore, processing chemicals, intermediate products, contact cooling water, and contaminated stormwater runoff. Mills that use froth flotation add chemical flotation reagents that may provide copper, zinc, chromium, and total phenolics to the wastewater. Cyanide may be used in froth flotation to help separate the mineral from the rock, and for leaching. The main wastewater constituents are (depending on the subcategory) the conventional pollutants pH and TSS; the inorganic pollutants aluminum, ammonia, arsenic, cadmium, copper, cyanide, iron, lead, mercury, nickel, radium 226, settleable solids, uranium, and zinc; and COD. Constituents in TSS may include asbestos fibers. The recommended treatment processes are lime precipitation and settling followed by impoundment and recycle or evaporation to achieve zero discharge (except in cases of unusual rainfall events), if required by the regulations.

ORGANIC CHEMICALS, PLASTICS, AND SYNTHETIC FIBERS (40 *CFR* 414). Organic chemicals, plastics, and synthetic fibers facilities use feedstocks derived from petroleum, natural gas, or coal tar condensates generated by coke production to manufacture up to 25 000 different products. The U.S. Environmental Protection Agency divided the industry into 10 subcategories, depending on the type of limitation. For the purposes of BPT regulations, seven subcategories were established based on the products accounting for most of each facility's production (40 *CFR* Subparts B through H): rayon fibers, other fibers, thermoplastic resins, thermosetting resins, commodity organic chemicals, bulk organic chemicals, and specialty organic chemicals. For BAT regulations, the agency divided the category into two subcategories based on the type of end-of-pipe treatment system (40 *CFR* Subparts I and J): direct discharge point sources that use end-of-pipe biological treatment and direct discharge point sources that do not use end-of-pipe biological treatment. Finally, all facilities were considered to fall under a single subcategory (40 *CFR* Subpart K), the indirect discharge point sources subcategory, for the purposes of establishing pretreatment standards. Subpart A of the regulation for this category contains general requirements.

Processes and product mix can vary weekly or even daily, and can include several continuous and batch operations. Estimated average wastewater production per plant is 4960 m^3/d (1.31 mgd) for direct discharges and 946 m^3/d (0.25 mgd) for indirect discharges. Some facilities have zero discharge. The highest wastewater flow in 2000 was 3.8 million m^3/d (1000 mgd). Wastewater is produced mainly via its use as the chemical reaction media for the product. Other process wastewaters are generated through such sources as air pollution control devices, boiler blowdown, steam condensate, vacuum pump seal water, wastewater stripper discharge, steam jet condensate, landfill leachate, contact cooling water, vacuum steam jet blowdown, bottom ash-quench water, and tank car washing. The main wastewater constituents are the conventional pollutants BOD_5, O&G; pH, and TSS; a wide variety of inorganic and organic toxic priority pollutants; and a large number of nonconventional pollutants. Many of the toxic and nonconventional organic pollutants are produced for sale or as byproducts of the production operations.

In-plant controls and technologies, used for segregated streams, include such processes as steam stripping to remove volatile organics, activated carbon to remove nonvolatile organics, chemical precipitation to remove metals (via hydroxide precipitation using caustic soda or lime), cyanide destruction by alkaline chlorination, and biological treatment. Plants with biological treatment systems typically have activated sludge and aerated lagoons, preceded by any pretreatment needed to enhance the biological system's performance, such as oil-water separation, dissolved air flotation, neutralization, and equalization. Plants with physico/chemical treatment systems typically include neutralization, oil-water separation with an American Petroleum Institute separator, dissolved air flotation, filtration, chemical precipitation, steam stripping, equalization, coagulation, carbon adsorption, distillation, air stripping, chemical oxidation (alkaline chlorination for cyanide destruction), solvent extraction, chromium reduction, and/or ion exchange.

PAINT FORMULATING (40 *CFR* 446). This category consists of facilities that produce interior and exterior paints for buildings and other structures; and/or chemical coatings for application at factories producing automobiles, aircraft, furniture, machinery, and other products. Only one subcategory is regulated, the oil-base solvent wash subcategory.

Most (80%) of the paint industry facilities use less than 38 m^3/d (0.01 mgd), but water usage may be as high as 1900 m^3/d (0.5 mgd). Wastewater sources include tank and equipment cleaning, bad paint batches, spill residues, contaminated stormwater runoff, tank truck cleaning wastewaters, steam condensate, and air pollution control devices in contact with water. In addition, other discharges include sanitary wastewater, non-contact cooling water, boiler blowdown, and non-contact steam condensate. The main wastewater constituents include conventional pollutants (BOD_5, O&G, pH, and TSS); COD; inorganic constituents (chromium, copper, lead, mercury, nickel, and zinc); and organic toxic compounds (benzene, di-*n*-butyl phthalate, carbon tetrachloride, ethyl benzene, di[2-ethylhexyl] phthalate, naphthalene, tetrachloroethylene, and toluene). Recommended treatment approaches before recycle include coagulation/flocculation and sedimentation plus biological treatment with aerated lagoons.

PAVING AND ROOFING MATERIALS (TARS AND ASPHALT) (40 *CFR* 443). The paving and roofing materials point source category consists of the following four subcategories, based on the type of product manufactured and the quantity of waste generated (40 *CFR* Subparts A through D): asphalt emulsion plants, asphalt concrete plants, asphalt roofing plants, and linoleum and printed asphalt felt plants. The wastewater flow rate varies by subcategory, with the asphalt concrete plants producing the least wastewater. Wastewater production results from the use of water for cooling, air emissions control, and/or cleanup purposes. The main wastewater constituents are O&G, phenols, TDS, total nitrogen, and TSS, depending on the subcategory. Treatment options include gravity oil skimmers (to treat and wet air scrubber water); and sumps, tanks, or settling ponds for solids separation with recycle to the wet air scrubber system, reuse in the process, or discharge.

PESTICIDE CHEMICALS (40 *CFR* 455). This category covers the manufacturing, formulating, and packaging of pesticides. The U.S. Environmental Protection Agency subdivided the industry, based on the type of product and operation, into four subcategories (40 *CFR* Subparts A through C and E): organic pesticide chemicals, metallo-organic pesticide chemicals, pesticide chemicals formulating and packaging, and repackaging of agricultural pesticides performed at refilling establishments. Subpart D contains the analytical methods to use for demonstrating compliance with the effluent limits.

Wastewater is produced as water formed during the chemical reaction, water used as process solvent or for process streams or product washes, spent acid/caustic, product/process laboratory quality control wastewaters, safety shower water, air pollution control scrubber blowdown, equipment and floor washes, shipping container cleanout, general shower waters, laundries washwater, contact cooling water, and contaminated storm water. Constituents include the conventional pollutants BOD_5, fecal coliforms, O&G, pH, and TSS; the inorganic pollutants barium, calcium, cyanide, iodine, iron, lead, manganese, phosphorus, potassium, silicon, sodium, strontium, and sulfur; and the organic compounds COD, TOC, pesticide active ingredients, and several VOC and SVOC priority pollutants.

In-plant or end-of-pipe treatment technologies for the pesticide chemical manufacturing subcategories include hydrolysis, activated carbon, chemical oxidation, resin adsorption, biological treatment, solvent extraction, and/or incineration. Zero discharge is required for several pesticide active ingredients. For the formulating, packaging, and repackaging subcategories, treatment before recycle or disposal may consist of emulsion breaking via temperature control and acid addition to remove surfactants, emulsifiers, and petroleum hydrocarbons; activated carbon adsorption; chemical oxidation via alkaline chlorination, possibly followed by air stripping, steam stripping, or activated carbon adsorption to remove chlorinated compounds, if formed during the process; chemical precipitation with sulfides (hydrogen or sodium sulfide) to remove metals (e.g., mercury, lead, and silver); and hydrolysis at high or low pH, and possibly high temperatures, to remove organics.

PETROLEUM REFINING (40 *CFR* 419). Facilities in this category process crude oil into various petroleum products via distillation followed by a series of other separation or conversion processes (e.g., cracking, coking, hydrotreating/hydroprocessing, alkylation, polymerization, isomerization, and catalytic reforming) (U.S. EPA, 1995c). Other supporting operations include sulfur recovery, additive production, and additive blending. There are three main categories of finished petroleum products: fuels, finished nonfuel products, and chemical industry feedstocks. Petroleum products are the raw materials for many products (e.g., fertilizers, pesticides, paints, detergents, rubber compounds, and plastics). The U.S. Environmental Protection Agency has divided the industry, based on the major types of processes and products, into five subcategories, as follows (40 *CFR* 419 Subparts A through E): topping, cracking, petrochemical, lube, and integrated.

Petroleum refinery wastewaters consist of process wastewater, cooling water blowdown or once-through cooling water, boiler blowdown, surface water runoff, and sanitary wastewater. The industry generates from 1500 to 30 700 m^3/d (0.4 to 8.1 mgd) of process wastewater. Sour waters are the main type of process wastewater generated, amounting to about 90% of the total wastewater produced. Processes that generate sour waters include distillation, fluid catalytic cracking, catalytic reforming, thermal cracking/visbreaking, catalytic hydrocracking, coking, isomerization, catalytic hydrotreating, and sulfur removal. Other process wastewaters include scrubber water from reformer catalyst regeneration, spent potassium hydroxide from alkylation, desalting wastewater, caustic wash water from isomerization, reformer catalyst regeneration wash water, quench wastewater, and leaks. The main wastewater constituents include the conventional pollutants BOD_5, O&G (i.e., petroleum oil), pH, and TSS; and amines, ammonia, chlorides, COD, hydrogen sulfide, mercaptans, phenol, solvents, and TDS. Chromates, phosphates, and other antifouling biocides may be present if used in cooling towers.

Wastewater treatment starts with segregation and treatment of sour water (containing dissolved hydrogen sulfide, other organic sulfur compounds, and ammonia) via gas or steam stripping before discharge to the wastewater treatment plant. End-of-pipe treatment typically includes separation of oil and solids in two stages, neutralization and equalization as needed, biological treatment and, in some cases, a polishing step. Oil and solids removal is accomplished through the use of gravity separators (e.g., American Petroleum Institute separators, corrugated plate interceptors, or other gravity separators) followed by treatment to remove emulsified oil via settling ponds or dissolved air flotation units, with or without the addition of coagulants. Biological treatment may consist of activated sludge systems, aerated lagoons or stabilization ponds, trickling filters, or rotating biological contactors. Polishing, if needed, includes treatment with activated carbon, anthracite coal, or sand filters.

PHARMACEUTICAL MANUFACTURING (40 *CFR* 439). The facilities covered by this category manufacture, extract, process, purify, and package chemical materials for use by humans and animals as medications. The U.S. Environmental Protection Agency divided the industry, based on the type of processes and activities, into the following five subcategories (40 *CFR* Subparts A through E): fermentation; biological and natural extraction; chemical synthesis; mixing, compounding, or formulating; and research. Most of the facilities produce wastewater in batches, during product changeover. The fermentation processes may take from several days to several weeks, with little or no wastewater produced until the process is complete.

The industry uses a number of solvents during its processes, in addition to detergents and disinfectants to clean the equipment during product changeover. However, most cleanup is performed with steam. A total of 297 pharmaceutical industries in the United States discharged 0.39 million m^3/d (104 mgd) of process wastewater in 1990.

Water is used as follows: as water of reaction or process solvent; to wash process streams, products, and equipment and floors; to control air pollution (discharged as scrubber water blowdown); to cool packing and lubricate pumps (pump seal water); for preparation of acid/caustic solutions that are discharged when spent; and as steam for sterilization and in steam strippers for solvent recovery and wastewater treatment (discharged as condensed steam). Additional wastewaters include discharged batches of process materials that were infected during the process. Research activities generate wastewater intermittently and may contain traces of the raw materials and the product being researched. Fermentation and chemical synthesis produce large volumes of water, while the other three subcategories produce small volumes of water.

The main constituents of the wastewater from each process are BOD_5, COD, and TSS at high concentrations (fermentation and chemical synthesis) or low concentrations (biological and natural extraction; mixing, compounding, or formulating). The characteristics of the wastewaters from research facilities are similar to those generated by the process that produces the chemical being researched. Pharmaceutical wastewaters may have acidic, neutral, or basic pH. Other regulated constituents include the inorganic pollutants ammonia and cyanide; and the organic compounds acetone, acetonitrile, n-amyl acetate, amyl alcohol, chloroform, benzene, n-butyl acetate, chlorobenzene, chloroform, o-dichlorobenzene, 1,2-dichloroethane, diethyl amine, dimethyl sulfoxide, ethanol, ethyl acetate, n-heptane, n-hexane, isobutyraldehyde, isopropanol, isopropyl acetate, isopropyl ether, methanol, methyl cellosolve, methyl formate, methyl-2-pentanone, methylene chloride, phenol, tetrahydrofuran, toluene, triethylamine, and xylenes.

In-plant treatment systems for segregated streams may include steam stripping with or without rectification columns for solvent recovery; alkaline chlorination, hydrogen peroxide oxidation, or hydrolysis to remove cyanide; and granular activated carbon to remove organics. End-of-pipe treatment consists of advanced biological treatment (single- or two-stage) with or without nitrification, effluent multimedia filtration, and polishing ponds (if needed). Advanced biological treatment typically includes equalization with or without pH adjustment, primary clarification, biological treatment unit (aeration tanks, aerated lagoons, trickling filters, rotating biological contactors, or anaerobic tanks), and secondary clarification. The wastewater from chemical synthesis may be too concentrated or toxic from the use of solvents to be handled by biological treatment, thus requiring physico/chemical treatment processes.

PHOSPHATE MANUFACTURING (40 *CFR* 422). This category encompasses facilities that process phosphate rock to produce a number of phosphate products that can be used to manufacture fertilizers and to produce calcium phosphate for animal and human food. The U.S. Environmental Protection Agency divided the industry into six subcategories, based on the processes and type of product (40 *CFR* 422 Subparts A through F): phosphorus production, phosphorus consuming, phosphate, defluorinated phosphate rock, defluorinated phosphoric acid, and sodium phosphates. Only the last three subcategories have effluent limits.

The industry uses large volumes of water, with total discharges of at least 0.16 million m^3/d (43 mgd). Wastewater streams include washing waters in flotation plants containing fine clays and colloidal slimes and some tall oil or rosin oil, condenser water bleed-off from phosphorus refining containing elemental phosphorus, water for transportation of ore to the process plant, classification water, heavy media separation water, solution water, air emissions control equipment water (which may contain fluoride), and equipment and floor washdown water. Other wastewater constituents are the conventional pollutants pH, temperature, and TSS, and fluorine, silica, and reducing substances.

Treatment processes for phosphate rock wastewaters involve settling of slime in ponds or removal of sand tailings in mechanical clarifiers before reuse. Overflow from containment and cooling ponds may be treated with lime neutralization, and double lime neutralization can be used to remove TSS, phosphate, radium 226, and fluoride from sodium phosphates manufacturing wastewaters.

PHOTOGRAPHIC (40 *CFR* 459). This category covers facilities that process photographic products using silver halide to produce continuous-tone black and white or color negatives, positive transparencies, and prints for delivery to external customers (U.S. EPA, 1981). Dichromate bleach may be used for processing, mostly for commercial movie films. Photographic processing is the only subcategory under this point source.

Wastewater is produced as waste chemical solutions and waste washwaters. The main wastewater constituent of concern is silver. Cyanide and chromium may be present if the facility uses bleach containing ferri-ferrocyanide or dichromate bleach, respectively. Other constituents include ammonia, BOD_5, iron, lead, pH, TDS, and TOC.

Silver recovery, which is practiced throughout the industry, is accomplished via metallic replacement or electrolytic recovery. Other processes include ion exchange, reverse osmosis, ferricyanide bleach regeneration, ferric EDTA bleach regeneration, and ferrous sulfate precipitation. Removal of chromium includes at-the-source segregation and treatment via chromium reduction, pH adjustment for chromium precipitation, and diatomaceous earth filtration. Ferricyanide precipitation may also be used, as well as water evaporation to minimize or eliminate discharges.

PLASTICS MOLDING AND FORMING (40 *CFR* 463). The facilities in this category add chemical additives to plastic resins to give them the appropriate characteristics; mold pellets, granules, powders, sheets, fluids, or preforms of plastic materials into their final solid or foam plastic shape; and finish the product through welding, adhesive bonding, machining, application of additives, or surface decorating (painting and metalizing). Homogeneous polymers without additives may also be produced. Processing of crude intermediate plastic material (i.e., plastic material formulated in an onsite polymerization process) for shipment offsite is excluded from this category and regulated under the organic chemicals, plastics, and synthetic fibers category (40 *CFR* 414). Based on the type of wastewater producing process, the U.S. EPA divided the industry into three subcategories (40 *CFR* 463 Subparts A through C): contact cooling and heating water, cleaning water, and finishing water.

As indicated above, wastewater is produced from water used to cool or heat plastic products, clean the surface of both the plastics products and the equipment used in production, and finish plastics products. The main wastewater constituents include the conventional pollutants BOD_5, O&G, and TSS; the inorganic pollutant zinc; and the organic constituents di-n-butyl phthalate, COD, bis(2-ethylhexyl) phthalate, dimethyl phthalate, TOC, and total phenols. Another pollutant of concern is plastic pellets released in the wastewater, which may be ingested by birds and other animal species after their discharge to surface waterbodies. Wastewater treatment technologies may include sedimentation, biological treatment, or activated carbon.

PORCELAIN ENAMELING (40 *CFR* 466). Porcelain enameling facilities apply glass-like coatings to metals to improve the resistance, stability, and appearance of the product's surface characteristics. The U.S. Environmental Protection Agency divided the industry, based on the basis material used, into four subcategories (40 *CFR* 466 Subparts A through D): steel, cast iron, aluminum, and copper basis materials. The industry may produce from 0.45 to 1360 m^3/d (0.00012 to 0.36 mgd) of process water (U.S. EPA, 2004). Water is used to remove undesirable material from the ware surface, as a medium for the chemical reactions, as a vehicle for coating application, as cooling water, and for plant cleanup and maintenance.

The main wastewater constituents are the basis materials (iron, aluminum, and copper), plus a number of other metals (e.g., antimony, barium, cadmium, chromium, cobalt, lead, manganese, selenium, titanium, and zinc). These metals may be contaminants of porcelain enamel, the basis material, or the incoming water, or may dissolve from the equipment used in the process. O&G, pH, and TSS are also constituents of concern. General treatment approaches include settling, and chemical precipitation with lime and settling for coating wastewaters; hexavalent chromium reduction for the aluminum subcategory; and settling and polishing filtration for the metal preparation wastewaters.

PULP, PAPER, AND PAPERBOARD (40 *CFR* 430). This category covers facilities that manufacture pulp, paper, or paperboard from wood or non-wood pulp. These raw materials are either manufactured onsite, obtained from other mills, or derived from pre- and/or post-consumer reclaimed fiber. Processes may include fiber furnish preparation and handling; pulping; chemical recovery; pulp processing; bleaching; stock preparation; and pulp, paper, and paperboard making. Based on the processes used and wastewater characteristics and treatability, U.S. EPA subdivided the industry into the following 12 subcategories (40 *CFR* 430 Subparts A through L): dissolving kraft; bleached papergrade kraft and soda; unbleached kraft; dissolving sulfite; papergrade sulfite; semi-chemical; mechanical pulp; non-wood chemical pulp; secondary fiber deink; secondary fiber non-deink; fine and lightweight papers from purchased pulp; and tissue, filter, non-woven, and paperboard from purchased pulp.

This category is the largest industrial process water user in the United States and, in the aggregate, discharged 7 million m^3/d (1800 mgd) of wastewater in 2000. Paper and/or paperboard making, bleaching, and pulping processes result in the discharge of an estimated 74% of the wastewater. Other contributing processes are chemical recovery, power operation, secondary fiber processing, pulp handling, wood preparation, pulp drying, and broke processing and storage.

The main wastewater constituents are BOD_5, TSS, COD, color, adsorbable organic halides (AOX), dioxins and furans, acetone, methyl ethyl ketone, chloroform, and chlorinated phenolic compounds. AOX is a measure of halogenated organic compounds that adsorb onto granular activated carbon. Chlorinated phenolic compounds include the following groups: chlorinated phenols, chlorinated catechols, chlorinated guaiacols, chlorinated syringols, and chlorinated benzaldehydes.

Treatment may be accomplished through equalization, neutralization, precooling, primary sedimentation, nutrient addition, aerobic biological treatment, and/or addition of flocculants to secondary clarifiers to improve settling. Multi-basin systems, some of them used as polishing ponds, may also be used. Multimedia filtration is recommended for the mechanical pulp subcategory. To dissolve as much of the lignin that holds the cellulose fibers together, either extended cooking or oxygen delignification may also be used if necessary in the bleached papergrade kraft and soda mills during the processing of the wood chips or after brown stock washing, respectively.

RUBBER MANUFACTURING (40 *CFR* 428). The U.S. Environmental Protection Agency divided this industry based on type of product, processing techniques, and product type. The resulting 11 subcategories are the tire and inner tube subcategory (40 *CFR* 428 Subpart A) and the following 10 rubber manufacturing and reclaiming subcategories (40 *CFR* 428 Subparts B through K): emulsion crumb rubber; solution crumb rubber; latex rubber; small-, medium-, and large-sized general molded, extruded, and fabricated rubber plants; wet digestion reclaimed rubber; pan, dry digestion, and mechanical reclaimed rubber; latex-dipped, latex-extruded, and latex-molded goods; and latex foam.

Synthetic rubber manufacturing facilities produce wastewaters during the cooling, heating, vulcanizing, and cleaning operations (U.S. EPA, 1995d). Wastewaters from fabricated and reclaimed rubber manufacturing plants result from processing solutions, washdown of plant areas, runoff from outdoor storage areas, spills and leaks of organic solvents and lubricating oils, vulcanizer condensate, discharges from wet air-pollution control devices, and dewatering liquor. Tire and inner tube facilities' wastewaters may consist of mill area oily waters, soapstone slurry and latex dip wastes, area washdown water, emission scrubber waters, contaminated stormwaters, once-through cooling water, boiler blowdown, cooling tower blowdown, and water treatment wastes.

The main wastewater constituents are BOD_5, COD, O&G, pH, and TSS . Color, TDS, surfactants, and the metals chromium, lead, and zinc may also be present. General treatment approaches for the tire and inner tube subcategory include: segregation of oily wastewaters and treatment in an API-type gravity separator, with a storage tank to handle large spills or leakage of a water supply line. For the synthetic rubber subcategories, treatment by equalization, neutralization, solids separation, and biological treatment, followed by dual-media filtration and activated carbon adsorption are recommended by U.S. EPA. Solids separation can be achieved via chemical coagulation and primary clarification or air flotation clarification of primary and secondary solids. Biological treatment systems may include activated sludge, aerated lagoons, and stabilization pond systems.

For the fabricated and reclaimed rubber subcategories, segregation of process wastewaters is encouraged. Treatment may consist of gravity separation or a filter coalescer to remove oil, coagulation and clarification to remove latex or holding ponds to remove other TSS, aerated lagoons and settling ponds to remove BOD, and chemical precipitation to remove metals.

SOAP AND DETERGENT MANUFACTURING (40 *CFR* 417). Soap is a type of detergent used for personal bathing or additives in lubricating oils, greases, rust inhibitors, and jellied fuels. It is characterized by its carboxylate water-stabilized group, with sodium or potassium as positive ions. Synthetic detergents are used to clean and launder, and contain surface-active (surfactant) compounds. Some liquid detergents use sodium citrate and sodium silicate. The U.S. Environmental Protection Agency divided this category, based on the type of process and final product, into 19 subcategories (Table 6.8). The industry uses low volumes of water and produces wastewater from the washing and purification processes (U.S. EPA, 1996). The main wastewater constituents are BOD_5, O&G, pH, TSS, COD, and surfactants, which can be removed via flotation with skimming and precipitation with calcium chloride.

STEAM ELECTRIC POWER GENERATING (40 *CFR* 423). This category covers the production of electric power via fossil fuel burning in boiler furnaces, production of steam using the evolving heat from the boiler furnaces, and use of the produced steam to move turbines' rotating blades, which then convert the imparted mechanical energy into electrical energy. The industry was not divided into subcategories for establishing the effluent limitations, but different limitations were imposed to each of the following major source of wastewaters: low-volume waste sources, fly ash and bottom ash transport water, metal cleaning wastes, once through cooling water, cooling tower blowdown, and coal pile runoff. The effluent limitations under 40 *CFR* 423 address all wastewater constituents except temperature.

Wastewater sources include regularly produced wastewater, primarily from water treatment system cleaning or regeneration processes; continuous or semi-continuous ancillary operations (e.g., cooling water systems, ash handling systems, wet-scrubber air pollution control systems, and boiler blowdown); wastewaters produced during cleaning of boilers, air preheaters, cooling tower basins, and miscellaneous small equipment; and wastewaters produced during rainfalls as drainage from coal piles, ash piles, floor and yard drains, and construction activities.

Wastewaters from steam electric power plants may contain a number of toxic VOCs and SVOCs, pesticides, metals (antimony, arsenic, beryllium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc), asbestos, cyanide, and residual chlorine. Recommended treatment technologies are ash settling ponds, lime precipitation, or evaporation. Oil skimming, equalization, filtration, aerobic biological treatment, and reverse osmosis may also be used if needed. Dechlorination can also be used to remove total residual chlorine, or ozone and ultraviolet light may be used for disinfection instead of chlorine.

SUGAR PROCESSING (40 *CFR* 409). The facilities in this category process raw cane into crystalline or liquid cane that are then refined to produce sugar, or beets to produce sugar. The U.S. Environmental Protection Agency divided the industry into eight subcategories based on the type of raw material, harvesting methods, harvesting conditions, availability and cost of control and treatment technologies, and manufacturing processes (40 *CFR* 409 Subparts A through H). The subcategories are beet sugar processing, crystalline cane sugar refining, liquid cane sugar refining, Louisiana raw cane sugar processing, Florida and Texas raw cane sugar processing, Hilo-Hamakua Coast of the Island of Hawaii raw cane sugar processing, Hawaiian raw cane sugar processing, and Puerto Rican raw cane sugar processing.

The industry uses 8000 to 100 000 m^3/d (2 to 26 mgd) of water, of which zero to 100% may be discharged as wastewater. Wastewater streams for the cane sugar industry may include, depending on water reuse and minimization practices, cane washwater, mill washwater, barometric condenser cooling water, boiler blowdown, filter cake slurry, fly ash slurry, acid and caustic wastewaters, floor washwater, and miscellaneous wastewaters. Wastewater in the beet sugar industry may consist of transport water, beet washing water, pulp-press wastewater, carbonation process residue, evaporator condensates, and wastewater resulting from sugar extraction.

The main wastewater constituents are BOD_5, COD, pH, TSS, and high wastewater temperature. Recommended treatment approaches for the raw cane processing subcategories include, depending on the subcategory, settling ponds with or without polymer addition followed by biological treatment, or containment of all wastewaters in evaporation ponds to achieve zero discharge except in unusual rainfall events. Beet sugar wastewaters can be treated via lagooning and land spraying, coagulation, sedimentation, and biological filtration.

TEXTILE MILLS (40 *CFR* 410). This category covers facilities that receive and prepare fibers; transform the fiber materials into yarn, thread, or webbing; convert these materials into fabric or related products, and finish these products. Based on raw materials, final products, and manufacturing processes, U.S. EPA divided the industry into nine subcategories (40 *CFR* 410 Subparts A through I): wool scouring, wool finishing, low water use processing, woven fabric finishing, knit fabric finishing, carpet finishing, stock and yarn finishing, nonwoven manufacturing, and felted fabric processing.

The industry may discharge between zero and 52 500 m^3/d (14 mgd), depending on the raw materials, processes, and products. Water is used for wool scouring, fabric washing, carbonizing, washing and rinsing during fulling, pre-scouring in sensitive dyeing, spillage, excess sizing dumps, cleanup of the slasher and other equipment, water-jet weaving, overspraying, desizing, cotton and cotton-synthetic fiber scouring, fabric washing, woven fabric dyeing and printing, bleaching, carpet backing, fulling of felted fabric, and finishing to improve resistance to various materials and environmental conditions.

The main wastewater constituents are BOD_5, COD, O&G, pH, TSS, color, chromium, copper, zinc, phenols, and sulfides. In addition, coarse suspended solids (e.g., lint, flock, fibers, rags, and yarn), other toxic metals, cyanide, and a number of toxic organic pollutants may be present. Wastewater treatment may be accomplished via preliminary screening, equalization, neutralization, biological treatment with extended aeration or aerated lagoons, chemical coagulation, post chlorination, and multi-media filtration or dissolver air flotation, as needed. Sulfide oxidation and oil-water separation are optional pretreatment processes for indirect dischargers.

TIMBER PRODUCTS PROCESSING (40 *CFR* 429). The facilities in this category process timber into a wide variety of finished products, including finished lumber and reconstituted wood fibers as a number of sheet-form flexible and rigid products. The U.S. Environmental Protection Agency has divided the industry, based on the process and products, into 16 subcategories (40 *CFR* 429 Subparts A through P): barking, veneer, plywood, dry process hardboard, wet process hardboard, wood preserving—waterborne or nonpressure, wood preserving steam, wood preserving—Boulton, wet storage, log washing, sawmills and planing mills, finishing, particleboard manufacturing, insulation board, wood furniture and fixture production without water wash spray booth(s) or without laundry facilities, and wood furniture and fixture production with water wash spray booth(s) or with laundry facilities. This discussion addresses the first eight subcategories and the last one, plus log washing and insulation board. Subcategory O (i.e., wood furniture and fixture production without water wash spray booth(s) or without laundry facilities) does not produce wastewater and no information was readily available for the other three subcategories.

Wood preserving plants reportedly produce an average of 53 m^3/d (0.04 mgd). Insulation board and wet process hardboard plants can produce between 190 and 15 100 m^3/d (0.05 and 4 mgd). Wastewater sources may include log conditioning wastewater, condensed steam, fiber dilution water and washwater, dryer washwater, glue spreaders and mixing tanks water, mat formation wastewater, pressing wastewater, dripped formulation mixed with rainwater and facility washwater, contact cooling water, boiler blowdown water, vacuum water, and water softener brine. Wood furniture and fixture production with water wash spray booth(s) or with laundry facilities generates wastewater from the latter two processes.

The main wastewater constituents of the wood preserving subcategories are the conventional pollutants O&G, pH, and TSS; COD; and organic solvents (e.g., benzene and toluene). Depending on the type of preservative used, other constituents are the polynuclear aromatic hydrocarbon components of creosote (e.g., anthracene, pyrene, and phenanthrene), phenol and phenol derivatives, pentachlorophenol, and heavy metals (arsenic, copper, chromium, nickel, and zinc). Wastewaters from the insulation board and wet process hardboard subcategories contain high concentrations of BOD_5 and TSS. Veneer and plywood plants produce wastewaters with high concentrations of the conventional pollutants BOD_5, pH, and TSS; COD, phenols, phosphorus, TDS, and TKN. Wastewaters from the wood furniture and fixture production with water wash spray booth(s) or with laundry facilities include any bleaching, straining, sealing, and/or topcoating agents removed.

Except for Subcategory P (wood furniture and fixture production with water wash spray booth(s) or with laundry facilities), all of the subcategories discussed recycle or reuse as much wastewater as possible, or evaporate them in cooling towers or in the process. The wastewaters from Subcategory P are treated via evaporation ponds, spray irrigation, burning with boiler fuel, or hauling to a landfill.

Recommended treatment processes for wood preserving plants include in-plant evaporation; or oil separation in two or more stages, chemical flocculation to break oil-water emulsions, slow sand filtration, neutralization, biological treatment, and (if necessary) hexavalent chromium reduction with sulfur dioxide followed by precipitation of metal hydroxides after pH adjustment with lime or caustic soda and possibly carbon adsorption. Treatment technologies for the other subcategories discussed, either before recycle or reuse or before discharge, may include (as needed) neutralization and settling before recycle or reuse; neutralization, primary clarification, biological treatment via extended aeration, secondary clarification, and recycle and reuse of a portion of the treated wastewater; aerated lagoons followed by settling lagoons with very long detention times; in-plant evaporation or evaporation through ponds; and spray irrigation.

TRANSPORTATION EQUIPMENT CLEANING (40 *CFR* 442). Tanks or containers in this category include tank trucks, closed-top hopper trucks, rail tank cars, closed-top hopper rail cars, intermodal tank containers, inland tank barges, closed-top hopper barges, ocean/sea tankers, and other tanks (excluding drums and intermediate bulk containers) used to transport materials or cargos that directly contact the interior of the tank or container. The U.S. Environmental Protection Agency divided this category into four subcategories, based on the type of transportation equipment and cargos (40 *CFR* 442 Subparts A through D):

- Tank trucks and intermodal tank containers transporting chemical and petroleum cargos,
- Rail tank cars transporting chemical and petroleum cargos,
- Tank barges and ocean/sea tankers transporting chemical and petroleum cargos, and
- Tanks transporting food grade cargos.

The industry generates about 56 800 m^3/d (15 mgd) of wastewater as a result of rinsing the tank interior before cleaning to remove residuals; cleaning the tank interior with hot or cold washes and/or rinses; cleaning the tank exterior; boiler blowdown; hydrotesting the tank for leaks; cleaning safety equipment; and stormwater contamination during tank and container cleaning. The main wastewater constituents vary depending on the type of facility and include any chemical transported in the tank or container, as well as the cleaning chemicals. Cleaning chemicals may include hydrofluoric acid, phosphoric acid, sodium hydroxide, sodium metasilicate, phosphate-based surfactants, glycol ethers or esters, diesel fuel, kerosene, other petroleum-based solvents, citrus oils and sanitizers, and oxidation inhibitors.

General treatment approaches vary per type of equipment. Recommended treatment processes for wastewaters from the tank trucks and intermodal tank containers transporting chemical and petroleum cargos include equalization, oil/water separation, chemical oxidation, neutralization, coagulation, clarification, biological treatment, and activated carbon adsorption. Treatment options for the food subcategory include oil/water separation, equalization, and biological treatment. Treatment for the other two subcategories may include oil/water separation, equalization, dissolved air flotation with flocculation and pH adjustment, and biological treatment. If the facility discharges to a POTW, biological treatment may not be necessary before discharge.

WASTE COMBUSTORS (40 *CFR* 444). Commercial facilities in this category use controlled flame combustion to treat or recover RCRA hazardous waste. Such facilities include industrial boilers, industrial furnaces, rotary kiln incinerators, and liquid injection incinerators.

Commercial waste combustors may produce from zero to more than 8 m^3/d (0.0021 mgd) of wastewater, consisting of air pollution control wastewater, flue gas quench wastewater, slag quench, truck/equipment washwater, container washwater, laboratory drain wastewater, and floor washings from the process area. Only the first three sources of wastewater are subject to the effluent limits under 40 *CFR* 444. The main wastewater constituents are TSS, pH, arsenic, cadmium, silver, chromium, titanium, copper, lead, zinc, and mercury. Aluminum, molybdenum, antimony, selenium, iron, and tin are also present in the wastewaters, but are not regulated because they are removed by the same treatment technologies that remove the regulated constituents. These treatment technologies may include chromium reduction, primary precipitation and solids removal, secondary precipitation and solids removal, and sand filtration.

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SUGGESTED READINGS

http://www.epa.gov/epacfr40/chapt-I.info/chi-toc.htm (Links to 40 *CFR* Parts 401–471)

http://www.epa.gov/nscep/ or http://yosemite.epa.gov/water/owrccatalog.nsf/.

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Chapter 7

Management Strategies for Pollution Prevention and Waste Minimization

(continued)

Waste management is a complex problem that affects all aspects of manufacturing businesses and "environmental considerations infuse everything from product design to marketing, from purchasing to product stewardship, from employee relationships to executive compensation" (Ditz, et al., 1995). Pollution prevention exists in three realms in the corporate world as a corporate philosophy, a managed team effort, and an engineered solution. Corporate philosophy sets the stage for concerted management efforts; which in turn, affect the ultimate selection of pretreatment technologies. This chapter focuses on some of the components of management systems that have been successful in reducing pollution loads while reducing production costs. Also included in this chapter is a discussion of pretreatment options as they relate to the overall pollution prevention effort.

CORPORATE PHILOSOPHY

Over the past several decades, the business response to environmental performance issues has tended to be one of three styles, each with different emphases on legal, market, and ethical considerations (Post and Altman, 1998):

- Compliance-based: corporations respond to regulations and find solutions that focus on "end-of-the-pipe" (Type 1);

- Market-driven: corporations anticipate regulatory changes and focus on solutions that involve manufacturing methods (Type 2);
- Value-driven: corporations seek environmentally sustainable products and processes and focus on stewardship of a product's entire life-cycle (Type 3).

In the United States, companies have tended to progress from reactive management (Type 1) to proactive management (Type 2). Not surprisingly, the reactionary style was a response to the environmental laws and regulations established in the 1970s (Wilson and Sasseville, 1999). These laws and regulations (e.g., the Clean Air Act, the Clean Water Act, and the Resource Conservation and Recovery Act) focused on protecting human health and environmental resources by limiting pollutant discharges into specific media (e.g., air, water, and soil). So, many industries responded by selecting processes that treated the "end-of-the-pipe" wastes and then proceeded with business as usual. Waste generation and treatment became established business costs and practices. As new dimensions to environmental controls were added to the corporate mix, costs became infused with non-environmental accounts and hidden from direct accounting measures. When the hidden costs were tallied, the burden could range from 19 to 21% of the cost of doing business (Lash, 1995; Heller et al., 1995).

Beginning in the 1980s with the 1984 Hazardous and Solid Waste Amendments of the Resource Conservation and Recovery Act (RCRA), the 1986 Emergency Planning and Community Right-to-Know Act (EPCRA) and the 1990 Pollution Prevention Act (PPA), it became increasingly clear that the mass of pollutants emitted to the environment could not be controlled by treatment alone. Also, treatment of one medium (air, soil, or water) that resulted in contamination of another medium was unacceptable. The first pollution prevention policy was introduced in the 1984 RCRA amendments, which stated that reducing or eliminating hazardous waste generation at the source should take priority over management after generation. Pollution prevention policy was formalized in the 1990 PPA with the establishment of a general hierarchy of prevention measures, as outlined in the U.S. EPA's *33/50 Initiative for Control of High-Volume EPCRA-Listed Compounds* (U.S. EPA, 1991; Allen et al., 2002; Dennison, 1996).

Many management systems are based on the waste-generation hierarchy. The hierarchy prioritizes the order for solving waste generation problems as follows: waste minimization/pollution prevention > recycling/reuse > volume/toxicity reduction > disposal. The waste management hierarchy (Table 7.1) may be applied

Table 7.1 Waste management hierarchy (ranked most favorable to least favorable).

Management option	Definition
Source reduction	Any practice that reduces the amount of any hazardous substance entering any wastestream before recycling, treatment, or disposal.
In-process recycle	Unreacted feedstock is separated and recycled to the process.
Onsite recycle	Waste from the initial process is converted into a commercial product in a second process performed onsite.
Offsite recycle	Waste from the initial process is collected and transferred to another facility, where it is converted into a commercial product.
Waste treatment	Waste is separated and treated to render it less hazardous.
Secure disposal	Waste is separated and sent to a secure site (e.g., a landfill).
Direct release	Waste is separated from product and released to the environment.

to one unit process or as a corporation-wide business philosophy (Allen et al., 2002). Specific definitions of the various terms vary from the original U.S. EPA descriptions in the PPA and interpretations from responding industries (e.g., API, 1993; ACC, 1999a). When enacted, these management systems tend to take on the proactive style of Type 2 business cultures.

Practical application of the hierarchal approach to pollution prevention by "evaluating waste reduction and releases at their sources before evaluating recycling and treatment programs" is exemplified by the chemical industry's success in dealing with the volatile organic carbon (VOC) regulations imposed by the Toxic Substance Control Act (TSCA) "right to know" air pollution regulations of 1976. The 1998 Toxic Release Inventory (U.S. EPA, 2000) data show that the total releases of listed hazardous compounds dropped from 1.6 bil. kg (3.6 bil. lb) in 1986 to less than 0.9 bil. kg (2 bil. lb) in 1998. The chemical industry has also tremendously improved in conservation, boasting a 21% improvement in electric efficiency (the amount of electricity demand per mass of product) between 1986 and 2000 (Chenier, 2002). A number of site-specific case studies for various industries and federal facilities are reviewed by Dennison (1996).

Industry trade associations are actively promoting progressive Type 3 management styles by offering stewardship training and certifications. One such program is offered by the American Chemical Council. "The purpose of the Product Stewardship Code of Management Practices is to make health, safety, and environmental protection an integral part of designing, manufacturing, marketing, distributing, using, recycling, and disposing of our products" (ACC 1999b). The program is based on the recognition that environmental responsibility is vested throughout the product's life-cycle.

MANAGING FOR SUCCESS

The 1984 Hazardous and Solid Waste Amendments and further U.S. EPA guidance identified the key elements of a successful program (Haas and Vamos, 1995). They reflect goals based on successful waste treatment at minimal cost. The revised list of guidelines for working groups is based on the premise that the incentives for success warrant a full understanding of the production process, not just a survey of the wastes generated. So, it is the project team's responsibility to identify the solution that provides the best cost-benefit tradeoff. A successful team will:

- Define the problem clearly and establish written goals;
- Obtain top management support for finding a solution to this problem;
- Include engineering, waste treatment operations, and production staff;
- Characterize the product and identify process changes that will minimize waste;
- Characterize the wastes generated;
- Generate options and prioritize solutions;
- Periodically assess waste-minimization options;
- Assess how process changes affect product quality or quantity;
- Create a cost-allocation system to fully load disposal costs back to the production unit;
- Encourage technology transfer (especially between operating divisions); and
- Provide program evaluation with effective feedback and incentives for improvement.

This list is not necessarily linear; the best results are obtained by repeatedly backtracking to reevaluate various elements. It is similar to the approach prescribed for companies creating the environmental management systems needed to obtain ISO 14001 certification (Wilson and Sasseville, 1999; Moxen and Strachan, 1998).

DEFINE THE PROBLEM WITH WRITTEN GOALS. One of a waste management team's first objectives is to define both the problem and the method for solving it. There are many reasons for establishing a waste management program, including:

- An industrial category wastestream needs to be brought into compliance;
- New environmental regulations limit a wastestream;
- A new or expanded production line has created new wastes;
- Downstream treatment problems have recently been associated with a specific wastestream;
- A desire to capture value;
- Downstream equipment needs protection;
- A desire to minimize water or energy use;
- Avoid capital expenditures;
- Recover or recycle resources, or minimize waste;
- Improve plant safety;
- Improve production rates; and
- Improve the product(s).

The more specific the goals, the better the team can evaluate its performance. A specific goal may be "reduce the TOC going to the industrial waste sewer by 50% while increasing product by 10%" or "cut the cost of surfactant in the parts-washing operation by better oil recovery."

OBTAIN TOP MANAGEMENT SUPPORT. For a waste-minimization project to succeed, top company managers must be made aware of all of its drivers and benefits. According to the National Research Council (1985), incentives for waste minimization strategies include reductions in liability and disposal costs. Good environmental management in the production line improves a company's bottom line, and the list of potential incentives should reflect this. When production wastes are controlled, the entire product line is probably in control. Some specific incentives for establishing a waste management team include:

- Reduce high disposal costs,
- Minimize secondary liability at the disposal site,

- Minimize third-party liability,
- Overcome adverse public relations,
- Improve product quality,
- Improve production rates,
- Improve worker safety, and
- Obtain industry certification (e.g., ISO 14001).

INCLUSIVE PLANNING. The most reasonable solution can only be found if all stakeholders (e.g., plant engineers, production-line staff, and waste-treatment staff) are included in the planning. If the waste-minimization program is a public relations response, then the planning team must include marketing or corporate relations staff. Pollution prevention requires innovative thinking and will generate many alternatives. A healthy debate of these alternatives will result in a prioritized list of options. An inclusive team also will make approval easier, because managers will be more confident that all stakeholders support the solution.

PRODUCT CHARACTERIZATION FOR WASTE MINIMIZATION. The best way to minimize waste is not to generate it. The waste-minimization team should evaluate production techniques and determine whether the facility can improve housekeeping; alter process technology; change materials; reformulate product(s); or recycle, recover, or reuse wastes before a pretreatment system is built. Following are generic options for good waste-reduction management (Haas and Vamos, 1995). Only a full analysis of political, environmental, marketing, and economic climate will reveal the winning strategy.

Improving Plant Operations. Housekeeping and preventive maintenance control wastes inexpensively. These methods include better monitoring of equipment leaks and losses, separation of wastestreams, better chemical handling, and covers to reduce volatile losses.

Altering Process Technology. Changes in process technology may include modernization, modification, and better equipment controls. These changes are moderately expensive and typically done when the process line is completely replaced.

Material Substitution. Facilities often can replace volatile solvents with less volatile ones, or non-degradable materials with biodegradable ones. The metalworking industry, for example, has largely transitioned from solvent degreasing to aqueous-immersion washers. Some parts-washing operations have switched to dry-ice blasting. Some replacements can be found after relatively inexpensive trials. However, finding an appropriate substitution may take extensive research and development if it is needed as a catalyst or solvent in a chemical reaction.

Product Reformulation. Sometimes products can be reformulated with more environmentally friendly ingredients. For example, volatile solvents in coatings and paints have been replaced with more water-soluble materials. Ammonia has replaced toluene in water-based ink formulations. However, without a determined and needy customer base, this is the most difficult change.

Recycle/Recovery/Reuse. This method is typically used to maximize the use of expensive materials. Keep in mind that some in-plant wastes may be another plant's raw material(s).

Pretreatment. Pretreatment is a necessary, but the least preferred, option. The U.S. Environmental Protection Agency has published a number of recommendations (U.S. EPA, 2004a; U.S. EPA, 2004b) for minimizing pollution in wastewater generated by specific industries (Table 7.2). (For more information on biological, chemical, and physical pretreatment methods, see Chapters 8 through 13.)

WASTE CHARACTERIZATION AND WASTE GENERATION. Waste characterization goes hand-in-hand with product characterization and is a baseline for any changes made to the production process. It is also an essential component of pretreatment system design. Waste characterization includes an in-plant survey, identification of categorical wastes, identification of waste-generating processes, identification of major water users, mass balances, in-plant control, and water minimization efforts. (For more information on waste characterization, see Chapter 4.)

In-Plant Survey. Detailed information on the facility's wastewater provides a baseline to help staff evaluate the effect of future production growth, water-conservation efforts, or changing regulatory requirements.

Identifying Categorical Wastestreams. Any wastestreams covered by categorical pretreatment standards should further be identified as subject to production-based standards, combined wastestream calculations, or both.

Identifying Wastewater-Generating Operations. The team should identify both wastestreams directly attributable to various processes and those generated via cross-media pollution control efforts (e.g., wet-air scrubber blowdown, sludge dewatering, product-change washouts, site-cleanup efforts, yard drainage, noncontact cooling water, or secondary containment spillage).

Preparing Mass Balances. The information obtained from the in-plant survey of wastewater-generating operations is used to prepare mass balances of the facility's flows and wasteloads. Mass balances confirm that all flows and pollutant loads have been accounted for.

GENERATE OPTIONS AND PRIORITIZE SOLUTIONS. The waste management team should provide facility managers with several alternatives and prioritize them so informed decisions can be made. Following are some available alternatives for in-plant control, water conservation and recycle, and pretreatment (Table 7.2).

In-Plant Control. Once a facility's mass balance is completed and the sources and loadings of various wastestreams have been determined, environmental engineers should consider options for controlling and reducing pollutants to reduce the concentrations and volumes of wastestreams that need pretreatment.

Ideally, specific pollutants should be eliminated by substituting raw materials that generate no wastewater at all or only wastewater that requires no pretreatment. Because it is often impossible or economically infeasible to eliminate pollutant-generating raw materials from the production process because of product specifications or other reasons, the possibility of recycling or reusing the wastewater generated during production should be evaluated. Sometimes the concentrated solutions obtained during cleanup operations can be recycled as raw materials in the next production run. If internal recycling is infeasible, engineers should evaluate the possibility of having an outside party reclaim or reuse the wastewater.

If efforts to eliminate, recycle, or reclaim wastewater via changes in production activities are unsuccessful, engineers should then focus on reducing the amount of wastewater that requires treatment. These steps include implementing good housekeeping practices, using spill-control measures (e.g., spill-containment enclosures and drip trays around tanks); eliminating any "wet floor" areas; and using either static rinses or those without overspray. Proper housekeeping should be practiced at all times, because it can be one of the most cost-effective measures for reducing pollutant loadings and maintaining compliance with regulatory requirements.

Table 7.2 Wastewater minimization or pollution prevention approaches used by the U.S. EPA to establish effluent standards for selected point source categories.[1]

Point source category	Wastewater minimization or pollution prevention approach
Aluminum forming	Water savings measures, including recycle of contact cooling water and scrubber liquor, countercurrent cascade rinsing, hauling or regeneration of chemical baths, alternatives to wet scrubbing for fluxing and degassing, and recycle of extrusion press hydraulic fluid leakage.
Battery manufacturing[2]	*Lead Subcategory:* In-process options (e.g., cascade and countercurrent rinsing) to reduce the volume of water, consumption of cleansed wastewater in product mixes, and substitution of nonwastewater-generating formation (charging) systems.
Carbon black manufacturing	Dry vacuuming of carbon black spills; recycling of dehumidifier blowdown or equipment and process area washdown as quench water. Evaporation/settling ponds or granular filters can be used before recycling.
Centralized waste treatment	None used.
Coal mining[2]	*Western Alkaline Coal Mining:* Best management practices to prevent erosion and sediment discharge, such as restoration of affected areas; stabilization of areas to prevent erosion; minimization of disturbances to the hydrologic balance; and installation of sediment traps, contour berms, terraces, diversion channels, check dams, interceptor ditches, mulching, straw bales.
Coil coating	*Steel, Galvanized, and Aluminum Subcategories:* In-plant controls to reduce wastewater flow. *Canmaking Subcategory:* In-plant controls to reduce wastewater flow.
Concentrated animal feeding operations	*Beef and Dairy:* Zero discharge of wastewater from the production area except during a 10-yr, 24-hr storm event. *Swine, Veal, and Poultry:* No allowance for excess discharge in case of storm events.
Copper forming	Flow-reduction measures, including recycling of solution heat treatment and annealing water, spray rinsing with recirculation of pickling rinse, and countercurrent rinsing of pickling rinse.
Electrical and electronic components	Solvent management, if applicable, through collection of used solvents for resale or contract disposal.

Point source category	Wastewater minimization or pollution prevention approach
Electroplating	Flow reduction measures such as use of countercurrent, spray, and fog rinses; avoidance of dilution; reuse of rinse tank overflow water; recovery of plating solutions or etchants through reverse osmosis, ion exchange, or evaporation; and process modification.
Explosives manufacturing	Reduction of wastewater flows through cleaning of spills, leaks, and equipment through sweeping and vacuuming; recycle of water used to transport explosive materials and to purify products; recycling cooling water; and separating process and non-contact waters.
Ferroalloy manufacturing	*Calcium Carbide:* Treatment of wet air pollution control scrubber wastewater and partial recirculation for covered furnace plants. For other types of furnaces, settling in ponds and recycle of wastewater to achieve no discharge. Plants using dry or no dust collection have no process wastewater discharge. *Electrolytic Ferroalloys:* Reduction of wastewater flow through in-plant recirculation and mechanical transport of filter residues.
Grain mills	None used.
Industrial laundries	Pollution reduction through activities such as refusal of items with free liquids, centrifuging of items to remove free liquids, steam/air stripping of volatile organics from items before washing, dry-cleaning of items before washing, change of laundering/dry-cleaning chemicals used, wash chemical addition through liquid injection system, water softening, improved housekeeping, equipment modifications, and recycling of laundry materials. Water conservation through actions such as prompt repair of leaks and faulty equipment, installation of laundering equipment that uses less water, reuse of noncontact cooling water as process makeup water, recycle/reuse of laundry wastewater before or after treatment.
Inorganic chemicals manufacturing	None used.
Iron and steel manufacturing	Water reduction measures, as applicable: Zero discharge for processes that don't generate wastewaters; wastewater disposal by coke quenching; high-rate recycle for direct-reduced ironmaking through solids removal using a classifier and clarifier, cooling, sludge dewatering, and treatment of blowdown with multimedia filtration; high-rate recycle for forging by using oil-water separation and treatment of the blowdown with multimedia filtration; emission control scrubber blowdown to coke quench stations.

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Table 7.2 *(Continued)*

Point source category	Wastewater minimization or pollution prevention approach
Landfills	Reduction of wastewater and toxic compounds is achieved through compliance with existing solid and hazardous waste Resource Conservation and Recovery Act regulations.
Leather tanning and finishing	Water use reduction.
Meat products	None used.
Metal finishing	Good management practices to prevent total toxic organics from entering the wastewater streams.
Metal products and machinery	In-process reduction of wastewater flows and pollution prevention through two-stage countercurrent cascade rinsing for all flowing rinses, centrifugation and recycling of painting water curtains; and centrifugation, pasteurization, and recycling of water-soluble machining coolants.
Mineral mining and processing	No discharge of wastewater because of no use of water in the process or as a result of recycling/reuse of the wastewater. Control of runoff, rainfall, and infiltration to reduce wastewater flows.
Nonferrous metals forming and metal powders	Reduction of wastewater flow, as applicable, through recycling contact cooling water, air pollution control scrubber liquor or turning, burnishing, and cleaning wastewaters; using dry air pollution control equipment and/or countercurrent cascade rinsing; improving housekeeping practices; improving maintenance practices to reduce water leakage; or reducing water flow by turning down flow valves. Recycling of lubricating emulsions.
Nonferrous metals manufacturing	Water use control through recycle of process water from air pollution control and metal contact cooling waste streams and other flow reductions. Zero discharge required for some subcategories, because no water is used in the process or complete water recycle is practiced.
Oil and gas extraction	Mostly zero discharge through reuse and/or recycling of wastes, fluids injection, and minimization of pollutants through reduction of oil spillage, segregation of deck drainage from oil leaks, diversion of uncontaminated rainfall, and similar measures. Solids removal (through shale shakers, high-G-force shale shakers, centrifuges, and squeeze presses) and recycling of drilling wastes.

Point source category	Wastewater minimization or pollution prevention approach
Organic chemicals, plastics, and synthetic fibers	Best management practices, such as solvent recovery, water reuse, at-the-source recovery of spills, process modifications, preheating or cooling of process wastes, sensors and alarms to warn of process upsets, and inspection and maintenance to prevent upsets, spills, or leaks.
Paint formulating	Solvents recycling when used. As applicable, in-plant controls (such as high-pressure water-washing of equipment, dry floor clean up, sealing of floor drains, or recycle of caustic rinses back into the caustic tank as make up and water rinses back into the product or rinse water) and contract hauling of non-recyclable wastes.
Paving and roofing materials (tars and asphalt)	Wastewater reuse and pollutant load reduction through practices such as use of product cooling water as white water makeup; and good housekeeping to prevent oil leaks from pump seals and packing glands and spills at loading docks, asphalt storage areas, and oxidation tower areas.
Pesticide chemicals	*Pesticide Manufacturing:* Zero discharge for several pesticide active ingredients (PAIs) based on closed loop recycle/reuse, recirculation of all process wastewater, or no use of water or of excess water in the manufacturing process. For the rest of the PAIs, pollution prevention and recycle/reuse practices. *Pesticide Formulating, Packaging, and Repackaging:* Pollution prevention to achieve zero discharge or to minimize discharges, through water conservation practices, good housekeeping, sweeping or vacuuming dry-production areas before rinsing with water, cleaning interiors of dry formulation equipment with dry carrier before water rinse; using recirculating wet scrubbers for air pollution control (if needed); reusing the rinsate of containers; or dedicating equipment to either water- or solvent-based products.
Petroleum refining	None used.
Pharmaceutical manufacturing	None used.
Porcelain enameling	*Coating Wastewaters:* Recycle all water except ball mill washout. *Metal Preparation Wastewaters:* Rinsewater reuse and flow controls, and spray or countercurrent rinsing.

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Table 7.2 *(Continued)*

Point source category	Wastewater minimization or pollution prevention approach
Pulp, paper, and paperboard	Flow reduction activities, such as increased reuse and recycle of pulp and paper machine white water through the use of gravity strainers and high-pressure, self-cleaning showers or disk savealls; paper machine vacuum pump seal water recycle; screen room closure; and/or reuse of deinking washwater after flotation clarification. Further organic load reduction through oxygen or extended delignification to reduce bleaching chemical demand; chlorine dioxide substitution for chlorine, totally chlorine-free bleaching, use of TCDD- and TCDF-precursor-free defoamers, or use of strategies to minimize TCDD- and TCDF-precursors in brown stock pulp to eliminate dioxins; effective brown stock washing; closed brown stock pulp screen room; and pulping liquor spill prevention and control.
Rubber manufacturing[2]	*Tire and Inner Tube:* Flow reduction by use of dry-type air pollution equipment or recycle of the solutions in wet air pollution equipment, elimination of soapstone solution discharges through recycling and reuse of water, and elimination of latex solution discharges through curbing and sealing of drains in the dipping area. *Synthetic Rubber:* Flow reduction options not evaluated because they may affect processing techniques or quality of the final product.
Steam electric power generating	Control on the use of chemicals as follows: (1) To reduce the total residual chlorine concentrations from chemicals used to prevent cooling tower biofouling, using no biocides, biocides other than chlorine, the minimum chlorine amount needed, or mechanical antifouling devices; (2) to reduce the amount of toxic pollutants resulting from chemicals used for cooling tower maintenance, using chemicals that do not contain toxic pollutants. Reduction of fly ash water volume by using dry transportation or recycling of fly ash water.
Timber products processing	As applicable, water volume reduction through: water reuse, minimization of water use and spray irrigation or evaporation of excess water, operation modifications, dry cleaning of spills, in-plant controls to prevent discharges from humidification, insulation of retorts and steam pipes, use of closed steaming, drying of the wood raw material before the treating cylinder, and segregation of contaminated and noncontaminated streams.

Point source category	Wastewater minimization or pollution prevention approach
Transportation equipment cleaning	Reduction of pollutant loads through such activities as maximum removal of heels before cleaning, use of dedicated tanks, use of less toxic cleaning solutions, and hot or cold water pre-rinse to remove heel and minimize contamination of the cleaning solution so it can be recycled. Water volume reduction through use of high-pressure, low-volume cleaning equipment; monitoring of water use; equipment maintenance to prevent leaks; dry cleaning for certain cargos; reuse of last rinses for the next first rinses; and reuse of other wastewater.
Waste combustors	None used.

Notes:

[1] From the U.S. EPA effluent limitations development document for each point source category. Table 6.7 presented the treatment approaches.

[2] There are other subcategories that may have different wastewater minimization and/or pollution prevention approaches.

A facility's pollution-prevention and waste-minimization efforts should be continuous rather than an isolated activity. For this type of program to succeed, specific measurable goals should be established and communicated to everyone at the facility. All successes should be recognized and publicized. Without continuous commitment and support from all levels of staff to achieve the goals of waste minimization via raw materials substitution, process modification, recycling (wastewater segregation and reuse), reclamation, and good housekeeping practices, chances for the long-term success of the program are decreased and any "significant" achievements may be only temporary. The management strategy for the control and treatment of a facility's wastes needs to be incorporated at the beginning of the plan and linked with all other components of the planning and implementation process. Benefits of a well-implemented plan include lower costs, improved product quality, increased production, improved public relations, reduced liability, and successful regulatory compliance.

Water Conservation and Recycling. Efforts to conserve and recycle water should be incorporated into a waste minimization program or initiated as a separate activity with its own specific goals. Reducing wastewater volumes via recycling, reuse, and other conservation methods may lower the pretreatment system's capital and operating costs and reduce fees for discharging to the POTW. However, simply reducing water may do little to reduce treatment costs unless higher pollutant concentrations are more efficient to treat. Increasing pollutant concentrations typically increases the risk of exceeding the system's treatment capability, resulting in discharge violations, but engineers should investigate the effect of any concentration change on the treatment process.

Water conservation alternatives include reusing cooling water as product makeup or cleanup water, collecting stormwater for noncritical water uses, using flow-restricting or water-saving devices, and recycling water in closed-loop systems. Once all internal applications for waste reuse, recycling, and conservation are maximized and implemented, environmental engineers should consider whether the treated wastewater could be used by outside contractors for irrigation, dust control, or other tasks that typically use fresh water. If the treated effluent is discharged to a POTW, engineers should consider whether any pollutants could interfere with the POTW's ability to reclaim its treated wastewater or use it for wetlands reclamation projects.

Pretreatment. Industrial wastewater may need pretreatment before discharge to a POTW for several reasons. Some industries are subject to federal or local pretreatment standards because they discharge organic or inorganic pollutants that can damage collection systems, inhibit or pass through POTW processes, or interfere with selected sludge-disposal alternatives (see Chapter 2). Other industries may voluntarily pretreat their wastewater to reduce or avoid POTW surcharges on pollutants (e.g., BOD and suspended solids). Occasionally, wastewater residuals (e.g., precious metals) may be valuable, and pretreatment systems can help reclaim them.

The type of pretreatment selected—physical, chemical, or biological—depends on wastewater characteristics, applicable pretreatment standards, and anticipated production changes that may affect wastewater characteristics (Table 7.3). Physical treatment methods primarily remove suspended solids, settleable solids, and oil and grease. Chemical treatment methods typically remove dissolved and colloidal solids, nutrients, heavy metals, and similar pollutants. Biological treatment removes biodegradable organics and nutrients.

Before selecting pretreatment options, industries must consider several factors. The U.S. Environmental Protection Agency has issued numerous pretreatment standards for specific industrial categories (both existing and new facilities) (see Chapter 6).

Table 7.3 Processes applicable to industrial wastewater treatment.

Pollutant	Appropriate treatment technologies
Biochemical oxygen demand (biodegradable organics)	Aerobic biological: activated sludge, aerated lagoons, trickling filters, rotating biological contactors, oxidation ditches, stabilization ponds, packed bed reactors, fluidized bed reactors. Anaerobic biological: anaerobic lagoons, anaerobic filters, anaerobic contact, fluidized bed reactors.
Total suspended solids	Sedimentation, flotation, screening, filtration, coagulation/flocculation/sedimentation or floatation.
Refractory Organics (COD, TOC) Nitrogen	Carbon adsorption, chemical oxidation, ammonia stripping, nitrification and denitrification, ion exchange, breakpoint chlorination.
Phosphorus	Precipitation, biological uptake, ion exchange.
Heavy metals	Membrane filtration, evaporation, electrodialysis, chemical precipitation, ion exchange.
Dissolved inorganic salts	Ion exchange, reverse osmosis, electrodialysis.
Fats, oils, and grease	Coagulation/flocculation/floatation, ultrafiltration.
Volatile organic compounds	Aeration, chemical oxidation, adsorption, stripping, liquid biological treatment, gaseous biofilters.

In addition, states and municipalities often supplement the federal standards with local pretreatment requirements. The publicly owned treatment works' National Pollutant Discharge Elimination System (NPDES) permit conditions or its treatment process characteristics may require more restrictive industrial discharge limits. The chosen pretreatment facility and its discharge must comply with all regulatory requirements. Long-term considerations also should be addressed, including provisions for more treatment in the future to meet changing regulatory requirements or the addition of modular systems to account for long-term flow variations. Sometimes field-scale pilot tests, modified production trials, or research and development must be done before a pretreatment program can be implemented.

Physical Separation. Physical separation processes typically include flow equalization, screening, sedimentation, flotation, filtration, aeration, and adsorption. Flow equalization dampens flow variation to achieve a fairly constant flow rate to the sewer system. It also dampens the concentration and mass flow of wastewater constituents, yielding a more uniform loading to the treatment plant. Flow equalization helps reduce shock hydraulic, organic, and nutrient loads and can reduce the required size of pretreatment facilities.

Screening removes coarse solids (e.g., rags or pieces of wood) and prevents damage to or clogging of downstream equipment. Manually cleaned screens work well, but cleaning them requires labor and may cause overflows because of clogging. Mechanically cleaned screens also perform well, but they may become jammed because of obstructions (e.g., bricks or pieces of wood).

Sedimentation removes suspended solids via gravity separation in a quiescent basin. Sedimentation is typically highly reliable, but the sludge collector mechanism may occasionally jam. The proper design of bottom slope and scraper blades and the appropriate number of arms will reduce this problem. Surface scum may cause odors that can be controlled by frequent removal. Short-circuiting and poor performance may occur if inlet and outlet designs are inadequate.

Dissolved air flotation (DAF) removes suspended solids by causing them to rise to the surface. One DAF process consists of saturating some or all of the wastewater feed or a portion of recycled effluent with air under pressure. The pressurized wastewater is held for up to 3 minutes in a retention tank and then released to atmospheric pressure in the flotation chamber. When exposed to atmospheric pressure, microscopic air bubbles are released and attach to oil and suspended particles, floating them to the surface where they are skimmed off as float solids. Dissolved air flotation systems are reliable, but chemical addition is often used to enhance performance. These systems require little land area, but air compressor noise must be controlled, and the sludge must be treated and receive proper disposal (Viessman and Hammer, 1985).

Filtration is a solid-liquid separation process in which the liquid passes through a porous medium to remove fine suspended solids. It is reliable and requires little land, but the backwash water must be treated, which will produce solids that require disposal.

Aeration strips volatile compounds from industrial wastewater. Diffused aeration or mechanical aeration typically are used. The aeration process is simple and typically reliable. It requires little land, and sludge is not generated in a system designed simply for aeration (not biological treatment). Proper design must ensure that offgases do not cause air pollution problems. A related process is stripping across a packed column. (For more information on air stripping and aeration, see Chapter 13.)

Adsorption accumulates a substance at the surface of a solid material (typically activated carbon), called an *adsorbent.* Carbon systems typically consist of vessels in which granular carbon is placed, forming a filter bed through which wastewater passes. Adsorption systems require little land. Under anaerobic conditions, biological activity in carbon beds may generate hydrogen sulfide, which has an unpleasant odor. Spent carbon may create a land-disposal problem, unless regenerated. However, regeneration systems are expensive and may cause air pollution. Many regeneration systems include catalytic converters to oxidize gases released during regeneration. Granular carbon systems often require pretreatment to reduce solids loadings to the beds. Powdered carbon may be used instead of granular carbon, but typically it is fed to wastewater using chemical feed equipment rather than being contained in a bed or column (Weber, 1972, and Corbitt, 1998).

Membrane filtration systems include reverse osmosis, electrodialysis, and ultrafiltration. Reverse osmosis is the pressurized transport of a solvent across a semipermeable membrane that impedes passage of solute (pollutants) but allows solvent (typically water) flow. Membrane fouling may result from the deposition of colloidal or suspended materials in the wastewater, so pretreatment typically is required to avoid frequent cleaning. Chemical recovery and wastewater reuse are possible.

In electrodialysis (a physical-chemical process), an electric current induces partial separation of wastewater components. The separation is achieved by alternately placing cation- and anion-selective membranes across the current path. When current is applied, the cations pass through the cation-exchange membrane in one direction, and the anions pass through the anion-exchange membrane in the other direction. Chemical recovery and wastewater reuse are possible, but power costs are typically high and membrane fouling may be a problem.

In ultrafiltration, wastewater is pumped past a membrane. Under the applied pressure, water and most dissolved constituents pass through the membrane pores, while larger molecules (e.g., colloids and emulsified oils) are retained. The process typically has high capital and operations and maintenance costs, and membrane fouling may be a problem. However, it seems to be a reliable technology for certain applications. (For more details on physical separation processes, see Chapter 5.)

Chemical Pretreatment. Chemical pretreatment processes typically include pH neutralization, chemical precipitation, oxidation-reduction, and ion exchange. Neutralization involves adding acids or bases to wastewater to adjust the pH to an allowable range, typically pH 5 to 9. Acidic wastewaters typically are neutralized with lime [$Ca(OH)_2$], caustic soda ($NaOH$), or soda ash (Na_2CO_3). Slaked lime is often used because it is less expensive than NaOH and Na_2CO_3. Sodium hydroxide is also sometimes preferred because of its lower maintenance requirements and ease of use. Alkaline wastewaters are typically neutralized via sulfuric acid, hydrochloric acid, or carbon dioxide. Neutralization is relatively simple and reliable but typically requires automatic feed equipment, pH monitors/controllers, and multiple mixing tanks. To reduce chemical use and costs, mixing of alkaline and acidic wastewaters should also be considered.

Chemical precipitation is another chemical treatment method often used to treat industrial wastewater. Chemical coagulation (rapid mixing) and flocculation (slow mixing) are used to precipitate dissolved wastewater contaminants and form floc particles, which settle readily in sedimentation basins. Chemical precipitation can effectively remove heavy metals and phosphorus from industrial wastewater. However, it may generate large amounts of inorganic sludge that must be dewatered and landfilled. If the sludge contains toxic levels of metals or is otherwise hazardous, it must be disposed of as a hazardous waste. In addition, close operator attention and rigorous cleaning are necessary to maintain a mechanically reliable chemical feed system (U.S. EPA, 1980; Viessman and Hammer, 1985; and Weber, 1972).

Oxidation-reduction is used occasionally to remove pollutants from industrial wastes; for example, to reduce chromium from its hexavalent form to its trivalent form before chemical precipitation. Ozone oxidation also may be used to remove dissolved organics and cyanide during pretreatment, but alkaline chlorination of cyanide is a more common practice than ozone oxidation. Hydrogen peroxide or potassium permanganate may also be used for some industrial wastes. Oxidation-reduction systems have a high mechanical reliability. Offgases must meet air pollution requirements, however, and oxidation-reduction may not be economically attractive in some cases (Eckenfelder, 1982; Weber, 1972).

In ion exchange, ions held by electrostatic forces to charged functional groups on a solid surface are exchanged for ions of similar charge in the wastewater. Ion exchange may be used to remove heavy metals, ammonia, and radioactive pollutants. The process is reliable and relatively easy to operate if automatic controls are used. Ion-exchange systems require periodic monitoring, inspection, and maintenance, and the wastewater may need pretreatment to prevent resin fouling. Scaling can occur when wastewaters high in magnesium or calcium are treated. In addition, disposal of waste brine and rinsewater is required. Recovery of valuable chemicals may be possible (Cherry, 1982; U.S. EPA, 1980; and Weber, 1972).

Biological Pretreatment. Biological pretreatment may be used to reduce BOD or suspended solids loads, degrade potentially toxic organic compounds, or reduce nutrient levels in industrial wastewater. Biological systems include activated sludge, lagoons, trickling filters, rotating biological contactors, and anaerobic processes. However, if the wastes are compatible, a POTW can treat biodegradable wastewater more cost-effectively than several biological pretreatment systems.

The activated sludge process uses an aeration tank in which wastewater and microorganisms are mixed. The microbes biooxidize the waste and synthesize new cells; the biological solids are then removed by final settling. Several modifications of the activated sludge process are available. The one selected should best meet the pretreatment requirements. The process typically is reliable, but sludge disposal, aerosol and odor potential, and energy consumption may cause problems. Skilled operators are required for optimum performance (Reynolds, 1982; U.S. EPA, 1980).

Aerated lagoons are typically 2- to 4-m (6- to 12-ft) basins that function similarly to the activated sludge process but without recycle. In addition to being reliable, aerated lagoons require only basic wastewater operator skills. Air emissions from the lagoons must meet air pollution requirements, however, and the potential effect on groundwater from lagoon seepage must be evaluated in design and operations. A liner may be required (Metcalf and Eddy, 1991). Facultative lagoons are typically 1- to 2.5-m-deep (3- to 8-ft-deep) basins in which wastewater is stratified into an aerobic surface layer, a facultative layer, and an anaerobic bottom layer. Facultative lagoons are also reliable and require basic operator skills. Like aerated lagoons, air and groundwater discharges must be evaluated and appropriately addressed.

Trickling filters consist of a fixed bed of rock or plastic media over which wastewater is distributed for aerobic biological treatment. Biological slimes that form on the media assimilate and oxidize substances in the wastewater. The biomass repeatedly falls off the media (sloughing) and must be removed in a settling tank following the trickling filter. Although not as efficient as activated sludge systems, trickling filters are typically reliable. However, they have limited flexibility, are susceptible to upsets, and may have difficulty operating in cold weather (Metcalf and Eddy, 1991; Reynolds, 1982).

Rotating biological contactors are fixed-film reactors typically consisting of plastic media mounted on a horizontal shaft in the tank. As wastewater flows through the tank, the media, approximately 40% immersed, are slowly rotated. Biomass on the media assimilate (oxidize) the organics. Excess biomass is stripped off the media by rotational shear forces and then removed during final settling. Rotating biological contactors perform well and reliably unless organic loads are high or temperatures are below 13° C (55° F). Odor may be a problem, and sludge treatment and disposal is required. Additionally, facilities with large flows may incur high capital and operating costs.

A packed-bed reactor consists of a reactor packed with a medium to which the microorganisms can become attached. Wastewater enters the bottom of the reactor through an appropriate inlet chamber. Air or pure oxygen necessary for the process is introduced with the wastewater.

Fluidized beds use a solid support medium (e.g., activated charcoal or sand) that is suspended in a high-rate upflow column. The high flow rate required to suspend the support medium is augmented by applying a high effluent recycle rate. These reactors remove low concentrations of relatively refractory organics. A great deal of study has gone into growth augmentation by adding small amounts of highly degradable organics to allow for treatment of the refractory waste fraction. Aerobic fluidized beds are typically operated using external oxygenation (pure oxygen) of the recycle water.

Anaerobic processes include contact, filters, fluidized-bed reactors, and lagoons. Anaerobic contact provides for separation and recirculation of seed microbes, thus allowing retention periods of 6 to 12 hours. The anaerobic filter promotes growth of the anaerobes on a packing bed and can be designed for upflow or downflow operation. For the fluidized bed reactor process, wastewater is pumped up through a sand or plastic bed, which supports microbial growth; effluent recycle is practiced. Anaerobic lagoons are typically used to pretreat meat-packing and other high-strength organic wastewaters. Anaerobic processes typically are reliable, but odor problems and process upsets may occur (Eckenfelder, 1989). Preference depends on waste strength, temperature, wastewater chemistry, and other factors (Speece, 1996).

Cross-Media Pollutants. When selecting pretreatment options, cross-media pollutant generation must be considered. Many pretreatment facilities generate sludge that requires handling, treatment, and disposal. The treatment and disposal of sludge, especially if it has hazardous waste characteristics, can be expensive and cumbersome considering the multitude of sludge and hazardous waste regulations at the local, state, and national levels. Some pretreatment processes may result in air emissions (e.g., offgases from air stripping of certain industrial wastewaters) that must comply with applicable air pollution standards. Other processes (e.g., ion exchange, ultrafiltration, and reverse osmosis) result in reject streams requiring disposal.

Safety Considerations. Selecting pretreatment options also involves safety considerations. If incorrectly installed, inadequately maintained, or improperly used, electrical and mechanical equipment can cause electrical shock or other bodily injury. Wastewater gases and pathogens can also be health hazards. Chemicals (e.g., chlorine, sulfides, or ammonia) in the wastewater or added during treatment can create noxious vapors or cause acute or chronic injuries to plant personnel or the public if control measures are inadequate.

Offsite Pretreatment. When formulating pretreatment strategies, offsite alternatives should also be considered. Offsite pretreatment typically means removing all or part of a facility's wastewater to another location and pretreating there so it is suitable for disposal. An offsite pretreatment facility may or may not be a RCRA hazardous waste treatment facility; it depends on whether the wastes accepted meet RCRA's definition of hazardous and whether the facility is RCRA-permitted. Typically, the offsite facility is nearby and designed to treat specific types of wastewater from several local firms (e.g., plating shops or printed circuit facilities) at a lower cost than comparable treatment by the facilities generating the wastestreams. Offsite treatment can eliminate the need to install a costly pretreatment system for a relatively small wastestream, but they are typically only conveniently and economically available in certain metropolitan areas and may be subject to strict regulatory requirements that can involve conditions and constraints on the wastewater-generating facility.

Residue Management (Disposal). Industry will always generate residues that are environmentally irreducible. Many companies directly discharge to a POTW, or provide some pretreatment before discharge to a POTW. Larger companies may handle waste residues in-plant. Contract firms are also available that collect and recycle certain metals, construction materials, oils and greases, and industrial solvents. The costs and short-term and long-term risks must be considered by the waste-minimization team and corporate managers. Some of the more common disposal methods include incineration, landfilling, landfarming, deep-well injection, storage lagoons, or discharge to a receiving stream.

PERIODIC WASTE MINIMIZATION ASSESSMENTS. The goal of any industrial wastewater pretreatment management strategy is to achieve regulatory compliance cost-effectively by implementing waste minimization, wastewater recycling, water conservation, and wastewater treatment via the most appropriate treatment processes. To determine whether this goal is being achieved, the strategy must include a monitoring component that provides information on the strategy's effectiveness and allows for necessary corrections. The primary purpose of monitoring is to ensure and verify that compliance with regulatory requirements (e.g., discharge permit conditions or categorical discharge standards) is consistently met.

However, the results from a properly designed discharge monitoring program (e.g., adequate testing frequency, rapid analysis turnaround times, and analysis for the appropriate parameters) can also provide information on the pretreatment system's efficiency and help improve its cost-effectiveness by offering process control data for reducing operating costs (e.g., chemical and power use rates).

Beside providing economic benefits, a good monitoring program helps assess the effect of process or raw material changes or other waste-minimization efforts, detecting potential system upsets that could cause discharge violations or slug discharges, and estimating loading surcharges that may be imposed by the receiving POTW. Monitoring incoming wastewater also allows for better process control, particularly in processes involving chemical addition or activated sludge. Industrial facilities are increasingly using statistical process control techniques to ensure compliance.

Wastewater effluent monitoring can be performed by either the industry (self-monitoring) or regulators. Facilities with limited laboratory capabilities may hire a contract laboratory for both sample collection and analysis. Regulators can require industrial self-monitoring to meet reporting requirements for baseline monitoring reports or periodic reports on continued compliance required by federal regulations, as well as to ensure that the pretreatment system is operated properly.

The results of any self-monitoring tests for regulatory purposes, whether performed in-house or by a certified laboratory, must be submitted to the regulator for review. Any violations may be subject to enforcement actions. Any self-monitoring samples collected for regulatory purposes in the United States must be analyzed in accordance with U.S. EPA-approved procedures. Informal self-monitoring is sometimes performed in-house to facilitate the pretreatment system's operations and check on its response to operating changes. This can be done via test kits or other rapid analyses, as long as the results are accurate. Rapid self-monitoring via test kits or onsite analytical instruments can provide a quick indication of pretreatment system upsets or problems. This feedback allows corrective measures to be implemented—including recycling or storing noncompliant effluent until the pretreatment system is operating properly again to prevent violations.

Results from self-monitoring via non-approved U.S. EPA methods do not have to be reported to the POTW unless specifically requested, and they do not count toward compliance determinations. However, all analytical discharge or effluent results obtained using U.S. EPA-approved methods become part of the compliance history and must be reported. The facility is subject to enforcement if these results violate the limits.

An effective monitoring system is integral to the pretreatment system design and should be planned at the conceptual stage. Including properly designed monitoring points and equipment as part of the total system design can significantly reduce future monitoring costs and improve pretreatment operations.

Compliance monitoring by a POTW or other regulator is the second type of monitoring most industrial facilities face. This monitoring can either be scheduled or unannounced. A publicly owned treatment works may require an industrial facility to install appropriate monitoring or sampling points that are continuously accessible to the POTW so it can set up sampling equipment or obtain grab samples unannounced or with short notice.

Finally, if spills, slug discharges, or chronic violations occur, a POTW may initiate a "demand" monitoring program against a facility. Once the problem has been resolved and continuous compliance is achieved, the demand monitoring program is typically rescinded and a normal monitoring schedule is resumed.

ASSESS EFFECT OF PROCESS CHANGE ON PRODUCT QUALITY AND QUANTITY. Pollution prevention may directly or indirectly focus on improving the quality or quantity and protection of downstream processes. For example, adding more efficient oil/water separation in parts-washing systems typically increases the washing efficiency, production rate, and enables better coating efficiency in downstream processes. To continually improve the target process, monitoring methods and evaluation techniques must be developed to track any effect on production and make periodic progress reports to managers. This task is best allocated to the production line manager, with feedback directed to the environmental engineer of record. Remember that environmental changes that decrease the product quality or manufacturing efficiency often become orphaned by managers.

CREATE A COST-ALLOCATION SYSTEM. In developing a management strategy to control industrial wastewater from a facility, it is important to develop a comprehensive cost analysis for the different options under consideration. Although cost figures strongly depend on local conditions and regulatory requirements, certain elements should be incorporated into the facility's management strategy before selecting a pretreatment option. Standard engineering methods for estimating costs should be followed. One method often used for evaluating waste treatment options (or evaluating waste contributions to the costs of a new production facility) is minimizing the present worth of options (Haas and Vamos, 1995; Allen et al., 2002).

A pretreatment system's performance and treatment capability will largely be driven by the regulatory requirements imposed on the discharge. Sometimes, however, when compatible pollutants are being treated, it may be more cost-effective for the publicly owned treatment works (POTW) to treat the wastewater even though a higher user fee is charged than for the industry to pretreat its wastewater and discharge lower pollutant loads to the POTW.

The costs that are well known or easily accessed are called "Tier 0" costs (Haas and Vamos, 1995; McHugh, 1990). These include determining the pretreatment system's capital cost, operating costs (e.g., chemicals, energy, labor, compliance, and residual disposal), and insurance and maintenance costs so the system remains in compliance. Improved production rates, improved quality, or higher recovery of materials must be considered at this point.

When developing a cost analysis, it is important to consider the many variables and factors in the pretreatment process, most of which will change over the system's life-cycle. An estimate of these changes, as well as the effect of any anticipated regulatory changes, residual disposal restrictions, and other applicable considerations should be incorporated into the cost analysis and, ultimately, the management strategy. All reasonable benefits must be considered. Benefits associated with the process are called "Tier 1" costs (Haas and Vamos, 1995; McHugh 1990). These include reductions in cost reporting, waste manifest requirements, wastewater surcharges, OSHA compliance costs, lower testing costs or monitoring costs. "Tier 2" costs are more subjective; they include the costs of future repairs, the risk of becoming a Superfund site, or the cost of litigation. "Tier 3" costs are even more subjective; they include public goodwill, shareholder value, or management risks.

Cost databases for industrial pretreatment are limited because of the almost infinite variety of industrial wastestreams. This variation makes it difficult to develop a large database of treatment costs. There are, however, sources of information on the more common wastestreams that can be used as a starting point for the estimates, a check on order-of-magnitude costs, or a rough comparison of treatment options. In addition, sources of information typically exist as case studies for specific wastestreams. However, these case studies typically are limited in the number of technologies compared. Industrial associations and trade groups (e.g., the American Petroleum Institute or the American Chemical Council) are also a good source of information on specific wastestreams, because they may track and record these data for their members. A limited number of studies are available for several production facilities (Ditz et al., 1995). Current and accurate cost and performance data must be used because technologies and treatment costs constantly change.

As discussed previously, many of the early environmental remedies were not well cost documented, resulting in huge hidden costs to the various industries. Now that pollution prevention is becoming more popular than pretreatment, extra care should be taken to properly isolate environmental costs (and benefits) and tie them directly to the product line. Minimizing production costs is a very attractive method of justifying pollution prevention. Unless all the costs are well understood, there is no method to take full credit for positive changes.

ENCOURAGE TECHNOLOGY TRANSFER BETWEEN OPERATING DIVISIONS. Technology transfer can occur on several levels. Company production may occur in several areas of the country, and similar solutions to common problems may be directly transferable. Large corporations often dedicate internal technical meetings that bring technical experts to discuss successes and failures at the various plant sites. Within one plant site, differing production lines may generate complementary or antagonistic wasteloads and some optimization of treatment processes may be gained by scheduling waste discharges. The waste treatment operators should always be made aware of production line changes that may affect any treatment or recovery operations.

PROGRAM EVALUATION, FEEDBACK, AND INCENTIVES FOR IMPROVEMENT. Each program that is implemented should be backed up with sufficient monitoring and cost analysis so the benefits (or lack thereof) are tracked. Successes and failures should be transmitted by internal memorandum, meeting minutes, or company newsletter to corporate management. Many of the simplest, most effective pollution prevention measures are generated by the production-line operators and many companies offer awards or bonuses for good ideas generated on the plant floor. Continual improvement should be the corporate philosophy of all environmental programs.

The following case study shows all of the important elements of good pollution prevention management (i.e., a clear problem statement, a solid management team, a means of measuring success, and communication of success through solid economic presentation). The Eastman Chemical Company facility at Kingsport, Tennessee, is a large producer of bulk organic acids, alcohols, cellulose esters, and PET bottle polymer. During the past decade, this facility reduced TRI emissions by 74% and EPA 33/50 Initiative chemical releases by 63%. However, these efforts did not result in a similar reduction in wastewater load (Barber and Bullard, 2002).

Designed to meet the 1984 RCRA requirements, the activated sludge plant with a rated capacity of 90 800 kg/d (200 000 lb/d) of BOD and 94 600 m^3/d (25 mgd) and a sludge-production rate of 59 000 dry kg/d (65 dry ton/d) was commissioned in 1988 (Johnson et al., 1988). By 1995, the BOD load was consistently 105 700 kg/d (233 000 lb/d) with a flow of 104 000 m^3/d (27.5 mgd) and a sludge production of 68 100 dry kg/d (75 dry ton/d). The constant high sludge production stressed the clarification, dewatering, and sludge incineration capacities beyond the limits. Before the current era of waste minimization, the normal solution for such an overload would have been plant expansion to increase the waste treatment capacity. An engineering study was performed, and it was determined that the costs of plant expansion ($60 MM) and improved sludge dewatering and disposal ($40 MM) were cost-prohibitive.

To overcome this challenge, a companywide management team was established to focus on permanent total organic carbon (TOC) load elimination, develop a long-range TOC philosophy for future products, and to focus on waste treatment improvements. A TOC reduction goal was established to limit the load to the waste plant at an average of 45 360 kg/d (100 000 lb/d) of TOC and a mass ratio of TOC generated to product sold of 0.0142.

Wasteload assessment data were used to pinpoint production buildings generating the highest loads, and many waste reduction programs were identified that could be implemented for little or no cost. Other reduction plans were identified that required some capital, while still others required intensive capital. Projects were evaluated on a net present value basis in three categories: those that exceeded 15%, those that fell between 0 and 15%, and those with negative return. From 1996 to 1997, most of the high-valued projects were completed with a net result of 6% drop in TOC load to the wastewater plant. At the same time, the overall plant production increased by 8%. As a measure of success, the team used the ratio of the mass of waste generation to the mass of product created, which fell initially from 0.0183 to 0.0159.

During the next 2 years, a capital improvement program of $1 MM per year was established to attack the mid-level and negative return projects. The team set priorities based on the expected TOC mass reduction per capital dollars expended. By 1999, the program was discontinued based on successfully exceeding the goal set for waste generation (0.0142) by reaching a ratio of 0.0131. During the same 4-year period, the wastewater treatment personnel focused on producing less biomass by changing from a constant MLSS activated sludge program to an SRT control program and by finding ways to remove more water from the waste sludge. As a result of the program, the overall plant load decreased 24% on a TOC basis and sludge production decreased 33%. The annual cost savings of $6 MM, based solely on wastewater treatment plant costs without consideration of production side material recovery or material savings, far exceeded the capital investment of $1 MM per year over the final 2 years of the program.

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Chapter 8

Flow and Load Equalization

Equalization is the process by which operating parameters (e.g., flow, suspended solids and other pollutants, and temperature) are made more uniform over a given time frame (typically 24 hours) to reduce their downstream effects. While the timing of these spikes depends on the situation, a 30- to 60-minute interval is common. This could be made faster or slower, depending on the specific flow/load/temperature variation, sampling ability, and on the measurement accuracy available.

CAPITAL COST AND OPERATIONS BENEFITS OF EQUALIZATION

When considering equalization in industrial pretreatment, the designer should include capital cost savings and operating stability as primary benefits. In situations where high flow peaks are common, equalization reduces the size of virtually all downstream systems in which flow rate is a design factor. These include process pumps, piping and valves, biological and chemical reactor vessels, activated carbon vessels, sand filters, and chemical feed systems. In situations where pollutant loadings spike, equalization will normalize these peaks, with the same impacts on reducing the size and cost of downstream facilities.

The principal operating benefits of equalization are stable operations and consistent effluent quality. Hydraulic spikes can lead to:

- Solids carryover in settling basins and DAF units;
- Unpredictable solids breakthrough in sand filters;
- Poor BOD and nitrogen removal and solids washouts from biological processes;
- Poor organics removal in granular activated carbon because of insufficient contact time;
- Poor process control in chemical reactions because of the lack of chemical feed mixing and reaction times.

These are just a few examples of the effect of hydraulic spikes on industrial processes. In addition to operating effects, equalization will reduce the size and capital costs of downstream processes by reducing the peak flow rates that must be handled.

Equalization also reduces pollutant spikes. Pollutant load spikes (e.g., suspended solids; fats, oils and grease (FOG); ammonia; organic compounds; heavy metals; acids and alkalis; and temperature) can cause the following problems in industrial pretreatment operations:

- High effluent solids and FOG levels from settling basins and DAF units because of high influent solids loadings;
- Failure of biological systems because of low dissolved oxygen, toxic conditions, organic overload, unacceptable pH and temperature levels;
- Effluent violations because of upstream process failure.

Equalization is often required in industries with manufacturing or production variations that result in wastewater flow and load variations. These variations cause serious difficulties in the performance of downstream treatment processes, so they must be dampened. Typical difficulties caused by spikes in flow and pollutant load—say, greater than 25% of the average daily value—include:

- Hydraulic overload of downstream pumping and process units;
- Solids carryover from sedimentation and flotation units;
- Difficulties in maintaining stable chemical feed systems and resulting unit processes;
- Dissolved oxygen deficits in biological processes;
- High differential pressure across filtration units, necessitating premature backwash or the use of more units; and
- Less contact time across activated carbon processes, reducing removal efficiency.

Industries that often require equalization include dairies, food processors, soft drink bottlers, chemical and petrochemical plants, pharmaceutical manufacturers, and industrial laundries. Large metal finishers with multiple streams at varying pH levels often use equalization to neutralize the streams before treatment.

The need for flow equalization is determined primarily by the wastewater's potential effects on the industrial pretreatment facility or the POTW. This effect is determined by two key components:

- The variability of the operating parameters to be equalized (e.g., flow rate, pH, BOD, COD, ammonia, and toxicity); and
- The volume of the flow being discharged.

Defining the need for flow equalization requires sufficient background information on these two factors, the relative cost of constructing and implementing effective flow equalization, and the anticipated cost savings by reducing the size of downstream treatment processes.

This chapter provides information on the proper application, design, and operation of equalization processes used to pretreat industrial wastewater.

TYPES OF EQUALIZATION PROCESSES

There are three basic equalization processes:

- Alternating flow diversion,
- Intermittent or off-line equalization, and
- Completely mixed on-line equalization.

These processes can vary from unmixed to completely mixed, depending on the constituent to be equalized or controlled. For example, hydraulic equalization of flows without solids would not normally require mixing. Flows with significant levels of suspended solids, temperature variations, or pH variations would benefit from mixing.

ALTERNATING FLOW DIVERSION. The alternating flow diversion system uses two or more basins (Figure 8.1). This approach is designed to collect the total effluent flow in one basin for a given period (typically 24 hours), while a second basin is discharging. The basins successively alternate between filling and discharging. The off-line basin's volume and pollutant characteristics vary throughout the fill process. Mixing should be provided so when the off-line basin is ready for discharge, the contents have constant pollutant levels as the basin empties.

This type of equalization is often used with sequencing batch reactors (SBRs) when two reactor basins are used. While this system provides a high degree of equalization, the land requirements and capital costs typically prohibit its use in industrial applications, except for two-basin SBR systems.

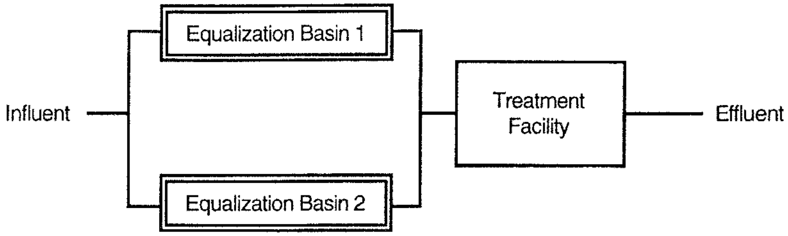

FIGURE 8.1 Alternating flow diversion equalization system.

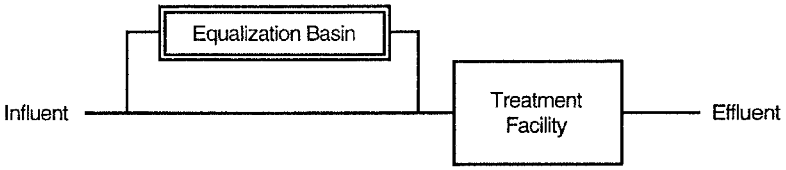

FIGURE 8.2 Intermittent flow diversion system.

INTERMITTENT FLOW DIVERSION. The intermittent flow diversion system is designed to allow any significant variance in wastewater parameters to be diverted to an off-line equalization basin for short periods (Figure 8.2).

The diverted flow is treated or bled back into the normal wastewater stream at a controlled rate. The rate at which the diverted flow is returned to the main stream depends on the diverted wastewater's volume and variance, and the level of treatment provided. Typically, the basin's contents would be sampled before discharge to determine the rate at which the basin can be emptied into the main process stream without harmful effects.

This type of equalization may be used when toxic or difficult-to-treat flows are occasionally expected because of certain plant operations. Industries that use this type of equalization include those with scheduled maintenance periods, refineries, metal-finishing operations with cyanide or hexavalent chromium batch operations, and food and dairy operations during clean-in-place operations.

High capital costs and land requirements make intermittent or off-line equalization unacceptable to many industries.

COMPLETELY MIXED EQUALIZATION. The completely mixed equalization system is designed to completely mix a single flow or multiple flow streams combined at the front end of the wastewater treatment facility (Figure 8.3). The

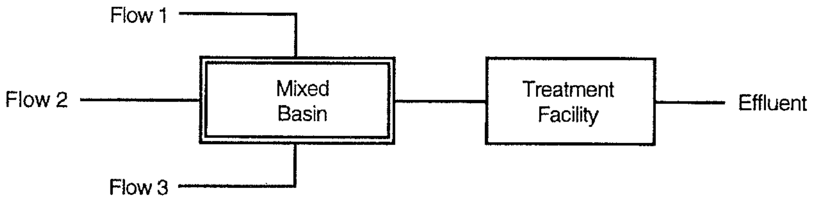

FIGURE 8.3 Completely mixed combined flow system.

equalization basin is on-line and receives flows continuously. This type of equalization is most often used by industry.

Completely mixed equalization can be used to reduce variances in each stream by thorough mixing with other flows. This system assumes that the flows are compatible and can be combined without creating more problems. This must be determined before using this system. For example, a metal-finishing operation should not equalize cyanide wastewater with acidic rinse waters because toxic hydrogen cyanide gas would be generated. Instead, the cyanide waste should be segregated and treated first.

One factor to be stressed in the design of this equalization process is ensuring that sufficient equalization capacity is actually provided. This is highlighted in an example of two different pumping controls in the same 750-m^3 (198,000-gal) equalization tank (Figure 8.4).

In Situation A, with the pump start control set at elevation 590, all volume above the pump-start level represents *live storage*—the storage available when the influent flow rate exceeds the effluent flow rate. In that case, the level rises at a rate of the difference in the inflow and outflow rates. All storage below the pump-start (300 m^3) is *dead storage*—storage that does not handle higher inflows than can be pumped out of the tank by the existing pumps.

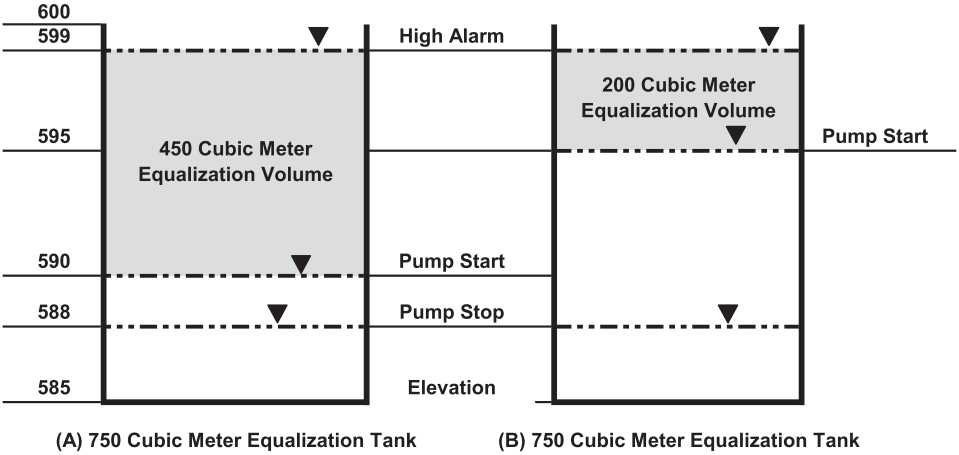

FIGURE 8.4 The pump placement's effect on capacity in a completely mixed equalization tank.

In Situation B, with the pump start controls set higher in the same tank, the *live* storage volume available to equalize influent flows is now reduced to 200 m^3. All storage below the pump-start (550 m^3) is dead storage, unavailable to equalize influent flows.

So, within an effluent pump's suction requirements, lower pump-start elevations maximize a tank's equalization capacity.

DESIGN OF FACILITIES

The design of equalization facilities begins with a detailed study to characterize the nature of the wastewater and its variability. This project team also should gather data on both flow and all pollutants of consequence.

DATA COLLECTION. The most significant variable when designing equalization facilities is the mass flow rate (flow × concentration). The project team must collect data on both flow and pollutant concentration (BOD, COD, etc.) on a time-series basis. Previous studies have indicated that these data tend to be normally distributed (i.e., most values are close to the average, and few are at the extremes), so the average of the sampled flows is a reasonable estimate of the true average mass flow. A safety factor is then applied to this value to provide for the extremes.

One exception to this approach is the equalization of waste streams with varying pH levels. Equalizing pH does not lend itself readily to mass balance calculations, because pH changes as functions of the pH levels of the combined streams and their respective alkalinities. So, more laboratory titration studies are recommended to estimate the effect of equalization on pH.

When developing flow and load data for equalization design, the team should collect at least two operating cycles to ensure that the data are representative. For example, if a dairy has two 8-hour production shifts and one 8-hour cleanup shift, the team should collect at least 2 days (48 hours) worth of data.

The data-collection intervals should be small enough to have a reasonable probability of measuring peak or minimum values. Hourly sampling via a flow meter and a flow-proportioned composite sampler is typical. If seasonal considerations are important, at least one sampling program should be conducted during each season, if possible. (Sometimes a design project's deadline prohibits this.)

Once a sampling program is completed, any anticipated changes in production, manufacturing techniques, or scheduling must be superimposed on the data, so the design is flexible enough to meet anticipated variations. These considerations, as well as economic and competitive uncertainty, require that a safety factor be applied to the final equalization design (see the design example in the next section).

ALTERNATING FLOW DIVERSION. Because the alternating flow diversion system is intended to hold the total flow for a fixed period (say, 24 hours), its design is based strictly on flow. Design criteria then are based on the average flow and its variability for the given timeframe.

For example, consider an industrial facility with the total daily flow and pollutant profile given in Table 8.1. Assuming that the 7-day period is the facility's operating cycle, the equalization basin can be designed using these data and a safety factor of 20% of the average weekly flow. The 7-day period assumes that the equalization facility can be operated everyday, although there is no process flow on 1 day. To express this in a general equation, the following should apply:

$$V_t = (Q)(T)(1+ SF) \tag{8.1}$$

Where

V_t = volume of each equalization basin (m^3);
Q = average flow rate (m^3/d) = 171;
T = equalization period (days) = 1; and
SF = safety factor (%) = 20%.

Each equalization basin would be designed to hold 205 m^3 (54 160 gal).

When evaluating the risk that a given flow or load will exceed the average daily flow, the project team may calculate the standard deviation using a standard statistics textbook or spreadsheet. The usefulness of this approach in predicting short-term variations in flow and load may be limited in industrial pretreatment applications by the lack of short-term flow and load data.

INTERMITTENT FLOW DIVERSION. Intermittent flow diversion systems are more complex because the project team must consider the variance of the pollutants to be diverted, the average length of the variance, and the discharge rate back to the system. Each factor must be evaluated with respect to its effect on downstream processes, especially if they are biological systems. This type of equalization system is best used when variances are easily detectable, infrequent, and could dramatically affect downstream processes (e.g., phenol levels in effluent).

The following steps should be applied to the system design:

- Step 1: Determine the frequency and duration of the variance to be diverted (this will allow design of the equalization basin).
- Step 2: Calculate the diverted flow's controlled release rate that will maintain normal operations.
- Step 3: Use the diverted volume to calculate the surge basin's volume so continuous flow to the treatment facility can be maintained.
- Step 4: Verify that the equalized flow meets desired discharge limits.

Data collection and system profiling are the keys to effectively designing this type of equalization system. An effective system is automated based on on-line monitoring of the stream, with diversions as necessary. Three examples of this technology are pH sensors to monitor for pH excursions, on-line gas chromatographs to monitor phenol excursions, and conductivity sensors to monitor total dissolved solids. Wide variations of these and other parameters can substantially damage biological systems or receiving waters (especially if only primary treatment is used).

In Table 8.1, the phenol levels vary substantially from day to day because of variances in plant operations. So, it may be necessary to divert flow from this facility to prevent permit violations and bleed the diverted flow back as the concentrations allow.

The phenol levels in Table 8.1 are 24-hour composite samples; the discharge limit is 500 μg/L. Further analysis of individual samples indicated that the problem was generated during two 3-hour periods over the course of the day (between 3:00 and 6:00 p.m. and between 11:00 p.m. and 2:00 a.m.), when the flow rate also increased to 0.250 m^3/min.

So, the total volume to be diverted is:

$$V = QTfk \tag{8.2}$$

Where

V = volume of flow to be diverted per time period (m^3);
Q = flow rates diverted (m^3/min);
T = time of diversion (hours);
f = frequency of diversion (number/day); and
k = conversion constant for unit (min/hr).

Table 8.1 Industrial facility daily flow profile.

Day of month	Total flow (m^3/d)	Phenol concentration ($\mu g/L$; ppb)	Phenol mass (kg/d)
1	350	2000	0.70
2	225	2750	0.62
3	200	3250	0.65
4	240	2500	0.60
5	300	2250	0.68
6	50	100	0.01
7	0	0	0
Average daily	171	1836	0.41
Minimum	0	0	0
Maximum	300	3250	0.70

Therefore,

$$V = (0.250\ \mathrm{m^3/min})\ (3\ \mathrm{h})\ (2/\mathrm{d})\ (60\ \mathrm{min/h})$$
$$V = 90\ \mathrm{m^3/d}$$

The controlled discharge rate can then be established as

$$f_c = V/Tk \tag{8.3}$$

Where

f_c = controlled discharge rate (m^3/min);
V = volume diverted (m^3);
T = time period for return (hours); and
k = conversion constant for unit (min/hr)

Therefore,

$$f_c = (90\ \mathrm{m^3}/24\ \mathrm{h})\ (1\ \mathrm{h}/60\ \mathrm{min})$$
$$f_c = 0.063\ \mathrm{m^3/min}$$

The equalization basin's volume can now be calculated. It was determined that 90 m^3 of the total flow will be diverted and fed back to the stream at a constant rate. So, the average flow for the remaining 18 hours is $(170 - 90) = 80$ m^3, or 0.056 m^3/min on a 24-hour basis.

To maintain this flow for the 6-hour diversion period, the surge basin must be large enough to hold the volume for the diversion time frame (6 hours in this case) at the average flow.

The volume is calculated as follows:

$$V = QT\text{k} \tag{8.4}$$

Where

V = volume of surge tank basin (m^3);
Q = average flow rate without diversion flow (m^3/min);
T = diversion time period (hours); and
k = unit conversion factor (min/hr).

Therefore,

$$V = (0.0.056\ m^3/min)\ (6\ h)\ (60\ min/h)$$
$$V = 20.16\ m^3$$

The diverted and mainstream flows can be recombined via in-line or flash mixing just before the downstream processes. The total combined flow (Q_T) would be:

$$\begin{aligned} Q_T &= Q_A + Q_c \\ &= 0.063\ m^3/min + 0.0.056\ m^3/min \\ &= 0.119\ m^3/min \end{aligned} \tag{8.5}$$

Where

Q_{A} = average flow rate without diversion (m^3/min) and
Q_c = controlled discharge rate (m^3/min).

COMPLETELY MIXED COMBINED FLOW. The completely mixed, combined flow equalization system is designed to address the variability expected when multiple flows from different sections of the plant combine, often generating impulse or step input changes to the wastewater treatment facility. This is the most common equalization process. This system continuously trims flow and load peaks, as well as changing operating parameters more gradually to optimize downstream processes.

The equalization basin's volume (V_e) is determined based on how changes in operating parameters will affect downstream systems. It is calculated as follows:

$$V_e = (\Sigma f_i)\, T_e\, k \tag{8.6}$$

Where

V_e = equalization volume (m^3);

f_i = individual flow rates (m^3/min);

T_e = equalization time (hours); and

k = conversion factor for units (min/hr).

If, for example, three flows enter the equalization basin at 1.98, 0.567, and 0.189 m^3/min, respectively, and the desired equalization time is 4 hours, then:

$$\begin{aligned} V_e &= \Sigma\,(f_1 + f_2 + f_3)\, T_e\, k \\ &= (1.98 + 0.567 + 0.189)\,(4\text{ h})\,(60\text{ min/hr}) \\ &= 656.6\text{ m}^3 \end{aligned}$$

Then, the relative change in each operating parameter can be calculated by using the formulas in the following section and converting the individual stream's variability to the total flow's variability, as follows:

$$Var_T = (Var_{Pi})\,\frac{f_i}{f_t} \tag{8.7}$$

Where

Var_T = variance in the total stream's concentration (mg/L or μg/L);

Var_{Pi} = variance in the individual stream's concentration (mg/L or μg/L);

f_i = the individual stream's flow (m^3/min); and

f_t = the total stream's flow (m^3/min).

For example, if the pollutant concentration in an individual stream changes by 50 mg/L, the concentration in the total stream would change by

$$Var_T = (50)(150/700) = 10.7\text{ mg/L}$$

This variance can be used in the calculation as the change in concentration of the combined and potential effect on the downstream system.

CUMULATIVE FLOW CURVE. While various techniques have been proposed using normal distribution flow and load profiles, confidence intervals, and coefficients of variation, these parameters are seldom precisely defined or predictable in most industrial operations.

Flow and load variations are often independent of each other in many industries, particularly those with significant cleanup operations (e.g., the food industry) or with significant process or product changes (e.g., food, pharmaceuticals, and petrochemicals). High flows may have low concentrations of pollutants, and vice versa.

The most common method for sizing equalization facilities is the mass balance approach, using a cumulative flow or mass diagram, sometimes called a *Rippl Diagram.* This graphic technique, which has long been used to determine a water reservoir's capacity, consists of plotting cumulative flow versus time for one complete cycle (e.g., 24 hours). Two parallel lines, with slopes representing the equalization tank's average pumping or outflow rate, are drawn tangent to the high and low points of the cumulative flow curve. The required tank size is the vertical distance between the two tangents.

The method is illustrated in Table 8.2 and Figure 8.5 for a hypothetical dairy. The example shows hourly average flows from a typical dairy industry, but the technique works for any industry. (Note: These flows could be measured more frequently or for a longer period, depending on the industry's characteristics.)

In Figure 8.5, the flow has accumulated starting at midnight and the cumulative flow is plotted as the curved line in Figure 8.5. The average flow for the day is represented by the line through the origin and the 24-hour cumulative flow value. This line also represents the rate of constant outflow from the equalization tank. The analysis determined that the equalization tank must hold at least 1700 m^3 (449 000 gal). Figure 8.5 also shows whether the equalization tank is emptying or filling. When the slope of the cumulative flow line is less than the average outflow line, the tank is emptying. When the cumulative flow curve slope is steeper than the average withdrawal rate, the tank is filling.

This procedure provides the tank size for the flow-time trace of a specific day or other operating period. Since the variability and, therefore, the amount of equalization required changes from day to day, care is required in selecting a daily or weekly flow or mass loading rate that is representative of the flow conditions to be equalized. Therefore, a safety factor of 10 to 20% should be applied to equalization volume calculations to allow for both operational variations and future flow or pollutant

Table 8.2 Flow data for Sunup Dairy.

Time	Flow rate (m^3/d)	Cumulative flow (m^3)	Percent of cumulative flow
Midnight	120	0	0.0%
1	100	120	2.3%
2	80	220	4.2%
3	70	300	5.7%
4	60	370	7.1%
5	70	430	8.2%
6	80	500	9.6%
7	150	580	11.1%
8	300	730	14.0%
9	350	1030	19.7%
10	400	1380	26.4%
11	400	1780	34.0%
Noon	450	2180	41.7%
1	350	2630	50.3%
2	500	2980	57.0%
3	450	3480	66.5%
4	400	3930	75.1%
5	200	4330	82.8%
6	200	4530	86.6%
7	150	4730	90.4%
8	150	4880	93.3%
9	100	5030	96.2%
10	100	5130	98.1%
11	200	5230	100.0%

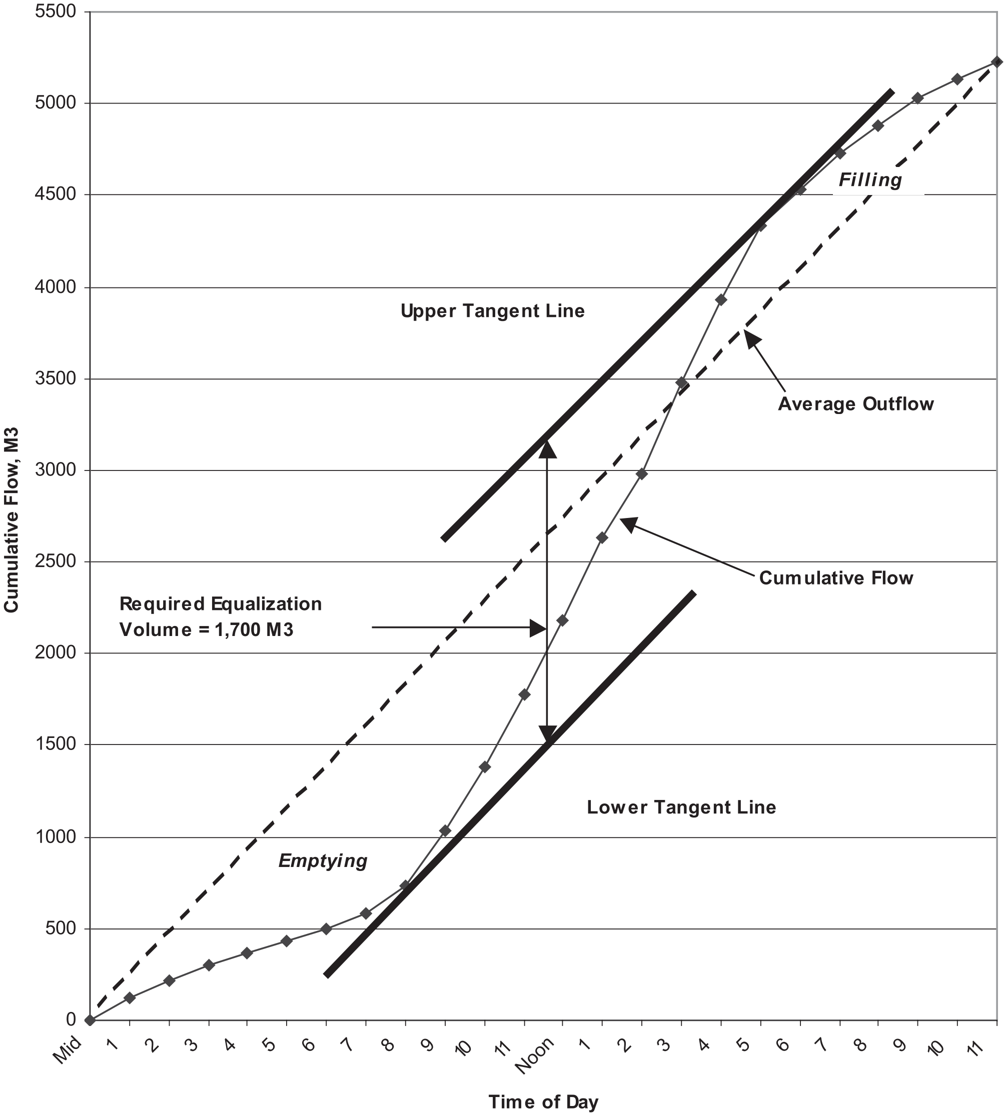

FIGURE 8.5 A mass diagram for Sunup Dairy.

changes. (The volume calculated is the live storage volume.) Alternatively, the average withdrawal rate could be increased instead if downstream processes can handle the higher flow rate.

OTHER DESIGN CONSIDERATIONS

MIXING REQUIREMENTS. An equalizing vessel often requires mixing, particularly if suspended solids are present. Typically, continuous mechanical mixing is better than attempting to mix incoming flows hydraulically. The exception is in the alternating flow diversion mode when suspended solids are not present.

When handling biodegradable wastes, the equalization tank may develop odor problems unless aeration is provided. The aeration and mixing systems may be combined (e.g., diffused air system). Although mixing power levels vary with basin geometry, an airflow rate of 0.5 to 0.8 $L/m^3 \cdot s$ (4 to 6.4 cu ft/min/1000 gal) of basin volume is considered the minimum to keep solids in suspension in diffused air systems.

In mechanically mixed systems, about 0.02 to 0.04 kW/m^3 (0.10 to 0.20 hp/1000 gal) is required to completely mix the heavier solids often found in industrial waste.

For both mechanical and diffused air systems, pilot studies should be performed on industrial wastes that are significantly more viscous than water because of high solids content or more viscous fluids.

Experience with mechanically mixed systems suggests avoiding the use of mechanical surface aerators in equalization basins, particularly with waste streams containing surfactants and soaps, and in cold climates. The spray from surface mixing creates major foaming and freezing problems in those applications. Also, floating aerators may not mix properly over the range of depths of basin operation, if the equalization basin's depth varies significantly. Submersible mixers are a better option because they can be located and relocated at any desirable depth. Also, the mixers can be oriented as required after installation to optimize mixing. Explosion-proof motors should be used when flammable gases or vapors are present.

A third method for mixing equalization basins is to recirculate the equalization basin's effluent via an effluent pump. Usually a throttling valve (butterfly or plug) is used for both the pump discharge line and the recirculation line to allow recirculated flows to vary from 0 to 100%. While more economical than mechanical or diffused air mixing, recirculation may be less effective in mixing basin contents because of vortexing. Baffles are recommended in tanks using recirculation for mixing.

AERATION. In addition to mixing, diffused air or floating mechanical aeration chemically oxidizes reducing compounds and physically strips volatile chemical compounds.

Some states require an air-discharge permit for emitting volatile organic compounds to the atmosphere or classification of the equalization tank as a process tank. Granular activated carbon or a chemical scrubber may be required to remove stripped gases before discharge to the atmosphere.

Waste gases from other processes may be used for mixing if no harmful substance is added to the wastewater. Flue gases containing large quantities of carbon dioxide, for example, may be used to mix and neutralize high-pH wastewater.

BAFFLING. Baffles are recommended in most mechanical mixing applications in equalization basins, except perhaps when the wastewaters contain appreciable settleable solids. Baffling prevents short-circuiting and vortexing. In circular tanks, four baffles are often installed on the walls to reduce swirling and improve mixing. The precise arrangement and size of the baffles depends on both the basin configuration and mixer manufacturer recommendations.

Over-and-under or around-the-end baffles may be used. Over-and-under baffles are preferable in wide equalization tanks because they provide more efficient horizontal and vertical distribution.

Influent should be introduced at the bottom of the tank so the entrance velocity prevents suspended solids from sinking to and remaining on the bottom.

TANK CONFIGURATION. Because equalization basins can be a source of odors, foaming, and freezing, the tank (basin) must be configured carefully with regard to freeboard (distance from the maximum water surface to the top of the tank), tank covers, piping arrangements, and auxiliary systems.

Freeboard. Equalization basins using diffused air should have a minimum freeboard of 0.5 m (20 in.), and up to 1.5 m (5 ft) in systems where foaming is expected. Systems with submersible mixers should have a minimum freeboard of 0.6 m (2 ft). Equalization basins with floating aerators should have at least 1 to 1.5 m (3 to 5 ft) freeboard.

Tank Cover. If freezing or significant odors are expected, equalization basins should be covered or put in a building with suitable ventilation. In addition, some form of odor control (e.g., chemical scrubber, activated carbon) should be considered for the off-gases.

Air Diffusers. If diffused aeration will be used for mixing or aeration, coarse-bubble diffusers are preferred over fine-bubble systems, to avoid solids clogging or coating with oil and grease. The diffusers should be mounted on the underside of the air header to minimize the possibility of settling solids clogging them.

Foam Spray. If the wastewater contains significant concentrations of soaps and surfactants, which is common at dairies, other food processors, and textile manufacturers, a foam spray system may help reduce foam. The foam spray system would normally use plant water or potable water sprayed under pressure through nozzles to break down the foam as it forms. Anti-foaming chemicals are also used.

Freezing. If freezing conditions are unavoidable, all external piping and valves should be heat-traced. If the equalization basin could freeze, one or more hot water sources should be provided near the basin. Covering the basin will also reduce freezing problems.

Draining and Cleaning. Equalization basins should be sloped to their drains, and a water supply should be provided for flushing without hoses. Otherwise, remnants in the tank after draining may cause odor and health issues.

Pumping Controls and Drives. Pump level controls establish true equalization of incoming flows and loads. In a simple one-pump (one-duty, one-standby) system, this typically requires the pump-start level to be set as low as possible, consistent with the pump's suction head requirements.

Equalization system designers must also consider the use of constant-speed pump drives versus variable-speed drives. In practice, the equalization pump often discharges to a nearby process with little variation in head (e.g., a weir). However, the pump's suction head varies significantly as the equalization tank level rises and falls, so static head is often the major hydraulic variable when designing equalization pumping systems.

Because a centrifugal pump's output varies inversely with head, large variations in pump output can occur as the equalization tank level fluctuates. To combat this effect, constant-speed pumps would normally use a flow-rate controller to adjust the pump head (and therefore its output) to a constant rate, despite a varying tank level.

A lower cost option may be to use a variable-frequency drive to vary the output of the equalization pump. This type of system would typically use a flow loop—a variable-frequency drive and a flow meter with a feedback loop—to adjust the pump speed to suit the desired flow rate. (For more information on feedback loops, see Chapter 14.)

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Chapter 9

Solids Separation and Handling

(continued)

BACKGROUND

Although publicly owned treatment works (POTW) are designed to remove and concentrate suspended solids, they typically should be removed from industrial wastewater before it is discharged to a POTW or receiving waterbody. Solids are often present in industrial wastewater in such large amounts that they would interfere with proper operation of downstream treatment units or POTWs. This is particularly the case with fats, oils, and greases (FOG) from such industries as food processors, refineries, and industrial laundries.

High suspended solids concentrations (more than 500 mg/L) can overload a POTW's grit chambers, primary sedimentation tanks, and solids management processes. High levels of FOG (more than 150 mg/L) can accumulate in primary sedimentation tanks and biosolids digestion tanks, clog pumps and collector mechanisms, greatly reduce oxygen transfer rates in aeration basins, and potentially lead to NPDES violations. FOG from refineries, industrial laundries, or other manufacturers with petroleum-based products can cause toxicity problems in a POTW's biological processes.

High concentrations of settleable solids and FOG also can clog sewer lines and pumping-station wet wells. Besides being difficult and expensive to remove at this stage, these materials can cause objectionable odors if they are biologically degradable.

Suspended solids in industrial wastewaters may be either organic or inorganic. These solids are typically classified based on size and removal technique:

- Large solids [objects at least 25 mm (1 in.) in diameter that will interfere with downstream flow and treatment operations];
- Grit [suspended matter (e.g., sand, gravel, metal particles, plastic particulates, products of incomplete combustion, and other dense materials) that settles more rapidly than organic solids do];
- Settleable solids [materials (e.g., particles with diameters between 1 μm and 25 mm) that settle out of wastewater during a standard Imhoff cone test]; and
- Colloids [particles with diameters between 10^{-6} and 10^{-3} mm (0.001 and 1 μm) and surface charges that must be neutralized to allow particle agglomeration, flocculation, and settling].

Grit can enter industrial sewers via stormwater runoff and washing operations at pulp and paper operations, timber products-processing, food processing, chemical manufacturing, etc. Mill scale from steel-pickling operations has the characteristics of grit (inorganic composition and high settling velocities) and is typically removed from wastewater via the same treatment processes.

Settleable solids and colloidal materials also may be organic or inorganic, depending on the process from which they originate. Dispersing agents (e.g., surfactants) may stabilize suspended solids, making them more difficult to remove. Such situations must be approached on a case-by-case basis. Chemical coagulation and flocculation with metal salts or synthetic polyelectrolyte are typically used to remove colloids.

SUSPENDED SOLIDS CLASSIFICATIONS

Water and wastewater solids are called *residue* (APHA et al., 2005). The total residue is the material left after a sample has been evaporated and dried in an oven at a defined temperature. It includes both filterable residue (the fraction retained by a filter) and nonfilterable residue (the fraction that passes through the filter). Suspended solids are filterable residue; dissolved and colloidal solids are nonfilterable residue.

Total suspended solids (TSS) are determined by filtering a sample through a defined filter medium, drying it in an oven, and then determining the residue's weight. The drying temperature is typically 103 to 105° C (217 to 221° F).

Total suspended solids include both "fixed" and "volatile" fractions, which are determined by filtering the sample through a filter disk until 200 mg of residue are collected on the filter. The residue is dried, weighed, and then ignited at a temperature of 550° C (1055° F). The weight of the residue after ignition is the fixed suspended solids fraction. The difference between the fixed and total suspended solids weights is the volatile suspended solids fraction.

Because of the high viscosity of sludge solids, its TSS and volatile suspended solids contents are determined by first calculating the total solids or total volatile solids, respectively, for a particular sample. Total solids and total volatile solids include both suspended and dissolved solids.

REMOVAL METHODS

Suspended solids removal methods are chosen based on the initial concentration of solids in the wastewater; the desired final concentration; and the particles' size, settleability, thickening characteristics, and discrete or flocculent nature.

Jar and pilot testing of a specific waste stream are often necessary to determine its solids characteristics and compatibility with a particular treatment process. Techniques typically used to remove suspended material from waste streams with TSS concentrations less than 1% (10 000 mg/L) include straining, gravity separation, and filtration.

STRAINING. Coarse or fine screens are used to strain solids from a waste stream. Coarse screens typically have openings that are between 6 and 50 mm (0.236 and 2 in.). Fine screens have openings less than 6 mm. The choice of screen depends on the particle size to be removed and the downstream operation(s).

Coarse Screens. The most commonly used coarse screens are bar screens, which are typically used to protect downstream equipment from damage or reduced efficiency because of large floating solids, wood, rags, stones, etc. Industries that typically use bar screens include food processors, pharmaceutical manufacturers, pulp and paper manufacturers, tanneries, chemical manufacturers, and textile manufacturers.

The two types of coarse screens are manual and mechanical (which refers to their method of cleaning). Manual bar screens are used in small applications and where cleaning is needed only infrequently. Manual cleaning may be cost-effective in a small system [less than 20 m^3/d (5000 gal/day)], but infrequent or improper cleaning schedules may result in high-velocity surges because of plugged openings. Screen plugging can decrease the screen's effectiveness and cause channel overflows.

Mechanically cleaned bar screens (Figure 9.1) are more common. They are used in larger applications or where frequent cleaning is necessary. Mechanical cleaning is done by rakes on loop chains or cables; the screens may be cleaned from either the front or back. Powered by overload-protected electric motors, the rakes move over and between the bars, pulling captured debris to a platform on top of the structure. Some mechanical screens have curved bars that are cleaned by a revolving rake.

Mechanical cleaning reduces labor costs, provides more constant flow conditions, allows better screening capture, and typically reduces odors. However, a parallel channel with a manual bar screen should be added to allow continuous operations while the mechanical screen is being serviced. Design considerations include the channel dimensions, bar spacing, depth of flow in the channel, cleaning method, and control mechanism (Table 9.1).

Head loss through screens depends on the quantity and type of screenings allowed to accumulate between cleanings. Design values should range between 0.2 and 0.8 m (0.7 and 2.6 ft) for clean to partially clogged screens. A clean screen's head loss may be calculated using conventional orifice formulas by considering the flow and the effective area of screen openings (i.e., the sum of vertical projections of the screen openings).

Fine Screens. Commonly used fine screens include static screens, rotary drum screens, tangential screens, and vibratory screens. They remove fine non-flocculent and non-colloidal particles.

Static Screens. A static screen is an inclined screen designed to remove fine particles without any moving parts (Figure 9.2). They are commonly used in the pulp and paper, mining, food processing, and textile industries.

FIGURE 9.1 Illustration of a mechanical screen.

TABLE 9.1 Typical design data for coarse screens.

Design parameter	Manually cleaned	Mechanically cleaned
Bar openings (mm)	25–50	15–75
Slope from vertical (deg)	30–45	0–30
Minimum approach velocity (m/s)	0.1	0.3–0.5
Maximum approach velocity (m/s)	0.3–0.6	0.6–1.0
Allowable headloss (mm)	150	150–600

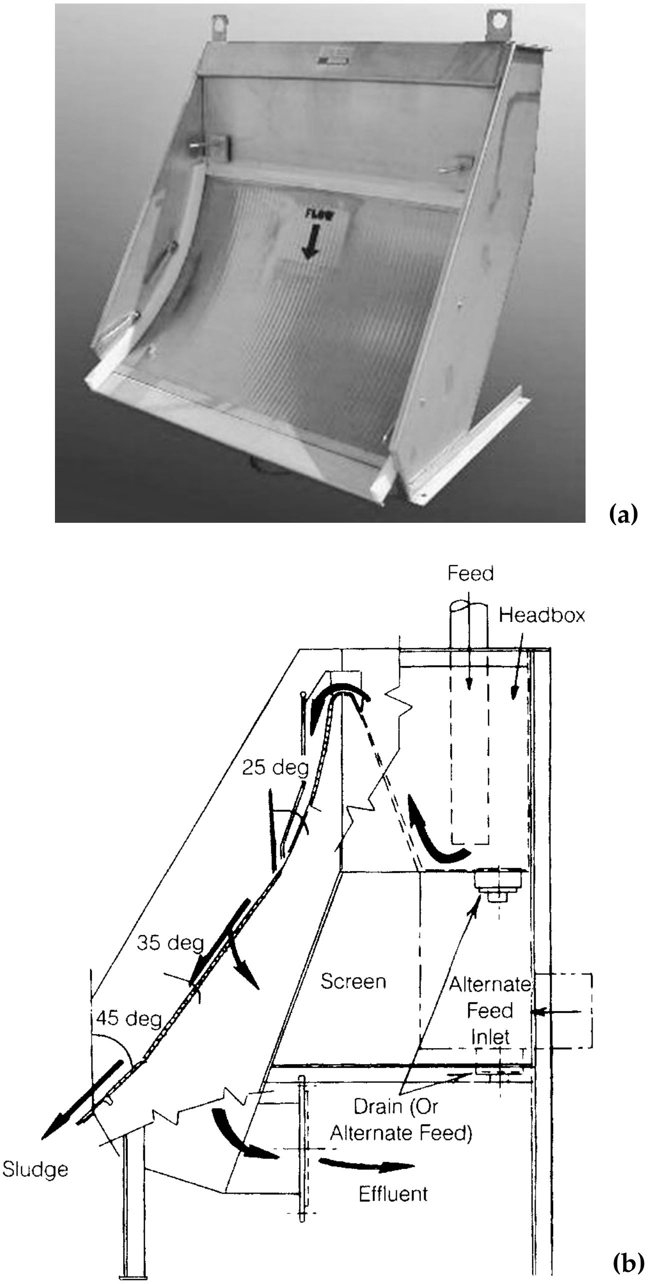

FIGURE 9.2 (a) An illustration of a static screen (courtesy of Screen Services) and (b) an illustration of an inclined self-cleaning static screen.

In one configuration, influent enters the screen via a head box and weir at the back of the unit. It then overflows the weir and discharges downward on the screen. The liquid passes through the screen, leaving the larger solids behind. These solids are discharged via gravity over the edge of the screen into a hopper.

Another configuration involves spraying the flow against the screen under pressure. In this case, the liquid passes through the screen, and the solids drop down its face.

Rotary Drum Screens. The rotary drum screen is mounted in a channel and operates partially submerged (Figure 9.3). It consists of a rotating cylindrical screen that revolves around the horizontal axis.

Two types are common: externally fed screens and internally fed screens. In externally fed screens, liquid enters the drum via a head box that distributes the flow along the length of the screen. It then flows via gravity through the rotating drum and out the bottom. Solids retained on the external screen are scraped off by a doctor blade. In internally fed screens, wastewater flows radially through the screen, and solids are deposited on the screening fabric.

Both types use water jets to clean (backwash) the screen to prevent blinding and clogging. Cleaning may be continuous or intermittent. In industries with high FOG content, hot water should be used to prevent grease from plugging the screen. The backwash may be actuated by increased differential pressure (head loss), time, or conductivity.

FIGURE 9.3 An example of a Rotostrainer® externally fed rotary drum screen (courtesy of Parkson Corporation, Fort Lauderdale, Florida).

Rotary drum screens are typically used in the food industry, where rapid protein recovery is desired, and in industries with large quantities of solids (e.g., the pulp and paper industry). They are commonly used ahead of dissolved-air flotation (DAF) systems to increase byproduct recovery and reduce solids loading to the DAF process.

One advantage of a rotary drum is low head loss or power needs. Head loss across the screen, including inlet and outlet structures, ranges from 300 to 480 mm (12 to 19 in.). Head loss through the screen itself should be no more than 150 mm (6 in.).

The screens are typically constructed of stainless steel, manganese bronze, nylon polyester, or alloy wire cloth. Openings range from 0.02 to 3 mm (0.0008 to 0.1 in.). The opening size does not account for overall solids removal. The mat of removed solids provides a mechanism for removing smaller particles. The drums are 1 to 4 m (3 to 13 ft) long and 0.9 to 1.5 m (3 to 5 ft) in diameter. They rotate at approximately 4 rpm.

Rotary screens with a screen or fabric whose apertures are between 0.01 and 0.06 μm (3.9×10^{-4} and 2.4×10^{-3} mil) are also used for microstraining. Though used infrequently, this type of screening can be used to polish effluent before discharge.

Vibratory Screens. Vibratory screens (Figure 9.4) are helpful in industries with very high solids (e.g., iron and steel, glass manufacturing, mining, food processing, and pharmaceuticals), and those requiring bulk separation of solids from water (solids classification).

FIGURE 9.4 An example of a vibratory screen (courtesy of Sweco, A Business Unit of M-I L.L.C.).

Vibratory screens include both circular center-feed units and rectangular end-feed units. In center-feed units, solids are discharged in a spiral toward the center or the periphery. In rectangular end-feed units, solids are discharged along the screen toward the lower end.

GRAVITY SEPARATION. Suspended solids may also be removed via gravity. This method relies on the natural tendency of solid particles to settle or rise under quiescent conditions, depending on their specific gravity. Those solids with a specific gravity higher than the liquid settle; those having a lower specific gravity will float.

Grit Removal. Grit is predominantly non-putrescible solids (e.g., sand, small gravel, metal shavings, ash, and soot) that settle faster than putrescible and other solids. Grit removal protects downstream pretreatment equipment and prevents heavy material from accumulating in sewers and equalization, neutralization, and aeration tanks. When designing grit-removal processes, the designer should consider putting this equipment close to the source of the grit to facilitate recovery and reuse, and help prevent onsite sewer plugging.

Four methods used for grit removal are velocity control, aeration, hydrocyclones, and sedimentation or dragout systems. In velocity-controlled systems, a control section in the downstream channel provides a nearly constant velocity over a range of flows to vary the flow depth in the channel as the volume changes. Control devices (e.g., proportional and Sutro weirs) are installed 150 to 300 mm (6 to 12 in.) above the grit channel invert to store grit and prevent settled particles from resuspending. A velocity of about 0.3 m/s (1 ft/sec) allows heavier grit to settle, transports most of the lighter organic particles, and tends to resuspend those that settle. These grit chambers are typically cleaned manually. Controlled-velocity grit removal requires more space than many industries can provide, although field applications in the vegetable and fruit industries may be effective and cost less than more complex equipment.

A more popular controlled-velocity option is the vortex-type grit chamber (Figure 9.5). In this unit, a vortex is generated hydraulically when inflow is introduced tangentially near the top of the unit. Grit is literally "spun out" of the wastewater to the bottom of the unit, where it is removed and dewatered via a conveyor-type device. Lighter organic solids remain suspended and are carried downstream to the next process. This unit has several advantages over other grit-removal devices. First, it has no mechanical parts in continuous contact with abrasive particles. Second, the system can be designed to remove even fine grit. However, a vortex grit

FIGURE 9.5 An example of vortex grit chambers (courtesy of Hans Huber AG).

chamber requires high hydraulic head, so pumping to or from the unit is typically required. Also, head loss increases as the desired grit removal (the fineness of the grit particles) increases.

Diffused air may be used to remove grit in a grit chamber. The heavy particles settle, while the lighter organic particles are suspended by the air and carried out. The airflow rates should be 5 to 12 L/s per linear meter of tank (3 to 8 cfm/ft), with provisions to vary the airflow. The higher airflow rates should be used in tanks with larger cross-sections. Detention times for effective removal range from 1 to 3 minutes at maximum flow rates. The grit chamber's inlet and outlet structures should be designed to prevent short-circuiting. The influent should be introduced directly into the air circulation pattern, and the outlet should be at right angles to the inlet. Dead spaces can be avoided by proper geometrical design of grit-collecting and air-diffusion equipment. Mechanical cleaning is recommended.

Hydrocyclones (see Figure 10.5 in this manual) are centrifugal separators with no moving parts. They work on the same principle as vortex grit chambers but are smaller because of the higher pressure and centrifugal force involved. A hydrocyclone separates two materials with different specific gravities (e.g. water and grit) via centrifugal force. It is used in industries where an inexpensive, low-maintenance method is desired for separating materials (e.g., grit and metal shavings). (For more information on hydrocyclones, which are also used to separate oily wastes, see Chapter 10.)

A hydrocyclone typically has a cylindrical top section mounted over a converging cone. Inflow is pumped into the unit along the inner wall, forcing it to rotate rapidly. The centrifugal force is directly related to the rotational velocity; it forces heavier material to the outside walls, and it discharges out the bottom of the hydrocyclone.

As the liquid swirls down the conical separation chamber, its velocity increases. It cannot exit the restricted discharge nozzle, so it reverses direction, forms an inner vortex, and moves to the clean liquid outlet at the top of the unit.

While used in many industries, hydrocyclones are most commonly used in the following applications:

- Oil and gas industry (to remove grit and cuttings from drilling muds, crude oil, and oil-water mixtures);
- Steel manufacturing (to remove mill scale from plant cooling water);
- Metalworking (to remove cuttings and grit from metalworking fluid);
- Vegetable and fruit processing (to de-sand wash waters and remove field dirt, pits, seeds, and other debris from juices and purees);
- Pulp and paper industry (to clean primary and secondary fiber stock);
- Any high-solids applications (to remove dirt and grit from seal water for pumps handling high-solids streams).

They can also be used downstream of other grit-removal processes (e.g., vortex grit chambers) to remove more liquid from a grit slurry before final solids disposal.

Hydrocyclone design is based on flow rate and the size and specific gravities of the particles to be separated. The sizing and specific design are typically provided by hydrocyclone manufacturers.

Sedimentation and a dragout tank are sometimes used by industries that handle large amounts of grit. The iron and steel industry, for example, typically handles mill-scale (which is high in both grit and oil and grease) in dragout tanks. The dragout tank is similar to a conventional rectangular sedimentation tank with a chain and flight collector mechanism. However, the solids are conveyed continuously up a sloped section out of the tank and into a hopper, avoiding the need to pump large quantities of grit.

Conventional Sedimentation. Conventional sedimentation involves holding wastewater in a quiescent (low-velocity) stage long enough for solids to settle. These solids' specific gravity is less than that of grit, so they need a longer settling time.

Sedimentation can be provided by ponds or tanks. Sedimentation ponds are also used for long-term solids storage, necessitating periodic solids removal. They are often used in the pulp and paper and chemical industries, where flows are high and land is available. The ponds are often lined with an impervious lining and surrounded by earthen berms. While cost-effective if inexpensive land is available, sedimentation ponds may be subject to odors and algae, and may attract vermin.

In contrast to sedimentation ponds, sedimentation tanks are used when flows are lower and land is less available. Settled sludge is removed frequently (ranging from hourly to once every 1 to 2 days). Design parameters include the tank's surface area, its depth, the detention time, the surface overflow rate, the weir overflow rate, and peak flow rates. The primary design parameter for sedimentation tanks is the *surface loading rate* is the wastewater flow rate over the tank's surface area. The design value for surface loading rate typically ranges from 80 to 120 $m^3/m^2 \cdot d$ (2000 to 3000 gpd/sq ft) at peak hourly flow rates. Other peak rates (daily, weekly) may be considered, depending on the wastewater's flow characteristics.

Once the tank's surface area has been established, the detention time can be determined based on the tank depth. Primary sedimentation tanks typically provide detention times of 90 to 150 minutes at average flow rates. Tank depths vary from 2 to 5 m (7 to 16 ft); 4 m (13 ft) is typically used. Enough depth is necessary to avoid scour along basin bottoms and for solids storage. However, excessive solids retention may result in anaerobic conditions, floating sludge, and odors.

Weirs are used to control the water surface in the sedimentation tank. The weirs used are usually rectangular or v-notch weirs. Weir loading should be about 250 $m^3/d \cdot m$ (20 000 gpd/ft) at average flow.

Tanks may be circular or rectangular. Circular tanks may be center-fed or peripherally fed. In a center-fed clarifier (Figure 9.6), the influent enters a circular well that distributes the flow equally in all directions. The cleaning mechanism (or solids scraper with two or four arms) is supported by a center shaft and turns about 0.03 rpm (one revolution every 30 minutes). Scum removal blades are typically provided and supported by the arms.

The peripherally fed design includes a suspended circular baffle near the tank wall. Influent is discharged tangentially at the base and flows spirally around the tank. The clarified liquid flows over a central weir, while scum and grease are confined to the surface of the annular space.

Rectangular sedimentation tanks (Figure 9.7) are used when space is limited, but unless they are properly baffled, they are more subject to short-circuiting than

FIGURE 9.6 An example of a circular sedimentation tank (courtesy of Walker Process Equipment).

FIGURE 9.7 An example of a rectangular sedimentation tank.

circular tanks are. Also, solids carryover can occur if the surface overflow rates are excessive. Rectangular tanks should be designed with influent channels across the inlet end and effluent channels at the outlet. Designers should consider using inlet, effluent, or mid-tank baffling to avoid short-circuiting and the resulting solids carryover.

The sludge-removal equipment may be a pair of looped conveyors or chains with fiberglass or wooden flights (Figure 9.8). Many plants have converted from redwood flights and iron chains to fiberglass to speed replacement or maintenance of the drive components. The flight and chain apparatus moves along the tank bottom slowly [between 0.60 and 1.2 m/min (2 and 4 ft/min)], scraping settled solids to the hoppers. Meanwhile, the returning flights move scum to the end of the tank for collection.

Another cleaning mechanism in rectangular basins with relatively light solids is a bridge traveling up and down the tank on rails supported on the sidewalls (Figure 9.8). It has one or more scraper blades that are lifted above the solids on return travel. Scum also may be moved by water sprays or scrapers attached to the bridge if the solids are light.

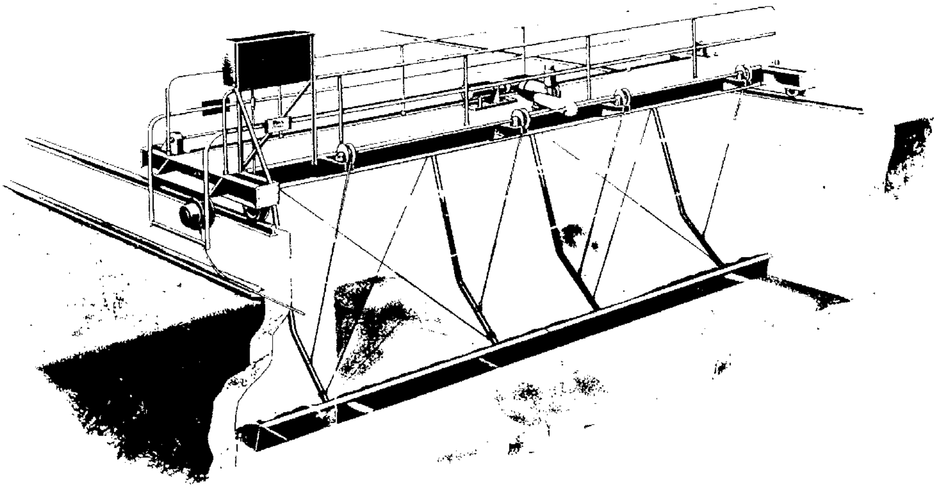

FIGURE 9.8 An example of a rectangular sedimentation tank with a traveling bridge collector.

Inclined-Plate Clarifiers. Inclined-plate clarifiers (Figure 9.9) are commonly used to settle solids in many industries (e.g., metal-finishing, printed circuit-board, and food processing). There are several types of these clarifiers:

- Plate settlers, which use parallel sheets of stainless steel or fiberglass, set about 50 mm (2 in.) apart at a 45- to 60-degree angle [lower angles are used for heavier solids (e.g., steel mill wastewater)];
- Lamella, clarifiers (a proprietary plate settler);
- Tube settlers, which use parallel tubes rather than plates and are typically used for drinking water treatment.

In this process, wastewater enters near the bottom of the plates and flows upward to outlet weirs or orifices. Solids settle down the plates and are carried by gravity to a solids thickening and storage area below. As in conventional sedimentation, the particles that are heavier than water typically settle, following the principles of Stokes' Law (see Chapter 10).

In conventional sedimentation, the overflow rate is used to calculate the required surface area of the sedimentation basins. So, all particles with a settling rate equal to or greater than the overflow rate will be removed. The tank depth does not affect solids removal effectiveness.

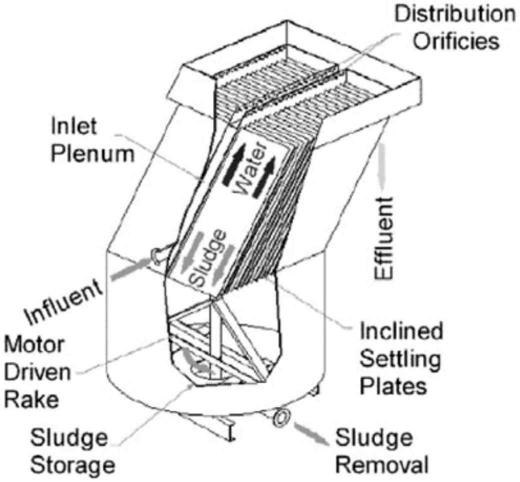

FIGURE 9.9 A schematic of an inclined plate clarifier (courtesy of Hoffland Environmental, Inc.).

The inclined-plate clarifier reduces the necessary settling depth from feet to inches, so it reduces the necessary settling area by up to 90% and is highly effective in removing suspended solids. However, because inclined-plate clarifiers substitute height for area, the 3.7 to 7.6 m (12 to 25 ft) tall units may not easily fit into existing buildings.

Inclined-plate clarifiers are designed based on areal loading, in units of L/m^2·min (gpm/sq ft). The area value used is the *projected area,* which is a function of the number of plates, the area of each plate, and the angle of the plates from the horizontal. The calculation for projected area is

$$A_p = nA \cos\alpha \qquad (9.1)$$

Where

A_P = projected settling area, m^2 (sq ft);
n = number of plates in the clarifier;
A = area of each plate, m^2 (sq ft); and
cos α = cosine of the angle α from the horizontal plane.

The effective surface area is a function of a manufacturer-specific design, so manufacturers should be consulted during unit design. Typical design loading rates are 10 to 40 L/m^2·min (0.25 to 1.0 gpm/sq ft). The lower value is typically applied to light solids (e.g., metal finishing). Higher rates are used for heavier solids (e.g., mill scale and pulp and paper solids).

Inclined-plate clarifiers are not usually used to clarify biological sludges because experience has shown that bacteria and other biomass can grow on the plates, plugging or reducing the settling area. "Sticky" sludges (e.g., oily solids) may also create plugging problems between the plates. Conventional sedimentation or flotation should be considered in these cases.

Chemical Coagulation and Flocculation. Gravity separation can be enhanced by coagulants and coagulant aids, which are added to wastewater to promote flocculation. Many solids produced in industrial processes are colloids, which are typically small (0.01 to 1 μm) and negatively charged. Chemical coagulation is often required because colloidal particles repel each other, and so resist settling and removal. [For detailed descriptions of colloidal chemistry and the mechanics of colloid destabilization (neutralization of colloidal charges), see the *Industrial Waste Treatment Handbook* (Woodward, 2001), *Principles of Colloid and Surface Chemistry* (Hiemenz et al., 1997), and *Wastewater Engineering: Treatment and Reuse* (Metcalf & Eddy, 2003).]

A *coagulant* is a chemical used to destabililize colloidal particles so a floc may be formed. A *flocculent* is a chemical used to further enhance floc formation into larger and heavier flocs. Coagulants and flocculants are often used together; the coagulant destabilizes the colloid, typically producing a pin floc, while the flocculent and a slow mixing mechanism (flocculation) make the flocs larger and sturdier so sedimentation or filtration can occur.

Coagulants are simple, water-soluble electrolytes (inorganic salts), inorganic acids, and bases. Iron, aluminum, and calcium salts are the most effective coagulants. Coagulants typically used in industrial pretreatment are lime, alum, polyaluminum chloride, ferric chloride, ferrous sulfate, ferric sulfate, and sodium aluminate. The meat processing industry sometimes uses sodium lignosulfonate and calcium lignosulfonate, when protein recovery is desired. These salts—byproducts of pulp and paper manufacturing—precipitate soluble protein for recovery at pH 3.5 to 4.0 in meat-packing and seafood-processing plants. Nonprotein BOD is also removed (up to 70 to 90% of soluble BOD).

Other naturally derived products are also used to recover protein in the food industry. Chitin (a byproduct of shrimp and crab processing) and carrageen (an extract of seaweed) are used as coagulant aids where metal salts or polymers would affect the quality and value of the recovered product. Bentonite and activated silica are other commonly used coagulant aids.

Jar Testing. A standard jar test (Figure 9.10) is an effective method for selecting a coagulant, flocculent, or coagulant aid and determining the optimum dosage and pH. Jar testing is particularly important for industrial wastes, whose characteristics vary substantially between processes and even between the functional units of one process. Also, waste characteristics change throughout the day because of batch processing and cleanup activities.

In the dairy industry, for example, pH fluctuations of up to 10 units are not uncommon when switching from processing to cleanup. Thus, jar testing should be performed on representative equalized samples where substantial variation is expected.

In the oilseed processing industry, the seed type and quality can significantly affect the resulting wastewater's characteristics, the treatment protocol, and the operating performance. In the dairy industry, pH fluctuations of up to 10 units are not uncommon when switching from processing to cleanup. So, jar testing should be performed on representative *equalized* samples when substantial variations are expected.

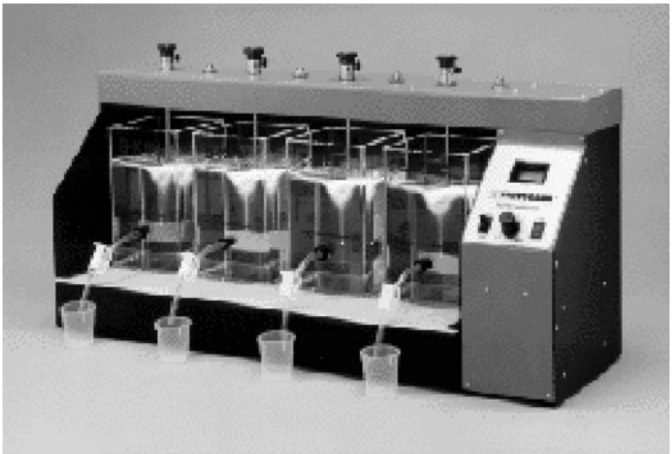

FIGURE 9.10 An example of a jar testing setup.

Chemical Feed Systems. A chemical-addition system includes facilities for chemical storage, chemical feeding, chemical mixing, rapid mixing of chemicals and wastewater, and flocculation. Chemical storage facilities depend on the chemical chosen, its state (liquid or dry), and the pretreatment system's size. Most coagulants can be purchased in bulk (railroad car or truckload lots), although they are also available in smaller quantities. The cost advantages of bulk purchase should be weighed against storage construction costs and potential chemical deterioration over time.

Chemical feed systems are designed for both dry and liquid feed. Solid coagulants are typically converted into a solution or slurry before being introduced to the wastewater. Some coagulants (e.g., alum) are non-corrosive as a solid and corrosive as a liquid, so the liquid-handling equipment must be corrosion-resistant.

A dry feed system consists of a hopper, feeder, and dissolving tank. The design must take into account the particular chemical's characteristics, as well as minimum and maximum wastewater flows. It also must protect the stored dry chemical from high temperatures and humidity. Some chemicals (e.g., lime and quicklime) require vibration or agitation to prevent bridging and promote continuous flow. A dry feeder may be volumetric or gravimetric; the latter is more accurate. At smaller facilities, dry chemicals may be added manually to the dissolving tank; in which case, a bag breaker is recommended.

Polymers are difficult to dissolve, and because of their diversity, no single dissolving and feeding system suits all applications. Polymer suppliers offer recommendations on dissolving and feeding their polymers. One widely used system is a dissolving tank with a mixer and metering pump. The powder is often wetted before being introduced to the tank to avoid "fish eyes," which lengthen mixing time and can reduce the polymer's effectiveness, so more must be used. After dilution, the polymer should be given time to "age" (i.e., allow the long polymer molecule to completely "unwind"). An aging tank with a 30- to 60-minute detention time is recommended.

Liquid-feed systems use a pump (e.g., piston, positive-displacement-diaphragm, balanced-diaphragm, peristaltic, and progressing-cavity) or rotating dipper to handle chemicals that are only available in liquid form; that are more stable and readily fed as liquids; or that are exceptionally fine (such as powdered activated carbon) or relatively dangerous such as sodium hypochlorite. The feed controls may be manual, automatic (flow-proportioned), or a combination of both.

The chemical must disperse rapidly throughout the waste stream so there is enough agitation and mix time. Dispersal and mixing typically occurs in a tank, where rapid mixing is facilitated by a mixer (an in-line mixer or propeller mixer mounted at an off-center angle). Mixing can also occur in pump-suction and -discharge lines if the chemical-injection point is at least 20 pipe diameters upstream of the flocculation process. While inexpensive, pipeline mixing is less predictable because mixing performance can be adversely affected by changing flow and velocity in the line.

A key variable in mixing is the energy needed to thoroughly mix the flocculant and waste stream without shearing or breaking the resulting floc. A *G* factor (velocity gradient) is often used during design to determine the power needed to produce the desired results (Camp et al., 1943). Desired *G* values for rapid mixing range from 500 to 1000 sec^{-1}. Typical detention times for flash mixing reactors are 30 to 60 seconds.

When calculating the necessary mixing energy, the key variables are the desired *G* value (based on experience), the reactor vessel volume, and the viscosity of the liquid being mixed:

$$G = \sqrt{P / \mu \forall} \qquad (9.2)$$

Where

G = desired specific energy input (sec^{-1}),
P = power required [watts (ft-lb/sec)],
μ = dynamic viscosity at design temperature [N-s/m^2 (lb-sec/sq ft)], and
$\forall$ = reactor volume [m^3 (cu ft)]

So, the required power for an application with a given detention time and viscosity at a specific G value would be calculated as follows:

$$P = G^2 \mu \forall \tag{9.3}$$

As an example, the required mixing energy (or power) can be calculated for rapid mixing of an industrial wastewater with a flow of 500 m^3/d (123 250 gpd) and an average temperature of 40° C:

Desired G value = 750 sec^{-1}
Dynamic viscosity (μ) at 40° C = 0.653×10^{-3} N-s/m^2
Desired detention time = 60 seconds

$$\text{Required volume} = \left[\frac{500\ Cu\,M / D}{1440\ Min / Day}\right] \times 1\,Minute \ = \ 0.35\ Cu\,M$$

$$\text{Required power} = (750^2)(0.000653)(0.35) = 128\ watts = 0.13\ kw$$

Following rapid mix, an area for slow mixing should be provided to permit flocculation of finely divided particles into heavier, denser flocs that may be removed via gravity or flotation. Typical G factor values for flocculation are 10 to 60 sec^{-1}. Detention times for flocculation should be 10 to 30 minutes at design flow.

The energy required to generate the needed velocity gradient for flocculation can be applied by hydraulic, air, or mechanical means. Mechanical agitation is preferred because it produces a more uniform energy distribution so delicate flocs will not be sheared at the full range of wastewater flows. Its efficiency and adaptability allows for modification at existing sites.

Flocculation may also occur in a tube flocculator (Figure 9.11). Tube flocculators are often installed before DAF units, but could be used wherever flocculation space is limited. The tube flocculator typically contains an in-line static mixer and multiple chemical-addition and sampling points. Its main advantages are that mixing and flocculation occur in one small area, there are no moving parts to maintain, and the process can adapt to changing wastewater characteristics.

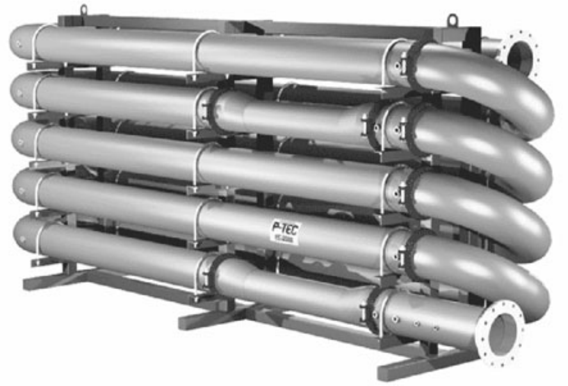

FIGURE 9.11 An example of a tube flocculator (courtesy of Piedmont-Technical Services, Inc.).

Centrifugal pumps typically should not be used for flocculation because the centrifugal rotation can shear flocculated particles before sedimentation or filtration. Likewise, avoid pumping flocculation effluent before settling or filtration.

Flotation. In flotation systems, light suspended solids or liquid particles are separated from the waste stream. Factors to consider during design include operating pressure, air:solids ratio, float detention time, surface hydraulic loading, and percent of recycle flow. Pilot testing should be done to develop reliable design criteria. (For more information on using flotation to remove fats, oil, and grease, see Chapter 10.)

Two conventional flotation methods are gravity flotation and dissolved air flotation (DAF). Both rely on the fact that materials with different specific gravities will separate. Gravity flotation relies on the natural tendency of light suspended solids, oil, and grease to float to the water surface. One common gravity separation device is a baffled tank designed to the standards of the American Petroleum Institute (API). These tanks may also contain coalescing plates to improve oil-water separation.

Dissolved air flotation introduces fine air bubbles into the liquid. The bubbles, which attach to or become entrapped within particles, float to the surface to form a solids layer that can be skimmed off. (For more information on DAF units, see Chapter 10.)

Chemical addition sometimes precedes sedimentation and usually precedes flotation processes and may enhance solids removal. Inorganic chemicals (e.g., alum and iron salts) help remove fine solids by precipitating hydroxides, carbonates, and phosphates and by enmeshing fine solids in precipitated solids. Some organic chemicals promote the flotation of the suspended solids by altering the surface properties of the solids, liquid, or air bubbles so the bubbles better adhere to the solids.

While improving solids and FOG removal, adding chemicals can generate substantial quantities of solids, which can be costly and difficult to process and dispose. If pretreatment standards are not stringent or solids and liquids separate easily, air-only DAF systems (without chemicals) may be preferred.

FILTRATION. Filtration removes suspended solids from a waste stream. Industrial wastewaters typically are filtered as part of a pretreatment system that includes

- Neutralization or precipitation of heavy metals,
- Biological treatment to decrease BOD and TSS levels,
- Solids removal before onsite biological treatment or discharge to the POTW.

The filtration system is used to "polish" suspended solids from the effluent (reducing them to extremely low levels) before discharging it to downstream processes or the POTW.

The metal-finishing industry and printed-circuit-board manufacturers often use filtration to capture the metal hydroxide or sulfide solids that escaped the sedimentation process. Filtration systems also have been installed after neutralization or precipitation systems when metal pretreatment standards became more stringent or a facility decided to reuse its water. Facilities also filter biological system effluent (to reduce suspended solids and insoluble BOD) before directly discharging it to receiving streams.

Both granular media filtration and pre-coat filtration are discussed below. For more information on filtration, see *Design of Municipal Wastewater Treatment Plants* (WEF, 1998) and *Wastewater Engineering: Treatment and Reuse* (Metcalf & Eddy, 2003).

Granular Media. Granular media filters are available with single- or multiple-size filtration media, continuous or interrupted operations, and various flow patterns. They contain two or more media (e.g., anthracite, sand, and garnet) with different specific gravities, and may have intermixing zones that gradually shift from one media to another.

Filter media are chosen based on their effective size and uniformity coefficient, which are calculated according to the relative distribution of grain sizes. This is determined by passing the media through a series of increasingly finer sieves and determining the weight of the media retained on each sieve.

The effective size of a filter medium, d_{10}, is defined as the media diameter at which 10% of the grains are smaller, and 90% are larger (by weight). The effective size is also approximately the average grain size. Specifying a media with a small effective size will improve solids capture, but shorten filter runs, increase backwash frequency, and increase recycle loads. Larger effective sizes would lengthen filter runs but reduce solids removal effectiveness. (Suggested sizing criteria are included later in this chapter.)

Filter media are also designed based on the uniformity coefficient (*UC*):

$$UC = \frac{d60}{d10} \tag{9.4}$$

Lower uniformity coefficients typically mean the media particles are more uniform, which result in slower head loss buildup (longer filter runs between backwashes). Very low uniformity coefficients produce more favorable filter operations, but are more expensive. (Suggested sizing criteria are included later in this chapter.)

Filter Types. Several types of filters are used to treat wastewater. Filters are typically characterized by the direction of flow through the filter (upward or downward); the nature of the flow (constant or variable); and the backwash operations (intermittent or continuous). The following four filter designs are predominantly used in industrial pretreatment:

- Downflow gravity filtration,
- Downflow pressure filtration,
- Upflow continuous backwash filtration, and
- Automatic backwash, shallow-bed filtration.

Filter Backwash. As a filter run progresses, the filter media fill with solids, causing the hydraulic head loss through the filter to increase. In gravity filters, the water surface rises. In pressure filters, the backpressure feeding the filter increases. In both cases, the increasing pressure drives trapped solids deeper into the filter bed until they eventually appear in the filter effluent (i.e., solids breakthrough). To prevent solids breakthrough and keep head loss within reason, the filter must periodically be backwashed (flow reversed through the filter). Typically, the design backwash flow rate is intended to expand the filter media by 10%. The precise flow rate is a function of wastewater temperature and media size; hotter water requires a faster backflow rate.

The backwash process is typically triggered in the following ways:

- Automatically, when the head loss reaches a predetermined point;
- Automatically, when the filter has run for a predetermined time without reaching the head loss limit (typically 24 hours);
- Manually, when an operator initiates the backwash cycle.

Filter Operating Characteristics and Design Considerations. *Conventional Downflow Gravity Filters.* Conventional downflow gravity filters are typically used in large municipal water and wastewater treatment plants and, to some extent, industrial pretreatment facilities (Figure 9.12). They can be procured in steel package plants or custom-designed and made of concrete.

The flow rate through these filters can be constant, or vary based on time or head loss. Backwashing is intermittent, as required to maintain filter performance. Although dependent on solids loading, backwashing should occur at least once a day, using filtered water at five to six times the filtration rate for short periods (typically 12 to 15 minutes). Spent backwash water is typically sent to the head of the pretreatment system.

While backwash water *volume* is typically small (3 to 5% of the total volume of filtered water), the high backwash water flow *rate* can cause hydraulic and performance

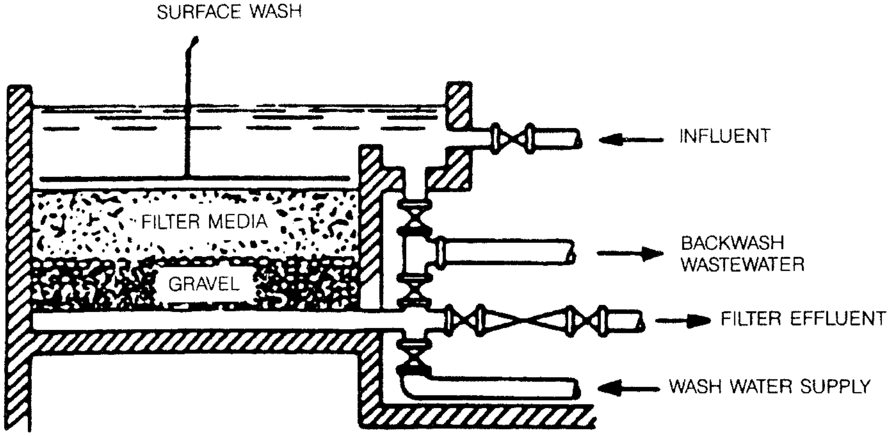

FIGURE 9.12 Cross section through a typical gravity filter.

problems in the pretreatment system. So, downflow gravity filter systems often consist of multiple units to minimize the effects of:

- Flow increases to the operating filters when one is taken out of service for backwash; and
- High spent-backwash flow rates on the pretreatment system.

However, the need for multiple units and the high backwash rates often make these units unacceptable for industrial pretreatment.

Downflow Pressure Filters. Downflow pressure filters are similar in configuration and design to gravity filters, except that the filtration vessel is closed and pumps typically provide the driving force (Figure 9.13). Pressure filters typically operate to higher head losses before backwashing, resulting in longer filter runs and smaller backwash volumes. However, they have the same high-backwash-rate issues as downflow gravity filters, requiring multiple units and equalization of spent backwash flow rates.

Pressure filters are made of steel and are typically procured directly from a manufacturer rather than custom-designed and constructed. They work best at lower flow rates [e.g., 75 to 1500 L/m (20 to 400 gal/min)], although larger sizes are available.

Upflow, Continuous Backwash Filtration. In an upflow, continuous backwash filter (Figure 9.14), the wastewater enters the bottom of the filter via a flow-distribution device and rises through sand media fluidized by compressed air. As the sand falls, it removes particles from the rising water. Clean filtrate is removed across a weir in the top of the filter.

FIGURE 9.13 An example of a typical pressure filter system (courtesy of Hoffland Environmental, Inc.).

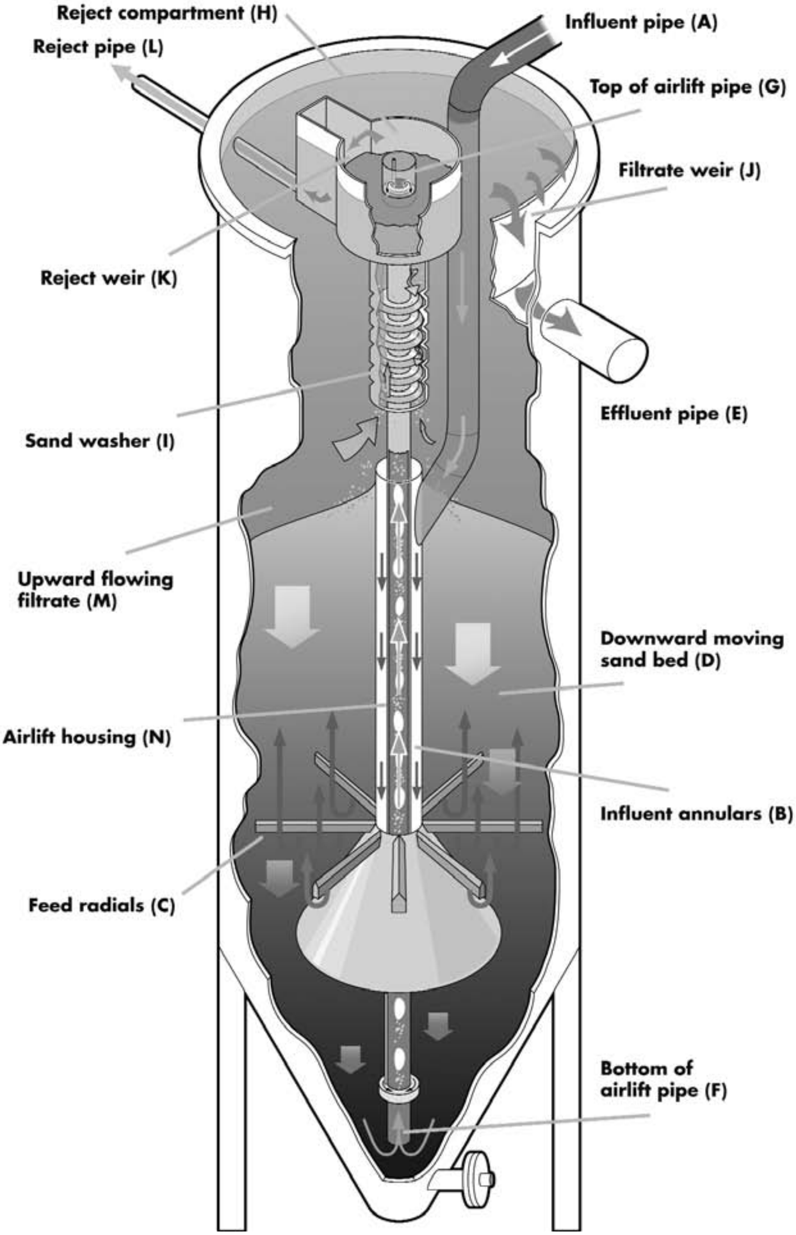

FIGURE 9.14 A schematic of a DynaSand® upflow, continuous backwash filter (Courtesy of Parkson Corporation, Fort Lauderdale, Florida).

The sand media and trapped particles are drawn into an airlift, where the particles are scoured from the sand as both rise in the airlift pipe. The particles are removed at the top of the chamber, and the cleaned sand is returned to the sand bed.

These filters typically operate at a constant rate, depending on the influent pumping scheme. They have similar loading rates as conventional downward filters, and produce similar spent-backwash volumes, but at a much lower backwash flow rate. So an industrial facility could use one or two units to handle all flows, without having large backwash rates and without requiring equalization of spent backwash water.

The filters are made of steel and are typically procured from equipment suppliers, rather than custom-designed. Their flow capacities range from 50 to 4500 L/m (14 to 1200 gpm).

Automatic Backwash Filtration. Automatic backwash (ABW) filters are also called traveling-bridge filters because of the mechanism that operates on a track above the filter (Figure 9.15). This type of filter is segmented into a series of small cells that are individually backwashed, as needed, by the traveling overhead assembly. It typically has a shallow media bed [media depth of about 280 mm (11 in.)], which keeps head losses low and may eliminate a pumping step. The flow to the filter is at a constant rate.

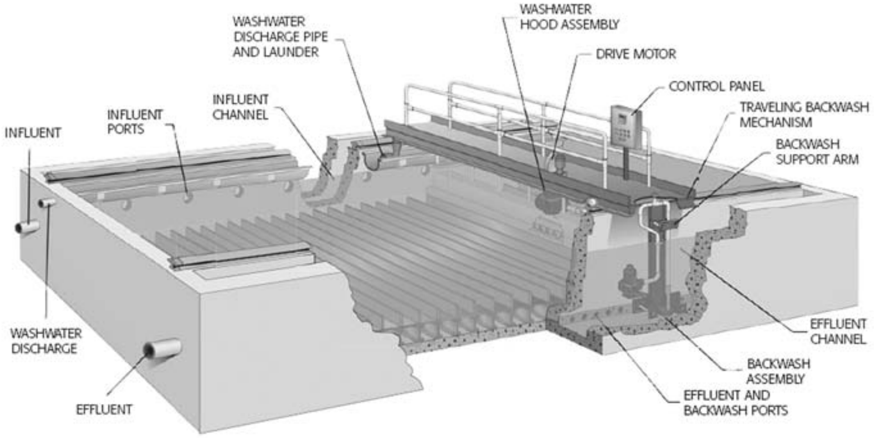

FIGURE 9.15 A schematic of an automatic backwash filter (courtesy of Degremont Technologies—INFILCO).

Table 9.2 Summary of typical industrial filter design criteria—single media.

Parameter	Downflow, gravity	Downflow, pressure	Upflow, continuous backwash	Automatic backwash
Media type	Sand	Sand	Sand	Sand
Media effective size (mm)	0.45–0.65	0.45–0.65	0.6–1.0	0.45–0.65
Media uniformity coefficient	1.2–1.6	1.2–1.6	1.2–1.6	1.2–1.6
Media depth [mm (in.)]	900 (36)	900 (36)	1000 (40)	280 (11)
Filtration rate [L/m^2·min (gpm/sq ft)]	200 (5)	400 (10)	200 (5)	80 (2)
Backwash rate [L/m^2·min (gpm/sq ft)]* (assumes surface wash or air scour)	400 (10)	400 (10)	10 (0.25)	800 (20)

The traveling backwash assembly is controlled by a programmable logic controller (PLC). The backwash cycle can be initiated manually or by the PLC based on time or head loss (water level). As with the upflow, continuous backwash filter, spent backwash flow rates are low.

These prefabricated steel filters have capacities ranging from 1400 to 7570 L/m (375 to 2000 gpm). Custom versions may be installed in concrete basins, with no practical flow limit. For recommended design criteria, see Table 9.2 and Table 9.3.

Table 9.3 Summary of typical industrial filter design criteria—dual media.

Parameter	Downflow, gravity	Downflow, pressure	Upflow, continuous backwash	Automatic backwash
Media type(s)	Coal/sand	Coal/sand	Sand	Coal/sand
Effective size (mm; sand/coal)	1.3/0.65	1.3/0.65	0.65	1.3/0.65
Uniformity coefficient (sand/coal)	1.5/1.5	1.5/1.5	1.5	1.5/1.5
Media depth [mm (in.); sand/coal]	600/300 (24/12)	600/300 (24/12)	750/900 (30/36)	200/200 (8/8)
Filtration rate [L/m^2·min (gpm/sq ft)]	200 (5)	200 (5)	200 (5)	80 (2)
Backwash rate [L/m^2·min (gpm/sq ft) (assumes surface wash or air scour)	800 (20)	800 (20)	4000 (100)	800 (20)

Note: The filtration rate assumes a water temperature of 25° C (77° F). Higher temperatures require higher backwash rates. A 1° C increase in water temperature requires an approximately 2% higher backwash rate.

Precoat Filtration. A pre-coat filter is typically a rotary drum vacuum filter that has been modified to handle wastewater containing fine or gelatinous solids. These filters also are used for "sticky" and other difficult-to-filter solids.

The filter media are coated with a layer of porous filter aid (e.g., diatomaceous earth or pearlite). This layer is typically approximately 3 mm (1/8 in.) thick. As wastewater flows through this filter, it leaves behind a thin layer of solids. The solids and a thin layer of filter aid are scraped off the drum, continually exposing a fresh surface of porous material to the wastewater.

A pre-coat filter may operate under pressure, in which case the discharged solids and filter aid collect in the housing and are removed periodically at atmospheric pressure while the drum is being re-coated with filter aid.

Vacuum-type pre-coat filters operate at loading rates of approximately 1.2 to 2.4 $m^3/m^2 \cdot h$ (0.5 to 1.0 gpm/sq ft).

Cartridge Filtration. Cartridge filters are typically upflow filters that use polypropylene cylindrical filter cartridges. Made of stainless steel, they are designed to hold a number of standard cartridges, which are nominally 250, 500, and 750 mm (10, 20, and 30 in.) long and between 70 and 115 mm (2.75 and 4.5 in.) in diameter. The cartridges' pore size ranges from 0.20 to 100 μm. Activated carbon cartridges may be substituted for conventional cartridges when taste, odor, lead, or chlorine removal is desired. Activated carbon also can adsorb toxic chemicals.

Cartridge filters are available in a variety of housings and flow rates [from 110 to 3000 L/m (30 to 800 gpm)]. They are widely used in industrial applications (e.g., process, drinking water, and liquid foods filtration) and in industrial wastewater pretreatment, particularly when suspended solids removal is critical (e.g., metal-finishing wastes).

These filters do not need backwashing. When head loss becomes excessive, the filter cartridge is removed and cleaned, or discarded and replaced. So, multiple units are typically required to ensure continuous service during cartridge replacement. An effective cartridge filter design for a waste stream with significant solids would typically include two filters in series, using both coarse and fine cartridges to extend cartridge life. To maintain process continuity, a four-unit system (two parallel trains of two filters in series) should be considered.

Cartridge filters provide more efficient filtration than bag filters, particularly when finer cartridges are used. They also have lower capital-cost and space requirements than those of granular filters. However, when cartridge replacement and labor costs are considered, cartridge filters may have higher life-cycle costs than granular filters, particularly when treating wastewaters with high solids concentrations.

Bag Filtration. Bag filters are similar to cartridge filters in both design and application. They consist of a stainless steel pressure vessel and fittings with a single or multiple polypropylene, polyester, or nylon filter bag. As with cartridge filters, the bag material must be compatible with the wastewater constituents. Polypropylene bags, for example, are incompatible with benzene, toluene, and xylenes, and may not be compatible with wastewater containing chlorinated solvents and ketones.

Bag filters range in size from 115 to 6800 L/m (30 to 1800 gpm) per vessel, and the bags' pore size ranges from 1 to 800 μm. In addition to solids removal, some bag filters can reduce oil and grease, as well as certain organic compounds.

As with cartridge filters, a flow train of at least two bag filters in series is recommended, using both coarse and fine bags if significant solids are expected. More than one train would be recommended to allow for continuous treatment.

Both bag and cartridge filters are used downstream of granular activated carbon columns to trap any escaped carbon fines and adsorbed organics. They have similar vessel costs, but bags cost less than cartridges. However, cartridges have more surface area than bags, so their run time may be longer. So, overall replacement frequency and costs must be weighed when comparing cartridge and bag filters.

Bag filters have lower capital costs than granular filters and provide comparable solids removal. So, the life-cycle cost of bag replacement and higher labor costs must be weighed against the granular filter's costs of backwashing and occasional filter media replacement.

Indexing Media Filtration. Indexing media filters (Figure 9.16) use a similar media to bag filters, but are intended for high-flow, low-head (non-pressurized) applications where frequent bag changes are impractical. They also can handle higher flows than bag filters.

This filter holds the media on a roll. As the media becomes plugged with solids, the waste stream rises until it activates an adjustable float switch for a conveyor drive motor, which rolls out fresh media and advances the plugged media into a tote box. The system is self-regulating: fluctuations in solids loading are reflected by how often the media roll advances.

FIGURE 9.16 An illustration of an indexing media filter (courtesy of SERFILCO, Ltd.).

SOLIDS HANDLING AND PROCESSING

Once solids have been generated and separated from wastewater, they typically must be further processed before disposal. Further processing is often necessary to reduce the volume for disposal or reuse, to modify the solids to be less odorous, and to kill pathogenic organisms prior to disposal.

Processes may include thickening, stabilization, conditioning, dewatering, heat drying, and volume reduction (Figure 9.17). The specific processes needed depend on the type of sludge [e.g., primary, secondary (biological), chemical, or other residual (e.g., grit, scum, or screenings)] and the planned disposal method.

Handling options must reflect the nature of the solids involved. For example, granular sludge (e.g., pulp and paper sludge) thickens and dewaters easily to 30 to 50% solids (by weight) or more, while biological or alum sludges (which retain water) are difficult to dewater to more than 15 to 20% solids. Also, industrial biological sludges often lack the primary fibrous sludge that greatly improves dewatering performance in municipal sludge, so industrial biological sludges may be the most difficult to handle.

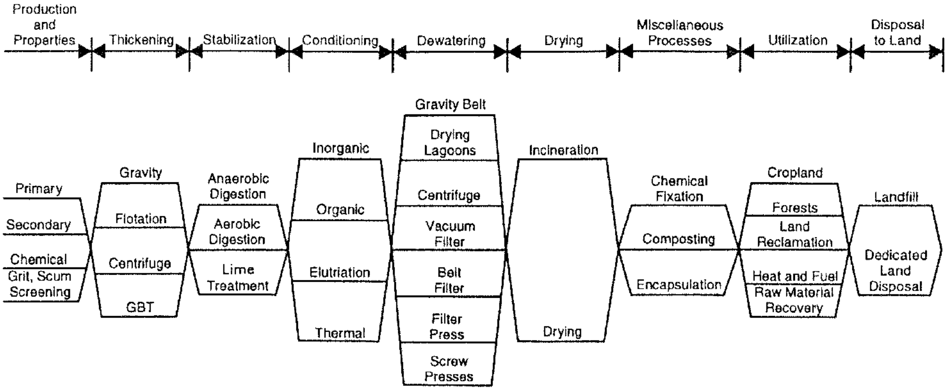

FIGURE 9.17 A classification of the solids-handling and solids-disposal options typically available for pretreatment systems.

Solids handling warrants careful consideration because the associated costs can constitute 50% or more of the entire pretreatment system cost. When choosing solids-handling alternatives, design engineers should consider the following:

- The sludge's properties (e.g., water-retention characteristics, oil and grease content, and hazardous or non-hazardous components);
- Its volume;
- Its solids content;
- Its handling and stabilization needs;
- Local land, energy, and labor costs;
- Local land availability and land-based disposal options; and
- Local, state, and federal regulations for solids treatment and disposal.

Early in the selection and design process, the project team should conduct treatability tests to identify the conditioning requirements and expected performance for each proposed process. However, even if few performance problems are anticipated, minor variations in waste stream composition can significantly alter the solids' characteristics.

SOLIDS CONDITIONING. Conditioning is typically required to improve an industrial sludge's thickening and dewatering performance. There are basically two types of chemical sludge conditioners: inorganic coagulants and synthetic organic polyelectrolytes. Inorganic coagulants (e.g., lime, alum, and iron salts) attract colloidal sludge particles and form an inorganic matrix in organic sludge, making it easier to dewater. However, they substantially increase the solids volume. Synthetic polyelectrolytes, which are typically used in smaller doses, may increase the solids particle size, thereby improving thickening and dewatering. The two conditioners often are used together to optimize dewatering while minimizing chemical costs.

Inert materials (e.g., fly ash, cement kiln dust, sawdust, bentonite clay, carbon-based byproducts, or other industrially generated materials) also may be used to absorb water and increase the solids' structural stability.

Bench-scale laboratory tests are typically necessary to determine the optimum dose and type of conditioning agent(s) required, the sequence in which to add them, and the nature of the material after conditioning.

SOLIDS THICKENING AND DEWATERING. Solids must be thickened (concentrated) and dewatered to comply with environmental regulations and minimize the volume to be disposed. Minimizing solids volume mostly helps to control disposal costs.

Thickening and dewatering are sequential processes: solids are thickened before dewatering because dewatering systems typically perform better if their influent contains more than 5% solids. Thickening processes are typically used on dilute solid streams, say 0.5-3% solids by weight. Typical thickening techniques include gravity thickening, dissolved air flotation (DAF) thickening, centrifugal thickening, rotary drum and gravity belt thickening. The output of a thickening process is typically 2 to 8% solids, depending upon influent solids concentration, chemical conditioning, the nature of the solids, and the process used.

Dewatering processes are typically used on more concentrated solid streams, often after thickening, at say 5 to 15% solids by weight. Typical dewatering techniques include pressure filtration, belt filtration, centrifugation, vacuum filters, screw presses, container filters, geotextiles, sand bed drying and drying lagoons. Although performance depends on the industry and specific technology involved, dewatering processes should yield an effluent that contains from 10 to 18% solids (biological sludges) up to as high as 50 to 60% solids [fibrous sludges (e.g., pulp and paper sludge)].

Thickening. Solids typically are thickened via gravity, flotation, mechanical squeezing, or drainage. Chemicals are often added before thickening to help release water bound in the solids. Thickening processes reduce solids volume before dewatering or disposal, as well as the size of the dewatering process needed. Improving thickening performance also typically reduces dewatering costs.

Gravity Thickening. Gravity thickening occurs in a circular clarifier with a slowly rotating rake mechanism that breaks up solids bridging and promotes solids settling and compaction.

The most important criterion in thickener design is the surface area required to achieve the desired thickening. It is calculated by establishing a solids loading rate (flux), expressed in kilograms of dry solids fed per day per square meter of thickener surface area (pounds of solids per square foot per day). The appropriate solids loading rate depends on the type of solids to be thickened (Table 9.4).

Effluent water is also pumped to the thickener to enhance thickening and reduce odors. Effluent water rates are typically 24 to 30 $m^3/m^2 \cdot d$ (600 to 750 gpd/sq ft). Effluent overflows the thickener's weirs and returns to the head of the pretreatment facility. Chlorination should be provided, particularly if the solids are biological or biodegradable.

Gravity thickeners typically range from 3 to 30 m (10 to 100 ft) in diameter, with sidewall depths from 2 to 5 m (8 to 18 ft). Gravity thickening is unusual at industrial facilities because of the space requirements, potential for odors, and high recycle flows. They are cost-effective for facilities that generate large quantities of solids (e.g., pulp and paper mills and steel mills).

TABLE 9.4 Typical thickening performance and design loadings for gravity thickeners.

	Solids concentration (%)		
Type of solids	**Unthickened**	**Thickened**	**Solids loading ($kg/m^2 \cdot d$)**
Primary	2–6	5–10	100–150
Chemical primary	4–8	6–8	30–40
Primary + WAS*	2.5–4.0	4–7	40–80
WAS	0.5–1.5	2–3	20–40
WAS—extended aeration	0.2–1.0	2–3	25–40

*WAS = waste activated sludge.

FIGURE 9.18 An example of a dissolved air flotation thickener (courtesy of Hoffland Environmental, Inc.).

Dissolved Air Flotation. Dissolved air flotation (Figure 9.18) involves pressurizing liquid (in thickening applications, this is typically clarified subnatant) and mixing it with influent sludge. When the mixture is released into a circular or rectangular flotation tank under atmospheric pressure, small air bubbles form that attach to and become enmeshed in the solids flocs. The bubbles reduce the flocs' specific gravity, so the solids float to the surface and are then skimmed off the clarified wastewater.

Dissolved air flotation typically is used on oily sludges, on very light sludges (e.g., biological sludges), and when space is restricted. Design variables include the air:solids ratio required for effective thickening, solids loading rate, hydraulic loading rate, and the feed solids concentration (Table 9.5).

TABLE 9.5 Summary of design values for DAF solids thickening.

	Solids loading (kg/m^2·d)	
Type of solids	**Without chemicals**	**With chemicals**
Primary	96—144	Up to 300
Primary + WAS*	72—144	Up to 240
WAS	58—72	Up to 240
WAS—extended aeration	58—72	Up to 240

*WAS = waste activated sludge.

Dissolved air flotation typically produces thicker solids than gravity thickening, but it is more mechanically complex, has more operating requirements (e.g., monitoring, maintenance, and chemical handling), and higher chemical and maintenance costs.

Centrifuges. Centrifuges are used to both thicken and dewater industrial sludges. They accelerate sedimentation via circular motion and centrifugal force. There are several types of centrifuges, but the one typically used in industrial wastewater applications is the solid-bowl centrifuge (Figure 9.19).

A solid-bowl centrifuge resembles a rotating horizontal bowl that is tapered at one end. A helical scroll rotates inside the bowl at a slightly different speed. Solids are pumped into the tapered end and, as they thicken, gradually "plough" up the conical "beach." Centrifugal force compacts the solids and expels the surplus liquid known as centrate. The thickened solids are then discharged from the bowl.

Centrifuges can thicken primary sludge to between 6 and 8% solids and waste activated sludge to 2.5% solids. They also can handle large flows, so fewer units are needed. However, they have high energy costs and require abrasion-related maintenance. The automotive and furniture-finishing industries use them to dewater paint sludge. Also, "three-phase" centrifuges separate oily solids into recoverable oil, dewatered solids, and water (for more information, see Chapter 10).

Gravity Belts Thickeners. Gravity belt thickeners (GBTs) are common and cost-effective thickeners. In the GBT process, the solids are placed on a moving porous belt, through which the water drains. Conventional coagulation and flocculation

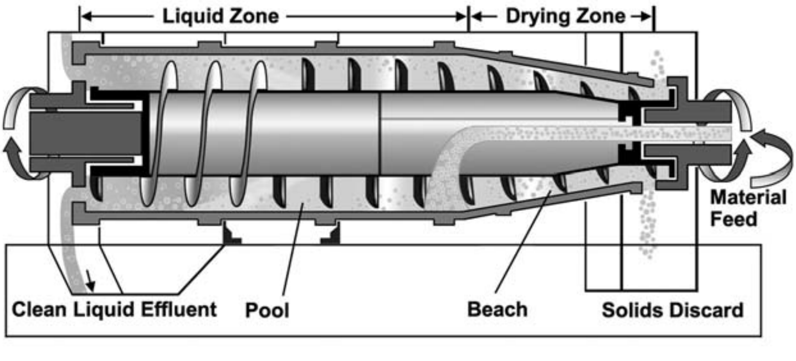

FIGURE 9.19 A schematic of a centrifuge (courtesy of Sweco, A Business Unit of M-I L.L.C).

techniques are used to free bound water from the solids. Chicanes (or plows) fitted on the press repeatedly turn over the solids to release more water through the permeable belt. The thickened material typically contains 4 to 8% solids.

Gravity belt thickeners are often less costly than other thickening options and produce comparable results. The units are typically sized based on solids loading, which is based on the type and solids content of the solids to be thickened. Fibrous sludges, which release water easily, may be loaded at higher rates than biological sludges, which are more gelatinous and difficult to dewater.

Solids-specific pilot testing is recommended, but if this is impossible, then a hydraulic loading rate of 600 to 800 L/m (150 to 200 gpm) per meter of belt width is recommended. Gravity belt thickeners are available in widths of 1 to 3 m (3 to 10 ft), with a maximum unit flow capacity of about 2800 L/m (750 gpm). Design solids loading rates can range from 200 to 600 kg/hr/m belt width (440 to 1300 lb/hr/m). Polymer is typically added to gravity belt thickeners at a rate of 1.5 to 4.5 kg/tonne of dry solids (3 to 10 lb/ton of dry solids), with higher rates used for waste activated sludge.

Rotary Drum Thickeners. A rotary drum thickener (RDT) is another thickening device. (Figure 9.20). The RDT functions much like the rotary drum screens discussed earlier in this chapter. Rotary drum thickeners consist of a rotating drum to which the chemically conditioned sludge is applied (typically to the inside of the drum). Solids are conveyed through the drum via a helical screw or gravity (by inclining the drum), and thickened sludge is discharged out the end of the drum. As water separates from the solids, it passes through the mesh screens and is returned to the head of the treatment plant. Water sprayed on the rotating screen removes any solids stuck to it and also passes through the screen.

The drum design is a function of the type of solids and concentration and is typically provided by the manufacturer for the specified condition. The RDT can thicken primary sludge up to 7 to 9% solids, and somewhat less when mixed with waste activated sludge. When thickening waste activated sludge alone, the RDT can achieve thickened solids concentrations of 4 to 9% solids, depending upon the feed solids concentration.

Compared to gravity belts, rotary drums are somewhat less efficient but have lower capital costs and similar operating costs, but need less space and operator attention.

Dewatering. Solids' moisture content must typically be reduced before it is incinerated or landfilled. Solids typically are thickened before they are dewatered.

FIGURE 9.20 An example of a rotary drum thickener (courtesy of Vulcan Industries, Inc.).

A thickened, dewatered cake will contain between 10% and more than 50% solids (depending on the type of industrial sludge involved). Common dewatering options include centrifuges, belt filter presses, pressure filters, screw presses, vacuum filters, geotextiles, and container filters.

Centrifuges. Centrifuges are used in certain industries (e.g., food and beverage, pharmaceutical, and chemical) to dewater solids (Figure 9.19). This is a complex technology that requires trained personnel to operate efficiently. Centrifuges also are relatively expensive to build and operate (e.g., high electrical, chemical, and maintenance costs). However, they may be the most appropriate technology for larger facilities with high solids loadings and high levels of FOG.

Most centrifuges are "two-phase" machines that separate solids and water. Special three-phase centrifuges are used to separate solids, water, and oil (for more information, see Chapter 10). A centrifuge's specific dewatering performance depends on the type of solids and the amount of prior thickening and chemical conditioning. The resulting cake can vary widely, between 15 and 35% solids, depending largely upon the characteristics of the feed solids, chemical conditioning, and operator skill.

Belt Filter Presses. Belt filter presses are widely available, widely applied, and relatively inexpensive to install (Figure 9.21). However, their operating costs (e.g., chemicals, labor, and periodic belt replacement) are significant.

Most belt filter systems consist of three stages: chemical mixing and conditioning, thickening via gravity, and dewatering via roller-based compaction. After chemical conditioning, the solids are placed on a moving belt, through which free water drains by gravity. After the free drainage zone, the solids are sandwiched between two belts and further compacted via the increasing pressure of rollers on the belts. Afterward, the two belts separate, and the solids drop into a hopper or a conveyance system.

Important design parameters for belt filter presses include chemical conditioning requirements, hydraulic and solids loading limits, and belt wash water requirements. The belts range from 0.5 to 3.5 m wide and are available in various weave patterns designed for specific types of sludges. The solids-loading and performance rates depend on the type of sludge involved (Table 9.6). Mining, pulp and paper, and textile sludges, for example, may produce dewatered cakes with exceptionally high solids concentrations.

As with centrifuges, a belt filter press's specific dewatering performance depends on the type of solids and the amount of prior thickening and chemical conditioning. The resulting cake is typically 18 and 25% solids, depending largely upon the characteristics of the feed solids and chemical conditioning.

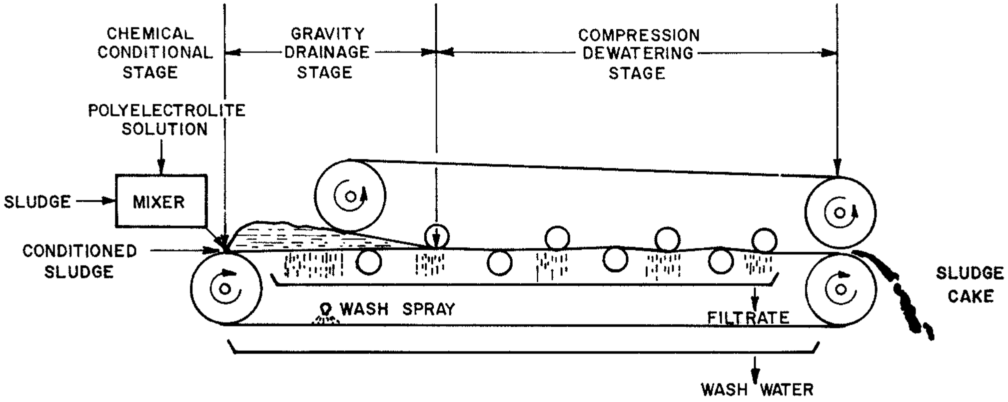

FIGURE 9.21 A schematic of a belt filter press.

Table 9.6 Design and typical performance data for belt filter presses (adapted from Metcalf & Eddy, 2003).

Type of solids	Dry feed solids (%)	Design loading (kg/m^2·d)	Dry polymer (g/kg dry solids)	Typical cake solids (%)
Raw primary (P)	3–7	360–550	1–4	28
Waste activated sludge (WAS)	1–4	45–180	3–10	10–15
P + WAS (50:50)	3–6	180–320	2–8	15–20

Recessed-Plate Filter Presses. Recessed-plate filter presses are a good choice when the dewatered sludge cake must have a high solids content, typically greater than 40% by weight (Figure 9.22). Also known as plate and frame presses, this technology is popular in industries that use heavy metals (e.g., plating and printed-circuit board manufacturing) and pay a premium to dispose of sludge in a secure landfill.

The process begins with high-pressure pumps that initially fill the press with solids, conditioned with an appropriate coagulant and polymer (Figure 9.23). Continuing feed pump pressure forces water from the sludge through the filter media. Filtrate then flows through flow passages formed on the plate surface or in open-mesh underdrain chambers to outlets in the filter plate.

Figure 9.22 An example of filter presses at a steel works plant (courtesy of Siemens Water Technologies).

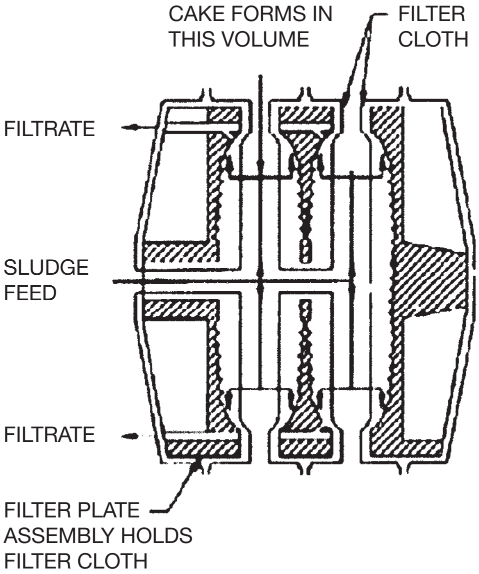

FIGURE 9.23 A schematic of a filter press plate.

A variation on the fixed filter media press is the "diaphragm press," or variable-volume press. An air- or water-actuated bladder or membrane behind the filter media increases the pressure to remove even more water from the sludge.

Once no more water can be forced from the sludge, the cycle is ended. The filter chambers are blown down with compressed air. The filter chambers are then opened, one chamber at a time, to discharge the filter cake to a hopper or conveyor belt. Cycle times range from 2 to 8 hours, depending on the type of sludge involved. Pilot testing is typically recommended to establish optimal chemical doses and cycle times.

If the sludge is difficult to dewater, the filter media may be coated with diatomaceous earth to increase the cake's achievable solids content. These systems operate at pressures ranging from 340 to 1550 kPa (50 to 225 psi).

Another option is to add inert materials (e.g., lime or silica) to the sludge to improve dewatering and reduce sludge "stickiness." However, the amounts needed can be significant, increasing the volume of sludge to be transported and disposed.

Pressure filtration typically can produce a cake containing 35 to 60% solids. However, the system is expensive and labor-intensive.

When designing a pressure filter, engineers first determine the quantity of sludge to be processed per cycle (9.5 Metric units) (9.6 English units):

$$Cu\ M\,Cake = \frac{(Total\,Cu\,M\ \ Liquid\,Per\ \ Cycle)(\%\ \ Solids)(Specific\ \ Gravity\ \ of\ \ Slurry)}{Sludge\ \ Cake\ \ Density,\ \ Kg\,/\,Cu\,M}(1{,}000) \tag{9.5}$$

$$Cubic\ \ Feet\ \ Per\,Cycle = \frac{(Total\ \ Gallons\ \ Per\ \ Cycle)(\%\ \ Solids)(8.34)(Specific\ \ Gravity\ \ of\ \ Slurry)}{Sludge\ \ Cake\ \ Density,\ \ lb\,/\,cu\ ft} \tag{9.6}$$

The specific gravity of liquid sludge typically ranges from 1.01 for biological sludges to 1.06 for chemical sludges. Sludge cake densities typically range from 240 kg/m^3 (15 lb/cu ft) for biological sludges to 400 kg/m^3 (25 lb/cu ft) for metal hydroxide sludges, excluding the effect of any additives.

As an example, to calculate the volume of a sludge press, assume the following conditions:

Projected sludge flow = 37.9 m^3/day (10 000 gpd)
Projected sludge concentration = 6% solids,
Specific gravity of feed sludge = 1.02,
Sludge cake density = 320 kg/m^3 (20 lb/cu ft), and
Assumed cycle time = 3 hours.

Then

$$Cu\ M\,Cake = \frac{(37.9)(0.06)(1.02)}{320}(1{,}000) = 7.2\ \ Cu\ M$$

$$Cubic\ \ Feet\ \ Per\,Cycle = \frac{(10{,}000)(0.06)(8.34)(1.02)}{20} = 255\,Cu\ Ft$$

If the facility wanted to run one cycle per 8-hour day and allow for cleanup, a 7.2- m^3 press (minimum capacity) must be provided. If the facility planned to run two cycles a day (19 m^3/cycle), a 3.6- m^3 press (minimum capacity) would be needed for two 3-hour cycles. Peak sludge days and press downtime must also be considered when sizing the press.

One proprietary system combines a pressure filter and a vacuum evaporator to produce almost completely dry sludge. The sludge is first dewatered to conventional levels in a filter press. Then, pressurized 80° C (180° F) water is pumped into the press chambers and evaporated under vacuum conditions (so water can evaporate at lower temperatures). The additional dryness is adjustable, depending on the additional cycle time used. This system may be useful for several industries (e.g., food and beverage, petroleum and petrochemical, pharmaceuticals, and metal-finishing).

Screw Presses. Screw presses typically are used to dewater pulp- and paper-manufacturing sludge. They are less effective for sludges with high volumes of biological solids.

In a screw press system (Figure 9.24), feed sludge enters the inlet and moves from a low-pressure (gravity drainage) zone to a high-pressure zone via a screw, which rotates at 0.5 to 6 rpm. The change in pressure gradient is controlled by the backpressure generated against the screw via a choke plate at the discharge end of the screw. Some screw presses have a steam-injection port at the inlet end of the unit. The steam is pressurized to between 7 and 345 kPa (1 and 50 psi) and applied to the screw to improve the sludge's dewaterability.

Before being introduced to the screw press, the sludge typically is thickened using polymers or alum. Polymer dosages range from 2 to 10 kg (4 to 22 lb) per ton of solids. Screw presses typically produce a cake containing 50 to 60% solids, thereby

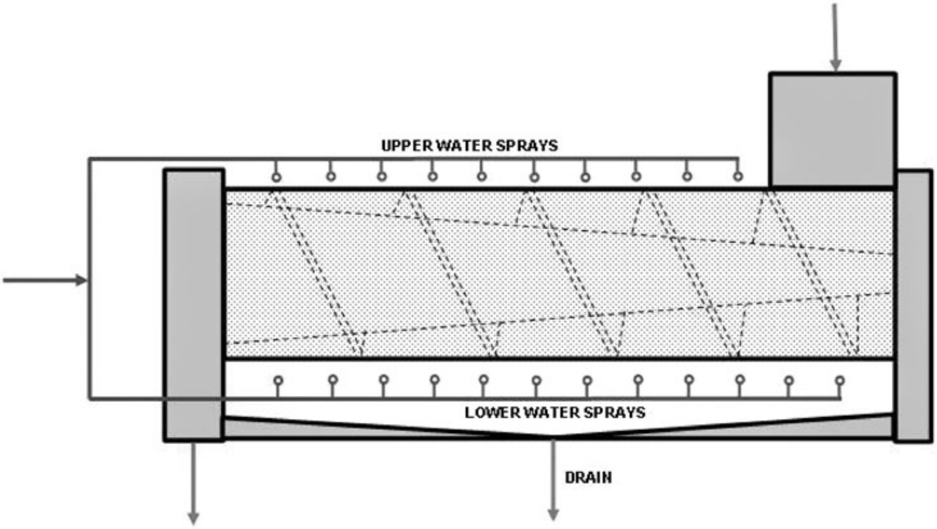

FIGURE 9.24 A schematic of a screw press.

lowering transportation and disposal costs. However, their capital costs are high, and they require more operational control.

Vacuum Filters. An older technology, vacuum filters are still used by industries with oily sludges (e.g., pharmaceutical, refinery, and food processing). In this process, a vacuum is applied to a large rotating drum that is typically covered with a polypropylene cloth. The drum rotates continuously through a vat of sludge, which it picks up and dewaters via its movement. At the end of each rotation cycle, the dewatered sludge is removed from the drum by a cutter blade and discharged to a container or conveyor. Filtrate and air flow through internal pipes and a rotary valve into a vacuum receiver, where the liquid is separated from the gas stream.

Industries that may benefit from using vacuum filters with pre-coat such as diatomaceous earth are:

- Corn syrup manufacturers,
- Fruit juice manufacturers,
- Wine producers,
- Pharmaceutical manufacturers,
- Petrochemical industries,
- Other food processors.

Vacuum filters are designed according to the type of sludge to be processed. Design loading rates are typically 7 to 12 $kg/m^2 \cdot h$ (1.5 to 2.5 lb/hr/sq ft) for difficult-to-dewater sludges, and 20 to 40 $kg/\ m^2 \cdot h$ (4 to 8 lb/hr/sq ft) for easier sludges.

Container Filters. A container filter is a combination of dewatering technologies in a simple roll-off container (Figure 9.25). This filter has three components: the container, the walls (which can be porous), and a porous floor. It operates on a batch basis. Sludge is pumped into the filter, and liquid drains via gravity through the floor and walls (if porous) to a cavity under the floor. (A vacuum pump may be added to speed the dewatering process.) The water is then pumped from the filter. When the sludge cake is dry, the filter may be picked up by a typical container truck, hauled to a dump site, emptied, and returned.

The filters range from 3.8 to 30 m^3 (0.5 to 40 cu yd). The filter media are available in stainless steel, nylon, polyester, and polypropylene, as well as materials that can handle oily wastes. The media's pore sizes range from 44 to 4,750 μm.

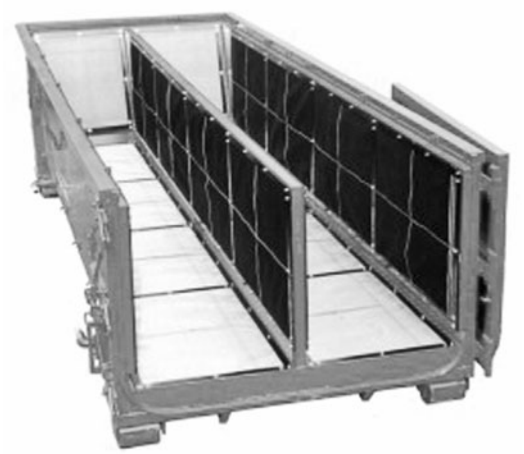

Figure 9.25 An example of a container filter (courtesy of Flo Trend Systems, Inc.).

The technology is simple, inexpensive, and best suited for relatively small waste generators. It has been used extensively at oil facilities and power plants (to dewater fly ash).

Geotextiles. Geotextile materials are a newer method for dewatering industrial sludges and sediments (Figure 9.26). In this process, sludge is conditioned with coagulants or flocculants and then pumped into a geotextile tube, which can be made to virtually any length.

Sludge remains in the tube for up to several months, depending on the type of sludge (e.g., suspended solids, fines, and bound water concentrations). Filtrate leaches from the geotextile into a confined area and then is treated or discharged. When the dewatering is complete, the geotextile is cut and the sludge is removed for disposal. The geotextile's dewatering performance is similar to those of the other dewatering methods in this section. The filtrate quality is similar to that of filter presses.

Sand Drying Beds. Facilities in rural areas that generate a relatively small amount of sludge may find sand drying beds an attractive dewatering option, especially if capital costs are a major concern. Drying beds are also popular in warm climates. In fact, most existing drying beds are in warm-weather areas.

FIGURE 9.26 An example of a typical geotextile system (Geotube®) (courtesy of TenCate™ Geosynthetics North).

Typically, 200 to 300 mm (8 to 12 in.) of wet sludge is applied to a sand bed and allowed to dry until it can be removed by pitchforks or front end loaders. The water leaves the sludge via percolation and evaporation. To reduce the drying time, the sludge can be chemically conditioned or special drying beds (e.g., vacuum-assisted, artificial media, and enclosed) can be used.

The principal difference between sand drying beds and mechanical dewatering systems is the significant influence of climate on system design and performance. However, the area required and the potential for odors can make them less attractive to industrial facilities.

Lagoons. Lagoons may be the simplest method for thickening, dewatering, and storing sludge. They treat sludge via evaporation. However, odors may be a problem, depending on the type of sludge involved. This method is popular in the pulp and paper industry.

Lagoon systems used only for dewatering typically have two treatment cells. Sludge is sent to one lagoon for several months. Then this lagoon is allowed to rest while a second lagoon is filled. Then, the second one rests while the first is used again. Solids loadings of 36 to 39 kg/m^3/yr (2.2 to 2.4 lb/cu ft/year) are suggested for biological sludges. If used for storage, sludge lagoons can vary significantly, though depths of 3 to 5 m (10 to 16 ft) are typical.

DRYING. Reducing sludge volume has become more important for industry, as sludge disposal costs have increased. Also, the U.S. Environmental Protection Agency (U.S. EPA) has designated drying as a *process to further reduce pathogens* (PFRP). To meet this PFRP designation, the sludge must be heated to more than 80° C (176° F), or the wet bulb temperature of the gas stream in contact with the sludge when it leaves the dryer must be more than 80° C (176° F). Also, the dried sludge must contain 10% moisture or less. Industrial solids that have been treated in a PFRP and that meet the 40 *CFR* 503 metals and nutrient criteria can typically be land-applied under most beneficial-use programs.

Several industries (e.g., pulp and paper, metal-finishing, chemical, pharmaceutical, and specialty steel) dry their sludge. In the pulp and paper industry, for example, dried biosolids are land-applied to forests or, because of its high concentration of volatile compounds, burned with bark or another solid fuel to produce steam and energy. The metal-hydroxide sludge produced by metal-finishing and steel industries is often hazardous; drying this sludge reduces its volume and, therefore, its handling and disposal costs.

The two major sludge-drying methods are direct-fired convection and indirect heat. In direct-fired convection, heated air or flue gas is passed over the sludge to evaporate water. The resulting gas-vapor mixture then is discharged to the atmosphere or (more commonly) scrubbed or condensed and returned to the wastewater treatment system. Direct-fired dryers include rotary-driven, flash, tray, fluid-bed, and belt.

In indirect heat drying, a heat exchanger and a heat source (e.g., steam, thermal oil, or hot air) are used. The heat source does not directly touch the sludge. Indirect dryers include thin-film, screw, paddle, and disc. A thin-film drying system, for example, uses a two-stage dryer. Dewatered sludge is pumped to the first stage, where it is dried to 40 to 65% dry solids in typically 5 to 10 minutes. Then, the sludge is sent to the second stage, which turns the material into pellets or granules (containing more than 90% dry solids) in approximately 1 to 2 hours. The water evaporated from the sludge is condensed and returned to the wastewater treatment process.

The choice of drying method depends on the nature of the sludge (solids content, volatile compounds content) and the availability and cost of energy. Direct-fired dryers are more efficient but create more off-gas and vapor than indirect dryers. If the sludge contains hazardous volatile materials, off-gas treatment costs make indirect dryers more attractive. Also, indirect systems recover heat, thereby reducing the overall energy input. [For more information on thermal dryers, see the *Design of Municipal Wastewater Treatment Plants* (WEF, 1998).]

COMPOSTING. Composting is a biological stabilization process used with certain in-process industrial wastewater solids from side streams for which beneficial use is possible. Composting typically is used for solids generated in the food, pharmaceutical, and pulp and paper industries.

In this process, dewatered sludge is mixed with a bulking agent (e.g., wood chips, sawdust, or previously composted biosolids) and allowed to further decompose. Composting is an aerobic biological process requiring a continuous supply of oxygen, provided either by frequent turning or mechanical blowers. The bulking agent enables air to flow uniformly through the pile.

The microbial decomposition generates heat, raising the materials' temperature to between 55 and 60° C (131 and 140° F). The solids' weight typically drops by more than 50% via evaporation and destruction of biodegradable solids.

The three most common types of composting systems are:

- Enclosed mechanical systems,
- Windrows, and
- Aerated static piles.

Enclosed mechanical systems are typically used for municipal wastewater solids. They are relatively expensive, complex, and not typically used in industry.

In windrow composting, special equipment turns mounds of the solids-bulking agent mixture about every 2 days by to aerate and expose the entire pile to microbial action. No mechanical aeration is used.

In aerated static-pile composting, mechanical blowers either draw air through or discharge air into the pile of solids-bulking agent mixture via piping underneath the pile. Otherwise, the pile is not moved for the entire 14- to 21-day aeration time.

One concern when composting industrial solids is achieving a proper nutrient balance. Typically, the optimal carbon-to-nitrogen (C:N) ratio is between 20:1 and 30:1. The bulking agent will produce the desired ratio in municipal biosolids, but industrial biosolids may need supplemental nitrogen. Also, toxic organic compounds can inhibit composting. If this is a concern, the project team should pilot test the material before implementing full-scale composting.

Campbell et al. (1991) provides a detailed evaluation of composting pulp and paper biosolids via an aerated static pile. Carr et al. (1990) discuss two successful composting studies for the food industry (an enclosed-mechanical system for poultry-processing waste and a windrow composting system for seafood waste).

For more information on designing each type of composting system, including land requirements, bulking agents, and nutrient requirements, see the *Design of Municipal Wastewater Treatment Plants* (WEF, 1998).

DISPOSAL PRACTICES AND TECHNOLOGY

GRIT AND SCREENINGS. Coarse screens typically collect rags, string, lumber, rocks, leaves, plastics, and facility-specific manufacturing materials. Grit typically consists of heavy, coarse solids (e.g., mill scale, gravel, sand, cinders, nails, and bottle caps), and well as large particles of organic matter. For example, field dirt, vines, leaves, and damaged product are often found in the grit and screenings at fruit and vegetable processors, which use water to both wash the product and move it from delivery to processing.

Although washing grit can reduce its organic content, it is rarely possible to completely separate inorganic and non-putrescible materials from odorous organics. Depending on the industry and waste, grit and screenings may be odorous and attractive to rodents and insects. Grit also can be abrasive and hard to handle in mechanical treatment systems.

Screenings and grit typically are disposed via landfilling or incineration. Incinerating grit and screenings keeps them out of other solids, reduces the disposal volume, and destroys any pathogens they might have contained. Depending on the industry, screenings and grit may contain putrescible materials that, if landfilled, should be covered often enough to meet requirements. Sprinkling with lime may reduce odors from temporarily uncovered solids. Because the residues of incinerated grit and screenings may contain relatively high concentrations of trace metals, facilities may have to take special precautions to landfill the incinerator ash.

CHEMICAL FIXATION. Chemical fixation is a method in which dewatered sludge cake is treated with lime, cement kiln dust, fly ash, or pozzolanic materials (volcanic ash and cement) to immobilize certain materials (typically heavy metals) so they will not leach from the cake after final disposal. These materials increase the sludge's weight and volume, but may be necessary for landfilling.

OILY SLUDGE AND RESIDUES. Oily sludge can be a challenge to handle and dispose. The conditioning, thickening, and dewatering requirements for oil-laden sludge depend on the source of the sludge and whether the oil is petroleum- or food-based. Sometimes suspended solids or chemical coagulants can be separated from sludge, but the dewatered solids typically contain a lot of oil. The disposal options include recovery, incineration, landfilling, and landfarming. Oily sludges are particularly problematic in the steel, refinery, petrochemical, and food-processing industries. The excess oil often prevents the solids from being land-applied or landfilled.

If the oils are being recovered for reuse, they must be separated from suspended solids when the solids make up more than 1% of the solids-oil mixture. Oil may be recovered via conventional clarifiers by heating the oil to approximately 88° C (190° F) for 4 to 6 hours and then settling it for 12 to 24 hours. The clarifier will then have three layers: a layer of clean oil at the top, a layer of secondary oil emulsions (called *rag*) in the middle, and a layer of water-containing soluble oil components, suspended solids, and oils at the bottom. The bottom two layers must be reprocessed or disposed via other methods. [For more information on recovery techniques for oily refinery solids, see the American Petroleum Institute's *Manual of Disposal of Refinery Wastes* (1969). For information on the requirements for sludge with hazardous constituents, see *The Land Treatability of Appendix VIII Constituents Present in Petroleum Industry Wastes* (API, 1984).]

Another effective method of separating and recovering oil from solids is a three-phase centrifuge (Figure 9.27). In this process, oily solids are pumped to a heat tank, where steam is directly injected to raise the solids' temperature to between 82 and 93° C (180 and 200° F). Then, the solids are fed to a special decanter-type centrifuge, which separates the material into oil, water, and dewatered solids. The oil typically is recovered for fuel blending or further refining, or (if food waste) sold to the rendering industry. The resulting solids may be sufficiently oil-free to permit less-expensive disposal options (e.g., conventional landfills or land application). The food industry's high-protein solids may be reused, sold, or given to renderers.

Incinerating oily sludge and then landfilling the ash may be an acceptable disposal method, although many industries avoid incineration because of the costs and environmental permitting issues involved. Fluidized-bed incinerators, rotary kilns, and multiple-hearth furnaces are all effective. Also, waste oils with virtually no suspended material can be incinerated in liquid burners if the waste-disposal regulations are met.

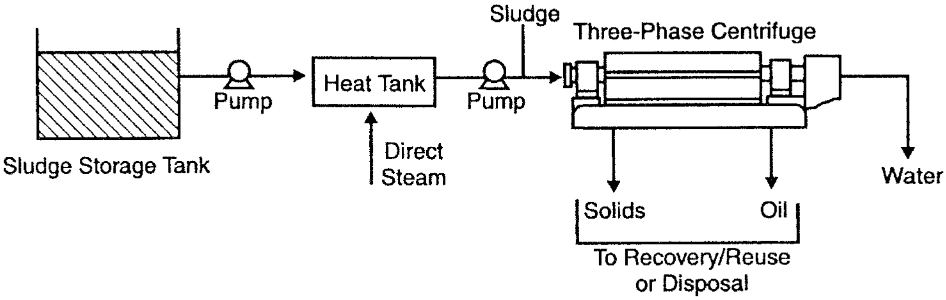

FIGURE 9.27 A schematic of a three-phase centrifuge.

Landfilled waste oils and oily sludge must comply with regulations promulgated under the Resource Conservation and Recovery Act (RCRA). Oily wastewater solids may only be disposed on soil if doing so does not contaminate groundwater or stormwater runoff, or is not a potential seepage problem.

Landfarming is a technique in which soil bacteria degrade oils. It involves spreading oily sludges in 100- to 150-mm (4- to 6-in.) layers, allowing them to dry for approximately 1 week, adding nutrients, and then disking them into the soil. The decomposition rates average 8 $kg/m^3 \cdot month$ (0.5 lb/cu ft/month) without nutrient addition and 16 $kg/m^3 \cdot month$ (1.0 lb/cu ft/month) with nutrient addition.

TOXIC OR HAZARDOUS WASTE. Some industrial sludges are classified as hazardous or toxic wastes in national or local environmental regulations (e.g., U.S. regulations promulgated under RCRA). Others may be classified as characteristic hazardous wastes because they are ignitable, corrosive, reactive, or toxic (as determined by the toxicity-characteristic leaching procedure). Neither characteristic nor listed hazardous wastes may be land-disposed without prior treatment to specific standards (see 40 *CFR* 257 and 40 *CFR* 261).

NONHAZARDOUS WASTEWATER SOLIDS

LANDFILLING. Landfills are designed to bury refuse, solids, and other solid wastes. In this process, solids are put in a prepared site or excavated trench and then covered with a layer of soil. There are three basic types of landfills:

- *Trench.* Trench landfills are used when the groundwater is deep beneath the surface, so the trench will not intersect the water table. The soil removed from the trench is typically used as the cover material.

- *Area.* In an area landfill, the solids are spread and compacted on the ground surface, and the cover soil is spread and compacted over them. The cover soil is brought in from somewhere else.
- *Ramp.* In a ramp landfill, the solids are spread and compacted on a slope, which was dug into the ground, and then covered by soil that was removed when digging the ramp.

When considering the landfill option, the project team must determine the volume of waste to be disposed, the production rate, and the waste's physical, chemical, and engineering properties. With this information, the designer can calculate the space needed, estimate cover requirements (if any), determine personnel and equipment needs, and design the landfill appropriately. Also, industries must comply with the relevant permit or licensing requirements. Performance standards typically address such topics as construction standards and general site-selection criteria. Such permits typically are issued by state regulators.

In addition, the solids must have enough structural stability to be worked conveniently via conventional earth-moving equipment. Solids can be made more structurally stable via dewatering; drying; mixing with dry, absorbent materials; chemical fixation; or a combination of these methods.

LAND APPLICATION. If enough land is available near the industrial site, then biological solids could be land-applied cost-effectively. In this process, stabilized solids (biosolids) in either liquid (2 to 5% solids) or dewatered cake (18 to 25% solids) form are applied to the land via spraying, subsurface injection, or manure spreaders. Nutrients in the biosolids help crops grow. Meanwhile, microorganisms in the soil oxidize constituents in the biosolids, thereby raising the soil's organic content.

To be suitable for this beneficial use, the solids should contain biodegradable constituents and not be subject to significant leaching during degradation. Solids from the food, pulp and paper, chemical, and pharmaceutical industries are good candidates. The land-application principles and design concepts are described in several texts (Crites et al., 2000; Crites et al., 2005).

INCINERATION. Multiple-hearth and fluidized-bed incinerators use thermal oxidation to convert waste into an inert ash and gases. In the process, they reduce the solids' bulk, toxicity, and potential for decomposition. Industries with high-BTU or hazardous wastes are good candidates for incineration.

Although incineration can be more expensive than landfilling or land application, their rising costs and potential long-term liability concerns make incineration an attractive disposal option for sludge with a low metal content. Incinerating sludge with a high metals content will probably produce ash that qualifies as hazardous waste, whose disposal is difficult and costly. [For more information on incineration technologies and design procedures, see the *Design of Municipal Wastewater Treatment Plants* (WEF, 1998). For more information on incineration and hazardous waste disposal regulations, see 40 *CFR* 257, 261 and 266.]

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Chapter 10

Removal of Fats, Oil, and Grease

This chapter examines the need for fats, oil, and grease (FOG) control in industrial wastewater, and the effectiveness and economics of control technologies. Past practices and newer approaches are critically examined so facilities required to remove FOG from their wastewaters can increase the advantages and economic benefits of pretreatment while protecting effluent quality. Pollution prevention options will be considered for some specific references and examples.

FOG CHARACTERISTICS

Fats, oil, and grease may be vegetable-, animal-, or mineral-based. Fats are mixtures of various triglycerides (the glycerol esters of fatty acids). They are found in both plants and animals and are important components of the human diet. Chemists classify fats, oils and greases according to their average molecular weight and degree of saturation. Fats have low, nonspecific melting points (which are lower when unsaturated fatty acid components predominate).

Oils are triglycerides that are liquid at room temperature. Common edible oils include cottonseed, palm, olive, corn, and soybean. Mineral oils include petroleum hydrocarbons (nonpolar FOG). Common fats are lard, tallow, and butter fat.

Soap is formed when animal fat or vegetable oil is boiled with sodium hydroxide (to produce glycerine) and sodium salts of fatty acids. Soaps are included in typical FOG analyses.

Waxes, which are the monohydroxylic alcohol esters of fatty acids, are much harder than fats at room temperature. Their biological function is typically to serve as a protective coating or structural material (e.g., beeswax). Natural waxes contain free acids, free alcohols, and some hydrocarbons. Waxes are included in typical FOG analyses.

Grease is a general classification for such materials as fats, oils, waxes, and soaps based on their physical (semisolid) forms or their effect on wastewater collection and treatment systems.

THE NEED FOR FOG PRETREATMENT

Many pretreatment programs require FOG control because industrial FOG can cause major problems at publicly-owned wastewater treatment works (POTWs). FOG-caused problems include:

- Blocked sewers;
- Excessive floating solids in pumping station wet wells;
- High scum concentrations in primary settling basins, causing carryover to downstream processes;
- Poorer performance of biological treatment processes;
- Coated multimedia and granular activated carbon filters;
- Difficulty thickening and dewatering biosolids; and
- Potential violations of NPDES permits, which prohibit discharges of visible oil sheens and floating solids.

Fats, oil, and grease are primarily regulated at the local level. Many sewer-use ordinances and WWTP discharge permits include FOG limits (either numerical or narrative).

The U.S. Environmental Protection Agency (U.S. EPA) considers animal- or vegetable-based FOG to be a conventional pollutant—along with biochemical oxygen demand (BOD), total suspended solids, pH, and fecal coliforms (U.S. EPA, 2002). The federal regulations that apply to FOG include

- 40 *CFR* 403.5(a)(1), which prohibits any pollutant that can pass through or interfere with WWTP operations;
- 40 *CFR* 403.5(3), which prohibits solid or viscous materials that could obstruct flow in sewers; and
- 40 *CFR* 403.5(b)(6), which prohibits the discharge of petroleum oil, non-biodegradable cutting oil, or products of mineral oil origin that will interfere with or pass through municipal treatment processes.

FOG CHARACTERISTICS

Fats, oil, and grease may be present in wastewater either as free floating oil, in an emulsion, or bound with solids (Table 10.1). Gravity will separate free-floating oils from water because their specific gravities are less than 1. Petroleum-based oils typically can be removed from wastewater by skimming them off the top of sedimentation basins. Such oils originate at refineries, petrochemical plants, steel manufacturers, and industrial laundries.

Emulsified oils are stable oil-water mixtures that typically will not readily separate by gravity without another influence (e.g., heat or de-emulsifying chemicals). Oil-water emulsions may be physical or chemical. Physical emulsions are mixtures of water and heavy oils or greasy materials (typically insoluble in water) that have been created mechanically (e.g., via high-speed, centrifugal pumping). They are less stable (more easily broken) than chemical emulsions, and can be separated via heat or a coagulant [e.g., aluminum sulfate (alum)].

Chemical emulsions are typically found in metalworking fluids used to machine parts in the automotive and machine tool industries. These fluids are mixtures of two immiscible liquids (mostly petroleum and mineral oils and water) that are stabilized by an emulsifying agent. To separate the oil and water, the emulsifying agent must be broken—often with an acid salt (e.g., alum).

Table 10.1 Types of oil in wastewater (adapted from the Arizona Department of Environmental Quality, 1996).

Type	Definition
Free oil	Oil present in water having little if no water associated with it. Separates by gravity.
Physical emulsions	Oil dispersed in water in a stable form as 5–20-μm droplets. Formed by mixing through pumping, piping, and valves.
Chemical emulsions	Oil dispersed in water as <5-μm droplets. Formed by detergents, alkaline fluids, chelating agents, or proteins.
Dissolved oil	Oil that is solubilized in liquid. Dissolved oil is detected by infrared analysis or other means.
Oil wet solids	Oil that adheres to the surface of wastewater or solids.

ANALYTICAL PROCEDURES FOR FOG

To implement an adequate pretreatment program, the project team must know which FOG compounds are in the waste stream. The degree of control, the treatment methods, and the environmental effects depend on the type of FOG involved. Compliance analyses alone may not provide enough data for pretreatment system design or operations.

TOTAL FOG. The U.S. Environmental Protection Agency has approved Method 1664 A, the n-Hexane Extractable Material Method, to analyze FOG in wastewaters. (This method replaced the Freon Extraction Method). It measures FOG as groups of substances with similar physical characteristics based on their common solubility in hexane. The fats, oils, and grease measured via this method may include hydrocarbons, fatty acids, soaps, fats, waxes, oil, and any other material that is extracted by the solvent from an acidified sample and that is not volatilized during the test.

Instrumental techniques (e.g., gas or liquid chromatography) also may be used to analyze FOG, but are not used routinely because of the expense and complexity involved.

FLOATABLE FOG. The “floatable” portion of FOG also can be estimated using Method 1664 A. This bench-scale test approximates the amount of readily floatable material in a sample. The results, while not used for compliance purposes, help determine the potential removal efficiencies of a gravity separator, which can only remove floatable FOG. It also can indirectly monitor a waste stream's potential to obstruct sewers.

In this test, a 1-L grab sample of the waste stream is allowed to settle for 30 minutes in a 300-mm × 70-mm-diameter (11.81-in. × 2.76-in.-diameter) glass tube. Then analysts withdraw the water from the bottom of the tube. The remaining "floatable" material is acidified ($pH < 2$), and then the FOG is extracted with hexane.

SAMPLING. Obtaining representative FOG samples is difficult. Fats, oil, and grease can adhere to various parts of automatic samplers rather than becoming part of the composite samples. Therefore, *grab* samples are taken for FOG analysis rather than composite samples. Samples should be collected and stored in sample containers provided by the laboratory.

Samplers should use a wide-mouth *glass* bottle and collect the sample below the wastewater surface. (Fats, oil, and grease can adhere to plastic.) Samples should not be collected from the overflow or immediately downstream of a weir, where FOG accumulations tend to be sloughed (APHA et al., 2005).

If a FOG sample cannot be analyzed immediately, it should be preserved with a few drops of concentrated sulfuric acid using standard preservation procedures (APHA et al., 2005). Separate samples should be collected for each FOG analysis. A total composite sample should not be subdivided in the laboratory because FOG tends to adhere to the sides and lid of the sampling container, and results may not be representative.

SOURCES OF FOG

FOG typically averages 30 to 50 mg/L in domestic wastewater, and represents as much as 20% of the organic matter measured as BOD. Industrial wastewater typically has higher FOG concentrations (Table 10.2).

FOOD-PROCESSING INDUSTRY. Potential sources of FOG in the food industry include meat processors and renderers, dairy processors, vegetable cookers and processors, edible oil producers, and nut and seed processors. Food-processing wastewater is largely due to cooking, cleanups (e.g., a cleanup shift) and changes in production (e.g., clean-in-place systems at milk producers). These flows often have high FOG concentrations, and show significant variations in flow rate and pollutant

TABLE 10.2 Industries that are major contributors of fats, oil, and grease to wastewater treatment plants.

Industry	Type of FOG
Vegetable oil refining	Vegetable
Soap manufacturing	Vegetable and animal
Milk processing	Animal
Dairy products, including cheese	Animal
Rendering	Animal
Slaughterhouse and meat packing	Animal
Candy manufacturing	Vegetable
Food preparation	Animal and vegetable
Eating establishments	Animal and vegetable
Laundry	Animal, vegetable, and petroleum
Metal machining	Petroleum
Metal rolling	Petroleum
Tanneries	Animal and vegetable
Wool processors	Animal
Petroleum refineries	Petroleum
Organic chemical manufacturing	Petroleum, animal, and vegetable

concentration. Gravity separation, pH adjustment, and coagulation are the most common types of FOG pretreatment in the food industry.

METALWORKING INDUSTRY. There are basically four types of metal-machining fluids (lubricants, coolants, and cutting oils):

- Straight oil (insoluble oils with little or no water);
- Soluble oils (oil-water emulsions);
- Synthetic metalworking fluids (an aqueous mixture of organic compounds); and
- Semi-synthetic metalworking fluids (a hybrid of synthetic metalworking fluid and soluble oil).

Oily wastewater can originate from various sources (e.g., machining plants, stamping plants, and machine shops). Metal pieces that are "worked" in manufacturing facilities such as automobile manufacturing. The metal pieces are frequently covered with machining fluids to cool and lubricate the cutting heads of the tools, as well as to transport metal removed from the piece. Such fluids are settled or filtered to remove metal cuttings, and then are typically reused. Metalworking wastewater consists of spent metalworking fluids, spent wash water, and spills. It is typically de-emulsified onsite before discharge to a municipal POTW.

Metalworking-fluid emulsions are typically treated by using an acid, an acid salt (e.g., alum), or a polymer to break the emulsion so oil and water can separate. Biological treatment also would de-emulsify such wastes. The treatment method depends on the metalworking fluid and is typically recommended by the fluid manufacturer.

Grease applied to metal surfaces for corrosion protection during storage and shipping can also end up in metalworking wastewater. Grease is typically removed via organic solvents or aqueous alkaline cleaning solutions. Vapor or immersion degreasing solvents (e.g., nonflammable chlorinated hydrocarbons or kerosene) can form emulsions or a floating film that may be toxic to microorganisms in POTWs. They also may be flammable or liberate toxic gases, so they cannot be discharged to public collection systems.

PETROLEUM INDUSTRY. Petroleum refinery wastes include free and emulsified oil from leaks, spills, tank draw-off, etc.; chemical treatment-related emulsions; oil-laden condensate; waters from distillate separators and tank draw-off; and oil-laden alkaline and acidic wastes and sludge. The combined refinery wastewater may contain crude oil, various crude oil fractions, or suspended solids coated with oil, soaps, and waxy emulsions. Petroleum FOG also includes light hydrocarbons (e.g., gasoline and jet fuel); heavy hydrocarbon fuels; and tars (e.g., crude oils, diesel oils, lubricants, asphalt, and cutting fluids).

OTHER INDUSTRIES. Other industries that typically generate significant amounts of FOG include industrial laundries, vehicle-washing facilities, iron and steel manufacturers, pharmaceutical manufacturers, aluminum can manufacturers, and printed-wire board manufacturers.

PRETREATMENT TECHNIQUES

In a pretreatment train designed to remove multiple pollutants, the FOG removal system should be installed as close as possible to the source to minimize the places where FOG can accumulate, and to reduce the size of downstream treatment units.

Free (non-emulsified) FOG is easy to remove from water because it floats to the surface and agglomerates, so it can be mechanically skimmed or lifted from the surface.

Emulsified FOG, however, stays in suspension and can be challenging to remove. To prevent free FOG from becoming emulsified, pretreatment system designers should avoid pumping oily wastewater (particularly with *centrifugal* pumps) wherever possible. When pumping is necessary, positive-displacement, *diaphragm* pumps should be considered to reduce the chance of creating physical emulsions. Designers also should avoid diluting FOG-laden wastes with non-FOG waste streams.

Before choosing a pretreatment process for emulsified FOG, system designers should characterize FOG and perform treatability studies. (For more information on treatability studies, see Chapter 5.)

There are two stages of FOG treatment. First-stage treatment separates free FOG from the waste stream. It removes fats, greases, and non-emulsified oils. Effective processes include gravity separation and gravity separation enhanced with coalescing media or parallel plates.

Second-stage treatment involves breaking emulsions and removing emulsified FOG. Emulsions can be broken via heating, distillation, chemical treatment and centrifugation, chemical treatment and pre-coat filtration, and filtration. Ultrafiltration also has been successfully used in cutting oil and fatty acid recovery systems. The most common second-stage system consists of gravity separation; chemical addition (e.g., alum, ferric sulfate, and ferric chloride); flocculation; and dissolved air flotation (DAF).

GRAVITY SEPARATION. Gravity separators range from small packaged restaurant units to large industrial product-recovery systems. One first-stage treatment system is an oil interceptor (grease trap), which is used at commercial establishments with small, intermittent discharges of FOG (e.g., restaurants, hotels, and service stations). Grease traps are designed to collect and retain the FOG typically found in kitchens. They are installed in the drainage system between sink or floor drains and the building sewer. Ideally, they are readily accessible for cleaning and maintenance.

Another first-stage system is a gravity separator with mechanical float removal and waste oil storage. It is used to treat industrial wastes from rendering plants, food processors, and oil refineries. Large separators may be operated on a batch or continuous basis, depending on the volume and type of waste to be treated. In the food industry, the oil may be recovered for reuse or for sale as animal feed. Food-grade materials degrade rapidly, however, so they must be removed and processed daily to be of value to renderers and farmers.

The standard criteria used to design gravity separators was developed and published by the American Petroleum Institute. A gravity separator should provide enough area, quiescent conditions, and time to allow the FOG to float out of the mixture. Major flow changes will affect oil-removal efficiency, so flow equalization may be required to avoid this problem. If steady flow is not anticipated because of other considerations, the trap should be oversized based on the peak sustained flow rate.

When designing a gravity separator, the design engineer must consider the unit's hydraulic capacity, the flow configuration, and cleaning ease and convenience. The distance between the trap's inlet and outlet should be sufficient to prevent grease from escaping via the outlet. This can be calculated by making some assumptions about the oil or grease to be removed, and the use of Stokes' law for a particle's terminal rise velocity. Assuming that the smallest oil globule to be removed is 0.15 mm (0.005 9 in.), the rise rate can be calculated as follows:

$$V_t = 1.224 \times 10^{-2} \left[(S_w - S_o)/\mu\right] \tag{10.1}$$

Where

V_t = rise rate of oil globules of 0.15 mm (0.0059 in.) or more—mm/s

S_w = specific gravity of waste at design temperature;

S_o = specific gravity of oil in wastewater at design temperature; and

μ = absolute viscosity of waste at design temperature—N·s/m.

This calculation is an approximation because it depends on an assumed oil droplet size that may, in fact, vary over time with temperature or the changing nature of the oil.

In gravity separation, a particle's terminal rise rate can be converted to an overflow rate by converting units. So, V_t can be used to design a oil-water separator as follows:

$$V_t = d/t = (d/LBd)/Q_m = Q_m/LB = \text{Overflow rate} \tag{10.2}$$

Where

d = depth of water in separator (m);

t = retention time in separator (seconds);

L = length of separator (m);

B = width of separator (m);

Q_m = waste flow rate (m^3/s); and

V_t = overflow rate ($m^3/m^2 \cdot d$), which is equivalent to the rise rate (m/s) of the smallest particle to be removed.

From the relationship between flow velocity and volume, the overflow rate can be used to estimate the surface area required:

$$A_H = F(Q_m/V_t) \tag{10.3}$$

Where

A_H = minimum surface area for gravity settling (m^2) [this is typically multiplied by a correction factor (F)], and

F = flow short-circuiting and turbulence factor (typically ranges from 1.2 to 1.8); the higher the (V_H/V_t), the larger the value of F.

The following are general rules for good gravity separator design:

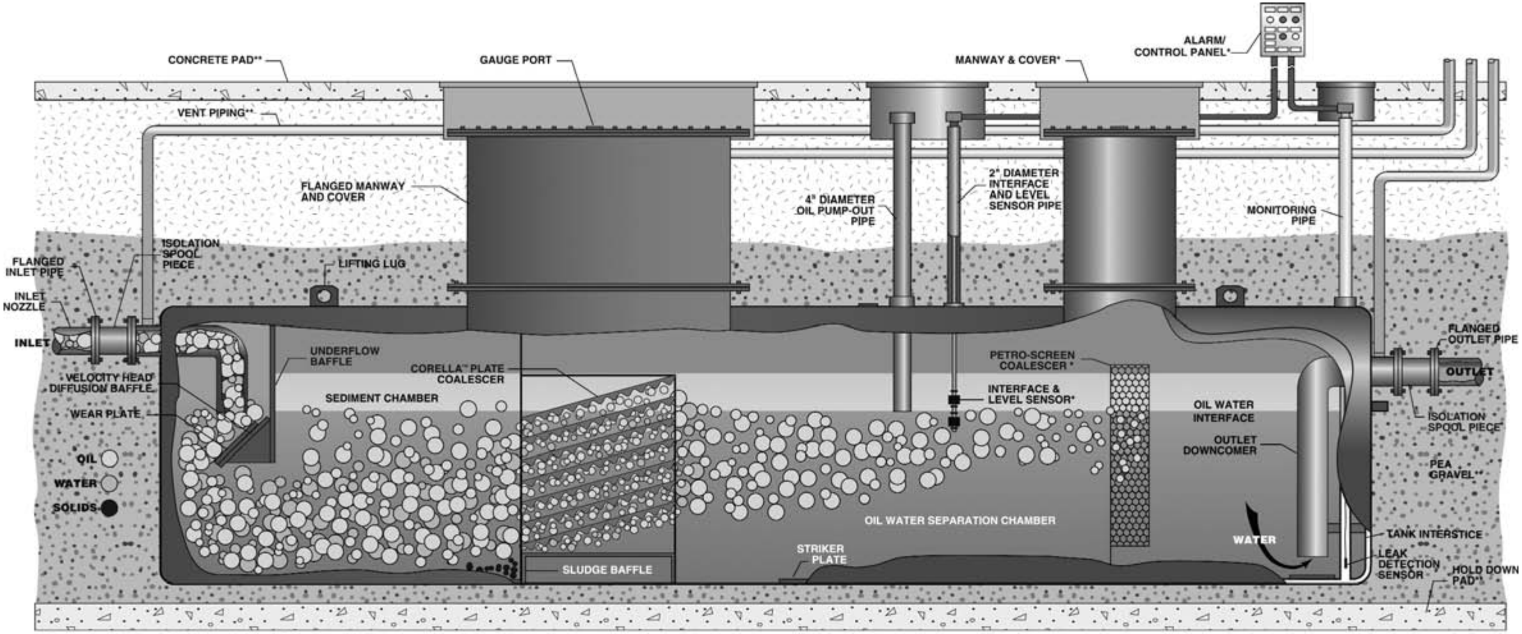
- A minimum cross-sectional area should be used, with a maximum horizontal velocity of 15.4 mm/s (3 ft/min) and a maximum ratio of oil rise rate to horizontal flow velocity of 15;
- The depth should be between 1.22 and 2.44 m (4 and 8 ft); and
- The depth:width ratio should be between 0.3 and 0.5.

Flow-control baffles are essential, and flow-control fittings may be needed on the inlet side of smaller traps to avoid overloading because of sudden wastewater surges. An effluent baffle or other device should be used to retain free-floating FOG. Internal baffling should not be used because it increases turbulence in the tank and may reduce effective surface area.

Coalescing Gravity Separators. There are commercial devices that remove oil from wastewater by passing it through a medium with a large surface area. The medium, often called a coalescer, is typically an oleophilic plastic that is arranged in a honeycomb or parallel-plate configuration. This coalescing oil-water separator (Figure 10.1) is typically best suited for petroleum hydrocarbons that are fluid, with suspended solids concentrations less than 300 mg/L.

As oily water passes through the medium, the oil rises, coalesces on the underside of the plate, creeps up the side, and ultimately rises into the floating oil layer on the surface. Flow continues through another separation chamber before exiting the separator. The combination of agglomeration resulting from flow path disruption, and impact of the oil with the media, causes the oil globules to grow in size. The resulting larger oil globules are removed easily by gravity.

The medium in the unit should be checked to ensure that it will not render the recovered oil unusable. If the captured oil is intended for human consumption or



* Optional equipment available from Highland Tank ** Installer supplied equipment

FIGURE 10.1 An illustration of a typical coalescing separator (courtesy of Highland Tank Co.).

animal feed, the design engineer should ensure that the coalescer is a material approved by the Food and Drug Administration. Also, many animal and vegetable oils are more polar than petroleum oils, so they may adhere to the plastic, thereby fouling the device. Coalescing separators work best with light FOG loads and require more maintenance than simple gravity separators to keep the medium free of blockages.

A number of coalescing separator manufacturers will size a separator based on flow data, oil type, and their own particular design. As a rule of thumb, however, a coalescing separator should be sized at an overflow rate approximately 0.762 $m^3/m^2\cdot d$ (0.013 gpm/sq ft).

Chemically Enhanced Separation. Emulsions are chemically treated to destabilize dispersed oil or destroy emulsifying agents. The process basically consists of rapidly mixing a coagulant with wastewater and then physically separating FOG from it via flocculation, flotation, etc.

The wastewater can be de-emulsified via coagulating salts (e.g., alum, polyaluminum chloride, ferric chloride, and ferric sulfate); acids; organic polyelectrolytes; heat; or salts and heat. Coagulating salts effectively de-emulsify oily wastes, but the precipitated solids may be difficult to dewater before disposal. Supplementing the inorganic salts with an organic polymer can facilitate separation and dewatering.

When acids are used to break emulsions, the clarified wastewater must then be neutralized before it can be discharged to a POTW.

Some organic polyelectrolytes de-emulsify FOG without creating significant excess sludge. In fact, the expense of the polyelectrolytes may be offset by reduced sludge volumes (i.e., lower handling and disposal costs).

The design engineer should conduct batch settling tests before selecting a method. A traditional "jar test" will identify both the type and dose of chemical required to remove FOG. Designers also should monitor the pH during testing for both optimum process control and acceptable discharge levels.

Jar tests may need to be repeated periodically to determine dose adjustments if the waste stream's chemical character changes. If the waste characteristics change rapidly and frequently without warning, equalization should be considered (as well as other treatment options).

If the chemically generated floc is not readily separated via gravity, dissolved air flotation (DAF) or centrifugation can be used. If the floc is unstable, however, these separation techniques will not work effectively.

DISSOLVED AIR FLOTATION. Dissolved air flotation (DAF) is the physical-separation process most often used to remove a chemically concentrated FOG. This process consists of pumping air into a waste stream under pressure, and then releasing the air-charged stream to atmospheric pressure in a tank (Figure 10.2). The oil and small solids cling to the minute air bubbles and float to the surface, where they are removed via skimmers. (For more detail on the use and design parameters of flotation systems with regard to solids handling, see Chapter 9.)

Similar flotation systems include:

- Induced air flotation (IAF), in which air is drawn into the flow via various methods based on venturi principle;
- Cavitation air flotation (CAF), in which a special recirculation pump draws air and recycles flow into the pump volute, uses high shear forces to mix them together, and then discharges the mixture into the flotation vessel;
- Dissolved nitrogen flotation (DNF), in which nitrogen is used in a sealed system to treat mixtures of explosive or volatile hydrocarbons—typically in refineries or petrochemical plants—to minimize the potential for explosion.

The air in a DAF system can be dissolved via direct pressurization or recycle pressurization. Recycle pressurization systems have become more popular because they operate at higher pressures, increasing the volume of air entrained and reducing the flow recycled (Figure 10.3).

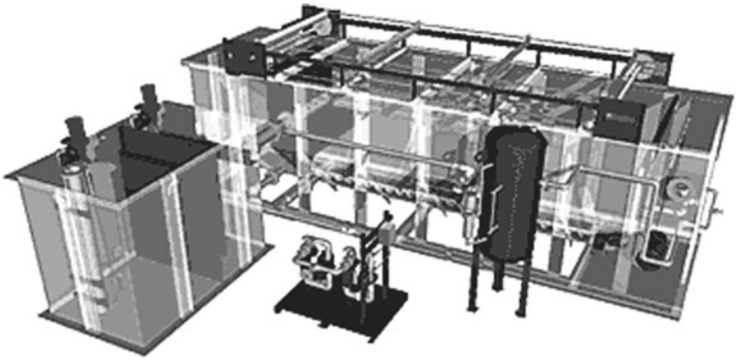


FIGURE 10.2 An illustration of a standard-rate dissolved air flotation unit (courtesy of Ellis Corporation).

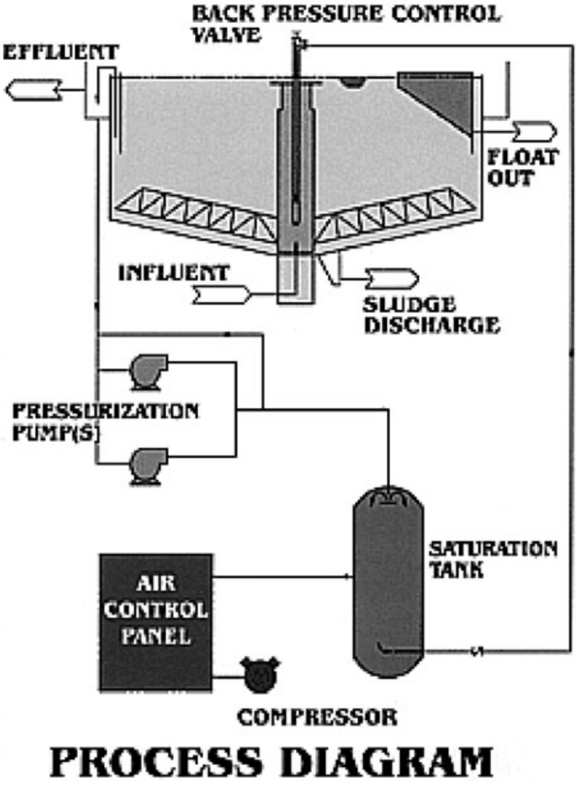


FIGURE 10.3 A schematic of air recycle pressurization for a dissolved air flotation unit (courtesy of Westech Engineering, Inc.).

Recycle pressurization involves pressurizing a side stream of DAF effluent with air before discharging the air-water mixture back into the DAF unit. The recycle pump is often a high-head, turbine pump that can handle air injection at 10 to 20% by volume without cavitating. The recycle pump typically operates at 550 to 825 kPa (80 to 120 psig).

When sizing DAF units, designers should consider the air:solids ratio (A:S); the operating pressure of direct or recycle flows; the pressurized flow rate; influent flow rate; and the air-oil mixture's rise velocity. The following two equations are used to determine the air:solids ratio.

$$\text{Recycle pressurization } A{:}S = [1.3 \times A \times (fP - 1)R]/QS \tag{10.4}$$

$$\text{Direct pressurization } A{:}S = [1.3 \times A \times (fP - 1)]/S \tag{10.5}$$

Where

S = influent suspended solids or FOG concentration (mg/L);
A = air solubility (cm^3/L);
R = pressurized flow rate (m^3/d);
Q = influent flow rate (m^3/d);
P = operating pressure (absolute) measured (atm) {$P = [p$ (gauge pressure, kPa) + 101.35]/101.35}; and
f = fraction of air dissolved at pressure P (typically 0.8).

The proper air:solids ratio depends on the concentration and characteristics of the influent FOG. Laboratory analysts can use a flotation cell to determine the optimal air:solids ratio. In municipal applications, the air:solids ratios typically were between 0.02 and 0.04 (by weight). Industrial data show that much lower rates may be possible with the newer recycle systems. Ross et al. (2000) reported that a DAF system at a rendering plant has been operated successfully at an air:solids ratio as low as 0.0006. So, pilot testing is important.

Variations in influent concentration will alter the air:solids ratio. To maximize process efficiency, operators must readjust the ratio by changing the recycle flow rate, the operating pressure, or both. An equalization tank will also optimize and stabilize inflow. Screening wastewater before equalization will reduce solids in the equalization tank and DAF units.

Design hydraulic loading rates for DAF units vary significantly, depending on the nature of the wastewater and whether the flotation device is a standard- or high-rate inclined-plate unit. Standard-rate units typically use recycle pressurization, a standard rectangular tank, and a surface skimmer. They remove about 90% of FOG.

High-rate DAF units, which are relatively new in industrial pretreatment, use inclined plates, more efficient air dissolution techniques, and tube flocculators (Figure 10.4). They need less floor space and handle higher flow rates, than standard-rate DAF units, but typically have higher capital costs and are much taller—typically 3 to 5 m (9 to 15 ft). This may make high-rate units difficult to fit in existing industrial buildings.

Some high-rate units have a plastic grid on the surface that allows floating sludge to be removed at a solids concentration of 6 to 12% (double typical DAF performance). They remove as much as 99% of FOG with chemicals, and 60 to 80% without chemicals.

Laboratory and pilot testing is strongly recommended before final design. The specific hydraulic and solids loading rates used to size the DAF will depend on the flow's temperature, the solids' specific gravity, the chemicals being used, the desired effluent parameters, and the residuals management.

FIGURE 10.4 An illustration of a high-rate dissolved air flotation unit with a tube flocculator (courtesy of FRC Environmental, Inc., www.frcenvironmental.com).

Chemicals typically allow for higher flow rates. Higher flow and solids loading rates, however, may result in more FOG, BOD, and suspended solids carryover in the effluent. Hotter wastewater requires more air and may hinder the removal of FOG that solidifies at lower temperatures. Smaller units with higher loading rates may require more frequent solids removal, which may make the float material wetter. All of these factors must be weighed when sizing a DAF unit, and are responsible for the wide design ranges provided.

Standard-rate DAF units are typically designed at 1.2 to 6.0 $m^3/m^2{\cdot}h$ (0.5 to 2.5 gpm/sq ft). The manufacturers' suggested solids loading rates range from 2.4 to 17 $kg/m^2{\cdot}h$ (0.5 to 3.5 lb/hr/sq ft).

High-rate units are rated at about 8.3 to 25 $m^3/m^2{\cdot}h$ (3.3 to 10.0 gpm/sq ft), using the unit's footprint area, rather than the *projected area* of the inclined plates. (The hydraulic loading rates are similar to standard-rate units when based on projected area.) The solids loading rates are similarly higher in high-rate systems.

Dissolved air flotation units are typically housed in a building to facilitate maintenance, reduce odors, and prevent freeze damage to the skimmer. Manufacturers recommend that the DAF process be preceded by screening and equalization processes to reduce solids loading and stabilize and optimize DAF performance, particularly when chemicals are used. This is especially true at facilities with high suspended solids (e.g., dairy and meat processors).

The decision to use chemicals in a DAF, or use only air, depends on a number of factors, including:

- FOG concentrations and removal rates with and without chemicals,
- BOD and TSS removal rates with and without chemicals;
- The facility's discharge limits for FOG, BOD, and TSS;
- The chemicals' dosage and costs;
- The quantity and disposal cost of extra sludge produced by the chemicals;
- Any potential use for the residuals (e.g., animal feed) that could be eliminated by using chemicals.

CENTRIFUGES. When chemically generated floc particles do not separate well, a centrifuge can separate them more efficiently. Centrifuges require more maintenance and energy than other types of separators but can be used when space is limited or significant flows must be processed. Pilot testing is required to determine whether a centrifuge will remove the FOG effectively.

Centrifuges are typically used to process industrial sludges (including FOG removal) rather than industrial wastewater. (For more information on using centrifuges to dewater sludges and recover FOG, see Chapter 9.)

HYDROCYCLONES. Hydrocyclones are an application of centrifuge technology that is becoming more popular at industrial facilities. They can be used to separate oil from heavier solids, oil from heavier water, and even oil from heavier oil. Hydrocyclones rely on centrifugal force for separation, so they need less space than conventional oil-water or oil-solids separation techniques.

In a hydrocyclone system (Figure 10.5), fluid is pumped tangentially into the hydrocyclone, which spins it, generating strong centrifugal forces that induce the solid and liquid (or two immiscible liquids) to separate. The forces generated vary over the hydrocyclone's length. The heavier phase (e.g., water, heavier oil, or solids) is forced outward toward the wall of the hydrocyclone tube and down to the underflow. The lighter phase flows toward the center, where it forms a core and exits via the overflow. The typical detention time is 2 to 3 seconds. Other than pumping through the hydrocyclone, the process has no moving parts. Multi-hydrocyclone assemblies are used for higher flow rates.

Hydrocyclones are typically used at refineries, offshore oil platforms, crude oil transfer facilities, vehicle washing stations, dairies, food processors, etc.

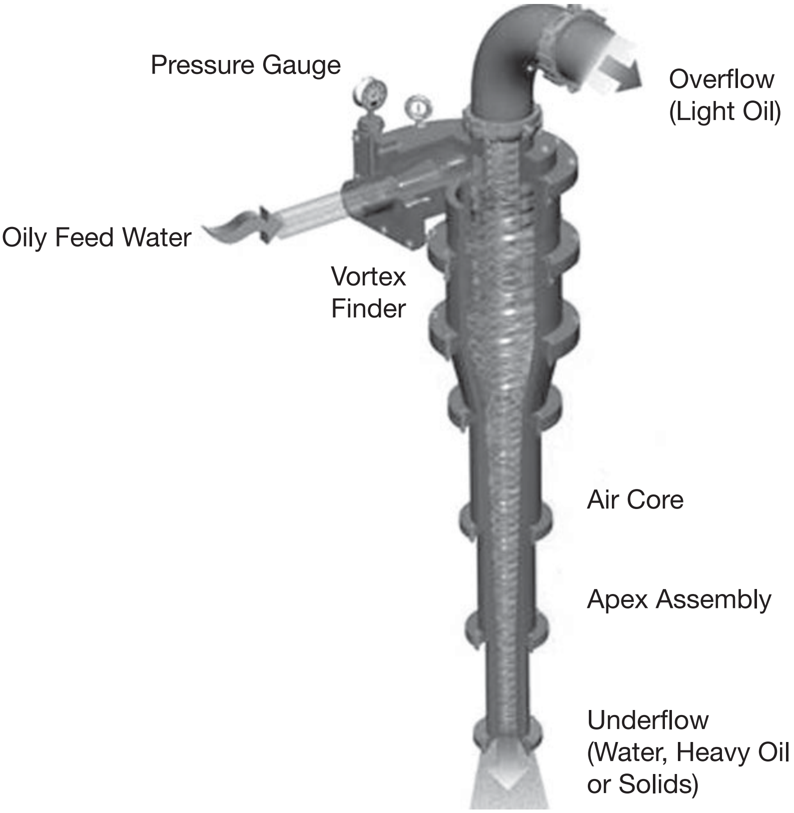


Figure 10.5 A schematic of a hydrocylone (courtesy of FLSmidth Krebs).

CONVENTIONAL FILTRATION. Cartridge filters, bag filters, pre-coat diatomaceous earth filters, and conventional sand filters remove FOG from wastewater effectively. Typically, oily wastes would be filtered after gravity settling (including DAF), to reduce the FOG concentration enough to avoid filter clogging. Diatomaceous-earth filters and sand filters are used for larger flows. They require significant space and must be backwashed to prevent clogging. Cartridge and bag filters are used for smaller flows; they require periodic replacement of their cartridges or bags.

ULTRAFILTRATION. An ultrafiltration system uses a fine membrane to separate FOG from water. It can treat emulsions as low as 0.005 μm. Ultrafiltration has been gaining popularity as membrane prices have dropped, and works well for facilities that want to reuse water, recover the oil, or discharge directly to a receiving water rather than to a POTW.

In a typical ultrafiltration system (Figure 10.6), screened or filtered influent is pumped to the process tank. A pump forces the solution through the membrane, which separates the constituents. The permeate (clean water) is discharged, typically at atmospheric pressure. In a "cross-flow" configuration, the water that does not pass through the membrane is recirculated to the process tank and mixed with the influent. As the removed oil accumulates on the membrane, the differential pressure across the membrane rises, and permeate throughput decreases. Once the membrane performance deteriorates to a prescribed level, the process is taken out of service and backwashed or chemically cleaned.

Membrane filtration typically must be preceded by gravity separation to reduce clogging and maintain a reasonable permeate throughput. Gravity separation may be followed by cartridge or bag filtration to reduce particle sizes to at least 5 μm.

Ultrafiltration breaks the oil-water emulsion but can only concentrate FOG, not remove it. Sometimes a gravity coalescing filter is used to remove the concentrated oil from the concentrate or reject stream. If this filter is impractical, the oil and water could be further separated via the addition of flocculants (e.g., alum and organic polymers). Also, heat can break oil-water emulsions at temperatures of 38° to 82° C (100° to 180° F), depending on the nature of the emulsion.

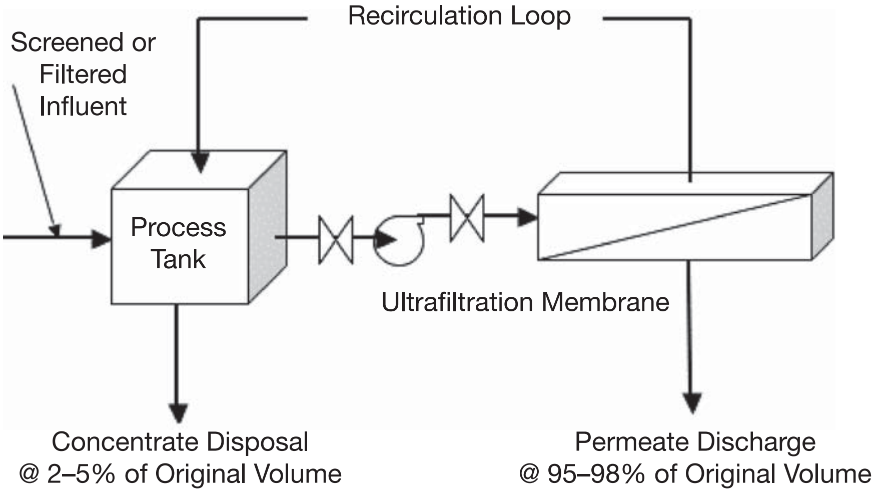


FIGURE 10.6 A schematic of an ultrafiltration process.

A major advantage of ultrafiltration is that the recovered FOG can be recycled or recovered. For example, it is currently used to recover machine oils in metalworking shops. The process's cost-effectiveness depends greatly on the value of the recovered material.

The disadvantages of ultrafiltration include high capital costs, membrane cleaning and replacement costs, and pretreatment requirements.

The design of an ultrafiltration system is based on a number of factors, including the waste characteristics (e.g., oil content, salt content, suspended solids), other chemicals that may be incompatible with a membrane, and other process conditions (pH, temperature, etc.) that may affect the process. Pilot testing is strongly recommended.

ORGANOCLAYS. Organophilic clay (organoclay) is a sodium bentonite clay that has been modified by exchanging a quarternary amine for sodium on the clay surface so it will adsorb insoluble organic materials. Both free and emulsified FOG bind tightly to the amine and so are removed from the wastewater. (The principal FOG-removal mechanism is adsorption, but physical straining is also a factor.)

Organoclay is used as a filter media in a conventional filter vessel, typically under pressure. It typically is mixed with anthracite (30% clay, 70% anthracite) to increase the filter bed's porosity, reduce head loss, and prevent the bed from plugging quickly. (The clay:anthracite ratio is manufacturer-specific and should be verified before final installation.) The filters are backwashed as required to remove suspended solids and improve throughput in the bed. A bed expansion allowance of 20% should be provided.

Organoclays are often used as a FOG polishing step, or as a pretreatment step before granular activated carbon (GAC) adsorption and reverse osmosis. As with membrane filtration, some level of pretreatment—typically, gravity separation—is often recommended to maximize bed life.

Organoclay and GAC adsorption systems have similar hydraulic loading designs. Typically, the design hydraulic loading rate is between 120 to 160 $L/m^2 \cdot min$ (3 to 4 gal/min/sq ft). Larger systems have a 1- to 2-m-deep (3- to 6-ft-deep) bed and an empty bed contact time of 15 minutes. Bag filters often precede organoclay filters to remove solids and reduce the backwash frequency.

Downflow filter designs are typical, but the outlet is higher than the inlet to prevent the media from draining when not in use. Duplicate units are typically provided to allow for periodic backwash (every 1 to 2 days) or media changeout. The media adsorbs about 60% of its weight in organics.

Depending on the waste treated, spent organoclay media may be hazardous and must be disposed of accordingly. However, nonhazardous spent organoclay (with adsorbed FOG) typically has a BTU value of 32 500 to 34 800 kJ/kg (14 000 to 15 000 BTU/lb), depending on the amount of adsorbed material at breakthrough, and may be used for fuel blending.

OPTIONS FOR USING RECOVERED FOG

There are many options for reusing FOG. For example, the oil recovered from edible oil refining, soap making, rendering, and meat processing can be salvaged and used in animal foods and in diesel engines. Many restaurants collect the spent FOG from frying vessels and sell it to rendering plants, where it is purified and then sold for industrial or animal feed use. Oil skimmed from gravity separators may be included or may be discarded with the restaurant's other solid waste and refuse.

Petroleum hydrocarbons with low water content can be used in refinery feedstock, reformulated for resale, or sold on the fuel market. Likewise, waste oil from certain industries can be collected and sold to waste oil refiners. Rising petroleum prices have made disposing such FOG less attractive.

REUSE. There may be other uses for recovered FOG, depending on its pH and the type and percentage of oil, fat, waxes, and foreign material present. To determine the potential marketplace, consult the industrial waste exchanges throughout the United States. Selling the FOG may help offset the process's operating costs.

For example, FOG may be reused in drilling-mud manufacturing, ore flotation, and asphalt manufacturing. Many drilling-mud manufacturers can use a variety of FOG materials as a raw material. Ore flotation—a process similar to DAF used to recover mineral ores after acid extraction—uses fatty acids from animal and vegetable fats and oils to enable the metal ions to float. Some asphalt manufacturers can use certain types of FOG to help emulsify other materials used to produce asphalt. (Suitability for these uses must be determined on a case-by-case basis.)

Polar animal- or vegetable-based FOG contains protein that can be recovered and sold or given away for use as an animal feed. When recovering FOG for animal feed, two considerations are critical: eliminating as much water as possible and making the material available for use within 1 day of collection. Using coagulants (e.g., alum or iron salts) to optimize FOG removal may make the material unacceptable to many renderers and farmers. Also, concerns about "mad cow" disease may make animal-based FOG unacceptable.

RECYCLE. Sometimes, the most economical alternative may be to return recovered FOG to the process that generates them. This requires that waste oil collection be separated from other wastewater processes, a stipulation that should be considered when designing new facilities as a means to prevent pollution. The ability to recycle, reuse, incinerate, or otherwise dispose of recovered FOG may be regulated under the Resource Conservation and Recovery Act (RCRA). Consult this regulation before choosing a disposal option.

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Chapter 11

pH Control

(continued)

Adjusting a wastewater's pH is one of the most common processes in an industrial pretreatment system. Because of various acids and bases used in industrial manufacturing, processing, and cleaning operations, most facilities need to adjust the pH of their wastewater before discharging it to surface waters or publicly owned treatment works (POTWs).

The optimum pH range is somewhat plant- and process-specific. For direct discharges, the effluent pH typically must be between 6.0 and 9.0 to protect the receiving waters. For indirect discharges, the effluent pH typically must be between 5.5 and 10.0 to protect municipal collection systems from corrosion and POTW processes from upset or failure. If a facility's pretreatment system includes biological treatment processes, however, the wastewater's pH typically must be within a fairly narrow range (between pH 6.5 and 8.5) before entering the biological reactor. If the biological system is designed to nitrify, the optimum pH range is typically 7.5 to 8.5. (These are the pH ranges typically used for biological treatment processes; some processes operate effectively outside of these ranges.) Also, the optimum pH range may change with differences in temperature, process configuration (e.g., batch processes versus continuous-flow processes), and technologies (e.g., aerobic treatment versus anaerobic treatment).

An acidic wastewater discharged into a collection system can trigger adverse chemical reactions. For example, when cyanide ions in wastewater come into contact with acidic industrial wastewater, the combination can produce hydrogen cyanide gas, which is highly toxic. Sulfides in wastewater may combine with acidic industrial wastewater to produce hydrogen sulfide gas. Both hydrogen cyanide and hydrogen sulfide are dangerous in low concentrations. In addition, hydrogen sulfide gas can be oxidized biologically to form sulfuric acid, which can corrode concrete pipes.

TERMS AND DEFINITIONS

Following are brief explanations of pH, pOH, acidity, alkalinity, and buffer capacity. This fundamental background information is necessary to understand the design and operations of pH-control systems. (For more information on these concepts, see McMillian, 1994; Snoeyink and Jenkins, 1980; and Stumm and Morgan, 1996.)

pH AND pOH. The term *pH*, which is used to describe a solution's acidic or alkaline condition, is defined as the negative logarithm of the active hydrogen ion concentration ($[H^+]$) expressed in moles per liter:

$$\text{pH} = -\log[H^+] \tag{11.1}$$

or

$$\text{pH} = \log 1/[H^+]$$

The pH scale runs from 0 to 14; the neutral point (pH = 7) is the pH of pure water at approximately 25° C (77° F). Alkaline solutions have a pH above 7, and acidic solutions have a pH below 7. Because pH is a logarithmic function, a solution with a pH of 5 has 10 times more active hydrogen ions than one at pH 6. Similarly, a solution of pH 2 has 1000 times more active hydrogen ions than one of pH 5. A solution of pH 1 contains 1×10^{-1} mole/L of free hydrogen ions, while a solution of pH 13 contains 1×10^{-13} mole/L of free hydrogen ions.

The hydrogen ion concentration varies inversely to the free hydroxyl ion concentration $[OH^-]$ expressed in moles per liter, as noted in the following equilibrium equation:

$$[H^+][OH^-] = 10^{-14} \tag{11.2}$$

In a liter of pure water at 25° C, approximately 1×10^{-7} moles of water dissociate, producing identical concentrations of free hydrogen and hydroxyl ions. The negative logarithm of the hydroxyl ion concentration is called the *pOH.* The relationship between pH and pOH can be derived from eq 11.2 by taking negative logarithms of both sides to obtain:

$$\text{pH} + \text{pOH} = 14 \tag{11.3}$$

Acids and bases dissociate in water, producing hydrogen and hydroxyl ions, respectively. An acid is described as weak or strong depending on the number of hydrogen ions liberated when the acid is added to water. A base is also described as strong or weak depending on the number of hydroxyl ions liberated when the base is added to water. For example, nitric acid (HNO_3) is a strong acid because nearly all of its molecules dissociate in water to produce hydrogen ions and nitrate ions. Acetic acid (CH_3COOH), on the other hand, is a weak acid because its molecules dissociate very little, producing few hydrogen ions in aqueous solution.

If an acid is added to water, the concentration of hydrogen ions in the solution increases. If 1×10^{-3} moles of a strong acid [e.g., hydrochloric acid (HCl)] are added to 1 L of pure water at pH 7, nearly all of the acid will dissociate, producing about 1×10^{-3} mole of hydrogen ions and a pH of about 3.

If a base is added to water, it releases hydroxyl ions that react with the hydrogen ions to form water, thereby lowering the hydrogen ion concentration and raising the solution's pH. For example, if 1×10^{-2} moles of a strong base [e.g., sodium hydroxide (NaOH)] are added to 1 L of pure water at pH 7, the hydroxyl ion concentration will be about 1×10^{-2} moles/L (pOH = 2) and the pH will be about 12 (using eq 11.3, pH = 14 − 2 = 12).

ACIDITY AND ALKALINITY. Acidity and alkalinity are useful concepts for determining neutralization requirements. More than a pH measurement is required to adequately determine how much base is needed to neutralize an acid or how much acid is needed to neutralize a base (Hoffman, 1972). In a nitric acid solution (strong acid), almost all of the acid's hydrogen ions are quantified by the pH measurement because the hydrogen ions are nearly completely dissociated. In an acetic acid solution, however, the acid's ions are available as both hydrogen ions and acetate ions (CH_3COO^-). As free hydrogen ions combine with an added base's hydroxyl ions to form undissociated water, more of the acetic acid will dissociate to maintain the hydrogen ion concentration that existed when the solution was at equilibrium. Therefore, a pH measurement alone will not indicate how much base must be added to neutralize the acetic acid solution.

A strong acid solution may have a lower pH than a weak acid solution, even if equivalent amounts of acid were used to prepare both solutions. However, the total acidity of both solutions will be identical, and equal amounts of a base will be required to neutralize the two solutions. Conversely, a dilute solution of a strong acid and a concentrated solution of a weak acid may have the same pH, but they will require different doses of a base to neutralize them, even if the volumes of the two solutions are equal.

Acidity. *Acidity* is a measure of a solution's capacity to neutralize a strong base (e.g., NaOH) to a designated pH. It is expressed as an equivalent amount (in milligrams per liter) of calcium carbonate ($CaCO_3$). Acidity is a gross measure; it can be interpreted in terms of specific dissolved substances only when the solution's chemical composition is known. Strong mineral acids [e.g., sulfuric acid (H_2SO_4)], weak acids [e.g., carbonic (H_2CO_3) or acetic acids], and metal salts (e.g., ferrous or aluminum sulfate) contribute to a wastewater's measured acidity.

The measured value of acidity varies with the designated endpoint pH used in its determination. In the titration of a single acidic species, the most accurate endpoint pH for acidity is obtained from the inflection point of a titration curve. The inflection point is the point at which the slope of the curve (pH change per milliliter of added reagent) is greatest. The point is determined by inspection of the titration curve. Because accurate identification of the inflection point of a curve is difficult in buffered or complex wastewater mixtures, the titration in such cases is carried to an arbitrary endpoint pH. The selected endpoint pH, however, has been standardized as either the "methyl orange end point" or the "phenolphthalein end point" (APHA et al., 2005). The methyl orange endpoint pH is approximately 4.3 to 4.5; the phenolphthalein endpoint pH is 8.2 to 8.4. These endpoints correspond to the carbonic acid system ($H_2CO_3/HCO_3^-/CO_3^=$), which is often the dominant buffering system in wastewater. The methyl orange endpoint corresponds to the pH at which carbonic acid predominates, and the phenolphthalein endpoint corresponds to the pH at which bicarbonate predominates.

The amount of base (expressed as $CaCO_3$) required to raise the wastewater's pH from its initial value to the methyl orange endpoint is the wastewater's *methyl orange acidity* (*mineral acidity*). The amount of base required to raise the wastewater's pH from its initial value to the phenolphthalein endpoint is the wastewater's *phenolphthalein acidity* (*total acidity*). Wastewaters with low pH (< 4.3) will have both methyl orange acidity and phenolphthalein acidity, while those with higher pH ($4.3 \leq \text{pH} \leq 8.5$) will only have phenolphthalein acidity. Wastewaters whose initial pH is more than 8.5 have no measurable (titratable) acidity.

A wastewater's titrated acidity (expressed as $CaCO_3$) can be determined as follows:

$$\text{Acidity} = (50\,000)(V_B)(N_B)/V_s \tag{11.4}$$

Where

Acidity = the wastewater's acidity expressed as $CaCO_3$ (mg/L),
50 000 = equivalent weight of $CaCO_3$ (mg/equivalent),
V_B = volume of base used to reach the endpoint (L),
N_B = normality of the base solution (equivalents/L), and
V_s = volume of sample (L).

In wastewaters without mineral acidity ($\text{pH} > 4.3$), carbon dioxide may furnish a large portion of any titrated acidity. Carbon dioxide is a normal component of all natural waters and may be produced via the biological oxidation of organic matter. The carbon dioxide equilibrium in natural waters affects the amount of acidity and alkalinity measured by titration. Salts of weak bases also contribute to the measured acidity because they consume base when titrated to the designated endpoint pH.

Alkalinity. *Alkalinity* is a measure of a solution's capacity to neutralize a strong acid (e.g., H_2SO_4) to a designated pH. Like acidity, alkalinity is expressed as an equivalent amount (in milligrams per liter) of calcium carbonate. It is a gross measure and can be interpreted in terms of specific substances only when the solution's chemical composition is known. The alkalinity of many wastewaters is primarily a function of their carbonate (CO_3^{-2}), bicarbonate (HCO_3^-), and hydroxide equilibria. The alkalinity is taken as an indication of the combined concentrations of these constituents (it may also include contributions from borates, phosphates, silicates, and other anions).

Alkalinity is measured by titrating wastewater with a solution of dilute sulfuric acid. Samples with an initial pH above 8.3 are titrated in two steps. The first titration step, which measures the *phenolphthalein alkalinity*, proceeds to the phenolphthalein endpoint pH (8.3 to 8.5). The second step, which measures the *methyl orange alkalinity*, is conducted to the methyl orange endpoint pH (4.3). The total alkalinity is the sum of the methyl orange alkalinity and phenolphthalein alkalinity. A wastewater whose pH is less than 4.3 has no measurable alkalinity.

A wastewater's titrated alkalinity can be determined as follows:

$$\text{Alk} = (50\,000)(V_\text{A})(N_\text{A})/V_\text{s} \tag{11.5}$$

Where

Alk = alkalinity of the wastewater expressed as $CaCO_3$ (mg/L),
50 000 = equivalent weight of $CaCO_3$ (mg/equivalent),
V_A = volume of acid used to reach the endpoint (L),
N_A = normality of the acid solution (equivalents/L), and
V_s = volume of sample (L).

Domestic wastewater is typically alkaline, with a slightly higher alkalinity than the local domestic water supply. Industrial wastewater alkalinity, however, depends on how process water is treated (e.g., softening, reverse osmosis) at the plant, as well as the raw materials, production processes, and cleaning agents used in the manufacturing process. An industrial wastewater's acidity and alkalinity can vary widely and should not be assumed to be the same as the domestic water supply.

BUFFERING CAPACITY. *Buffering capacity* is a solution's capacity to resist changes in pH. It results from the presence of a weak acid and its conjugate base, or a weak base and its conjugate acid. Such compounds (e.g., carbonate, bicarbonate, and salts of phosphoric acid) dissociate into conjugate pairs and provide a good buffer system in wastewater. The following equations illustrate these concepts using bicarbonate (HCO_3^-; a weak base), carbonic acid (H_2CO_3; its conjugate acid), a strong acid (H^+), and a strong base (OH^-). The relationship between bicarbonate and carbonic acid under equilibrium conditions is:

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \tag{11.6}$$

If a strong acid is added to this buffered solution, its hydrogen ions react with the bicarbonate ions to form more carbonic acid:

$$H^+ + HCO_3^- \rightarrow H_2CO_3 \tag{11.7}$$

If a strong base (OH^-) is added to the buffered solution, its hydroxyl ions react with the carbonic acid to form bicarbonate and water:

$$OH^- + H_2CO_3 \rightarrow HCO_3^- + H_2O \tag{11.8}$$

As long as the solution contains enough buffering capacity (bicarbonate ions), the addition of a strong acid or base will not significantly affect its pH.

Strong acid and strong base solutions, on the other hand, have negligible buffering capacity because these compounds, by definition, dissociate nearly completely in water:

$$H_2SO_4 \rightarrow 2H^+ + SO_4^= \qquad (11.9)$$

Adding a strong acid (H^+) to this solution will increase the hydrogen ion concentration, lowering the pH. Adding a strong base (OH^-) to this solution will cause water (H_2O) to form, thereby consuming hydrogen ions and raising the pH.

Sometimes, water's natural buffering capacity has been destroyed via the addition of strong acids or bases or the intentional softening of the water for process use. A wastewater with a low buffering capacity is difficult to neutralize and maintain within a relatively narrow pH range because adding small quantities of a reagent will greatly change the pH. A well-buffered solution resists changes in pH, so reagent additions have less effect, making the reaction easier to control. In some cases, adding a buffering agent to a poorly buffered wastestream may result in a more economical and controllable neutralization system.

pH MEASUREMENT PRINCIPLES

A pH measurement device has three components: the pH sensor or probe, which includes a measuring electrode, a reference electrode, and a temperature sensor; a preamplifier; and an analyzer or transmitter. The sensor components are typically combined into one probe. The measuring electrode is typically made of glass (recent developments, however, have replaced glass with more durable solid-state sensors). A glass measuring electrode has a pH-sensitive glass bulb at the end and a silver chloride wire in the center, which is surrounded by a potassium chloride (KCl) electrolyte solution. The reference electrode typically is a chamber that surrounds the measuring electrode. It contains a silver chloride wire surrounded by an electrolyte solution of potassium chloride saturated with silver chloride. A porous liquid junction in the reference electrode allows the electrolyte solution to make physical and electrical contact with the liquid being monitored and to develop a potential (voltage) that the electrodes can measure (Oakton, 1997).

The measuring electrode, which is sensitive to the hydrogen ion concentration, develops a potential directly related to that concentration. The reference electrode provides a stable potential for comparison. When immersed in a solution (e.g., wastewater), the reference electrode's potential remains constant, while the measuring electrode's potential changes in proportion to the hydrogen ion concentration (Griffiths, undated).

The preamplifier is a signal-conditioning device. It modifies the high-impedance pH electrode signal so the analyzer can accept it. The preamplifier also strengthens and stabilizes the signal, making it less susceptible to electrical noise.

WASTEWATER CHARACTERISTICS

Before designing and implementing a pH-control system, engineers should define the important wastewater characteristics. Numerous characteristics [e.g., alkalinity/acidity, flow rate(s), chemical composition, and desired pH] affect the performance and cost of pH control. The following evaluations should be conducted to establish design criteria for pH-control systems.

TITRATION CURVES AND ANALYSIS. Although the pH value is used to control the neutralization process, the wastewater's acidity or alkalinity is the true measure of the amount of reagent required for neutralization. To determine the wastewater's total acidity or alkalinity, a titration must be performed. This is a necessary first step when designing a pH-control system. The data obtained define the reagent required, the expected dose, and the process-control characteristics.

An *acid-base titration curve* graphically depicts the change in wastewater pH per reagent dose. The shape of this curve depends on the wastewater's composition (e.g., concentrations of buffering compounds) and the type and concentration of the reagent used for pH adjustment. This shape provides important information about the wastewater's response to the reagent.

The titration curve's *inflection point* is the point where the curve's slope is steepest. Also called the *equivalence point* (because the solution contains equal amounts of acid and base at this point), it defines the level at which the pH changes most dramatically per unit of reagent added. If a strong acid is mixed with a strong base, the equivalence point is at pH 7.0. Near the equivalence point of a strong acid-strong base titration curve, a small addition of an acid or a base will change the pH by several units. Because a strong acid-strong base reaction provides no buffering capacity, maintaining a narrow pH target is difficult.

The equivalence point of a titration of a strong acid with a weak base (or a weak acid with a strong base) occurs at a pH less than 7. The equivalence point of a titration of a strong base with a weak acid (or a weak base with a strong acid) occurs at a pH greater than 7. When a weak acid or weak base is involved in the titration, the pH change per unit of acid or base added is less pronounced than in the strong acid-strong base titration because strong acid-weak base reactions and strong base-weak acid reactions produce salts that buffer the pH change (eqs 11.6 to 11.8). Therefore, a reaction involving a weak acid or base typically proceeds in a more controlled manner, resulting in improved pH control. An advantage of using the salt of a weak base [e.g, sodium bicarbonate ($NaHCO_3$)] to neutralize a wastewater containing strong acid is that the weak base bicarbonate ion (HCO_3^-) provides buffer capacity and produces a flatter titration curve within the acceptable range of pH control.

Table 11.1 presents typical titration data for two hypothetical wastewaters containing a strong acid (e.g., sulfuric, nitric, or hydrochloric acid). The table shows titrations with a strong base (e.g., sodium hydroxide) and with a weak base (e.g., sodium bicarbonate). Figure 11.1 depicts the titration curves for the data in Table 11.1. The strong acid-strong base curve is steep near its equivalence point (pH 7.0). The strong acid-weak base curve, however, is flatter near its equivalence point (pH 5.5). The typical range for pH control is within the range of 6.0 to 9.0. The strong acid-strong base system would be more difficult to control within this range than the strong acid-weak base system.

Diprotic acids and bases [e.g., carbonic acid (H_2CO_3)] have two equivalence points. Tripotic acids and bases [e.g., phosphoric acid (H_3PO_4)] have three equivalence points. Solutions containing several acids and bases may have multiple equivalence points. Many industrial wastewaters have complex compositions—including a variety of acids or bases—so their titration curves will also be complex, with multiple equivalence points. Therefore, a well-planned, comprehensive wastewater-sampling program should be conducted to provide accurate information on the type and amount of reagent needed to neutralize high- or low-pH solutions. The samples should be representative of the full range of expected wastewater variations, and titration curves should be developed to determine the maximum chemical doses required for pH control.

WASTEWATER VARIABILITY. Defining how wastewater characteristics vary over time is as important as the titration analyses. Few industrial wastewaters are discharged uniformly over time, and significant variations may occur within minutes. Variations are especially pronounced in industries with frequent production cleaning cycles—particularly if they alternate between acidic and basic cleaning agents. The wastewater may vary in its flow rate; specific composition (e.g., BOD,

Table 11.1 Typical titration data of a strong acid (see Figure 11.1).

Strong base units added	Measured pH	Weak base units added	Measured pH
0.00	2.0	0.00	2.5
1.25	2.5	1.00	3.0
2.75	3.0	2.50	3.5
3.75	3.5	3.20	4.0
4.25	4.0	3.40	4.5
4.50	4.5	3.55	5.0
4.65	5.0	3.65	5.5
4.75	5.5	3.75	6.0
4.80	6.0	3.85	6.5
4.80	6.5	4.15	7.0
4.80	7.0	4.65	7.5
4.80	7.5	5.40	8.0
4.80	8.0	6.40	8.5
4.85	8.5	7.80	9.0
4.95	9.0		
5.10	9.5		
5.35	10.0		
5.85	10.5		
6.85	11.0		
8.35	11.5		

pH, TSS, dissolved solids, and temperature); and acidity, alkalinity, and buffering capacity.

To evaluate how wastewater characteristics vary over time, design engineers should implement an in-depth monitoring program. This program should provide continuous or intermittent flow rate data, as well as collect grab (discrete) wastewater samples at specific intervals (e.g, days, hours, or minutes, depending on the specific wastewater). Production facilities with similar processes that operate continuously for long periods may require minimal characterization. Those with numerous processes, that operate with short cycles, or that discharge in large batches, often require a more elaborate analysis (e.g., continuous flow monitoring and discrete sampling at 5- or 15-minute intervals). Where wide variations exist, titration curves

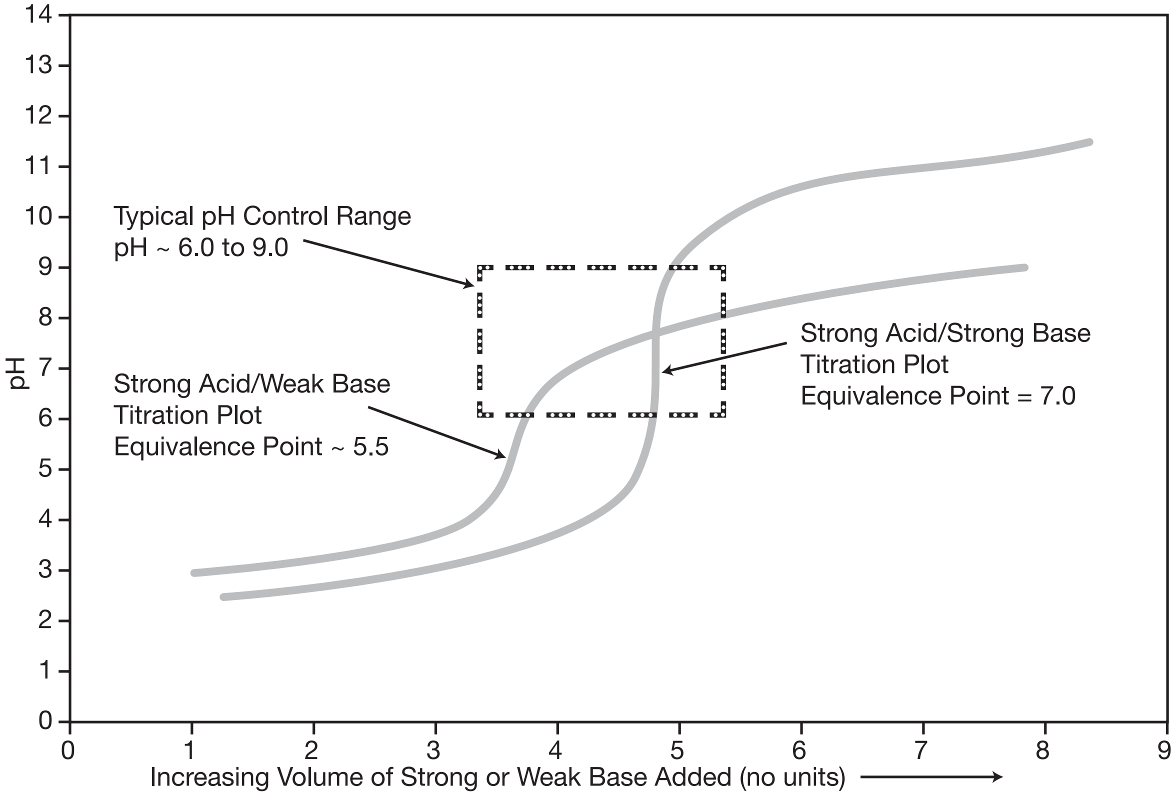

FIGURE 11.1 Typical titration curves—strong acid-strong base and strong acid-weak base.

should be developed using numerous samples to evaluate and define neutralization reagent dosages at a variety of wastewater conditions.

SOLIDS PRODUCTION POTENTIAL. Solids are produced when certain compounds precipitate as a result of a change in pH. Design engineers should evaluate the solids-generation potential by using multiple neutralizing agents at various doses. The following types of solid precipitations are frequently encountered in pH-control processes.

Calcium carbonate ($CaCO_3$) deposits are generated when a solution is oversaturated with $CaCO_3$ and the pH is higher than approximately 8.5. Calcium carbonate precipitation is common when the wastewater is relatively hard (high calcium concentration) and significant bicarbonate alkalinity exists. Bicarbonate alkalinity may result from biological action (CO_2 generation) or the addition of a bicarbonate [e.g., sodium bicarbonate ($NaHCO_3$)] or carbonate (e.g., soda ash, Na_2CO_3) to neutralize an acidic solution.

Calcium sulfate ($CaSO_4$)—also called *gypsum*—is slightly soluble (2 to 3 g/L) and is generated when alkaline wastewater containing dissolved calcium is treated with sulfuric acid, or acidic wastewater containing sulfates is treated with lime compounds.

Calcium chloride ($CaCl_2$) is highly soluble and generated when alkaline wastewater containing dissolved calcium is treated with hydrochloric acid, or acidic wastewater containing chlorides is treated with lime compounds. Because of its high solubility, the available calcium (Ca) is more likely to precipitate with other salts (e.g., $CaSO_4$ and $CaCO_3$) than with chloride.

Metal hydroxides will precipitate upon neutralization of acidic wastewater containing dissolved metals using lime or caustic soda, especially at elevated pH values in the 9 to 11 range. Some metals that typically precipitate as hydroxides at a higher pH are co-precipitated with another metal hydroxide that is formed at a lower pH. For example, in acidic wastewaters that contain dissolved iron, ferric hydroxide [$Fe(OH)_3$] will precipitate upon addition of a base (OH^-) at a pH of approximately 7. Under these conditions, ferric hydroxide will tend to increase sludge generation through flocculation of suspended solids and colloidal solids (WEF, 1998).

Typically, fewer solids are generated at low pH levels than at high pH levels. Solids produced during neutralization often must be removed from the wastewater via sedimentation or filtration and then processed (e.g., thickening, dewatering, and storage). So, generated solids may significantly affect a pH-control system's capital, operating, and maintenance costs.

SELECTION OF NEUTRALIZING AGENTS

The following criteria may be used to help select neutralization chemicals. These criteria should be evaluated based on bench-scale jar tests and titration curves prepared under various test conditions using representative wastewater samples.

TYPE OF NEUTRALIZING AGENT REQUIRED. The first question to answer is whether a base or acid (or both) will be needed to control pH. Both are often needed, especially when the wastestream characteristics are highly variable and the target pH range is narrow.

OPERATING COSTS. An economic evaluation of neutralizing agents should include several alternatives. For example, an acidic wastewater's pH can be raised by either a strong or weak base. The strong base will require a lower dose, but its reactions may be difficult to control within a narrow pH range. Also, the strong base may cost more per unit than the weak one. The overall chemical cost is a function of both the unit cost and the required dose. Related labor and maintenance costs must also be evaluated to compare total operating costs for each chemical.

When evaluating chemical costs, one appropriate comparison is the cost to provide a unit of alkalinity or acidity for each chemical. The following equation can be used for this evaluation:

$$C_{\mathrm{alk/acid}} = (C_{\mathrm{bulk}})(\mathrm{EW})/[(P_{\mathrm{bulk}})(\mathrm{EW}_{\mathrm{CaCO_3}})] \tag{11.10}$$

Where

$C_{\mathrm{alk/acid}}$ = cost per unit weight of alkalinity or acidity (as $CaCO_3$),
C_{bulk} = cost per unit weight of bulk chemical,
EW = equivalent weight of chemical,
P_{bulk} = fractional purity of bulk chemical,
$\mathrm{EW}_{\mathrm{CaCO_3}}$ = equivalent weight of calcium carbonate = 50.

CAPITAL COST. The installation costs should include chemical storage tanks and buildings, pumping/metering equipment, construction materials, safety considerations, and required instrumentation for process control.

REACTION TIME. The reaction time will affect the number, size, and mixing requirements of the pH-control vessels. The system controls will also be affected by the reaction time.

DISSOLVED SOLIDS PRODUCTION. The concentration of dissolved solids produced during neutralization depends on the type and amount of chemicals used. Also, soluble salts may be objectionable in the effluent.

SOLIDS PRODUCTION. The amount of solids generated during neutralization is typically a function of the wastewater's composition, the reagent(s), and the wastewater's final pH. Precipitated solids must either be discharged to downstream treatment processes (or a POTW) in suspended form, or else removed, processed, and disposed. (For more information on solids handling and processing, see Chapter 9.)

SAFETY. Some chemicals must be handled with more caution than others. Any precautions needed to reduce skin contact, accidental eye contact, and vapor inhalation should be considered during the selection process. The quantity of chemical(s) required affect storage and secondary containment requirements, which may raise other safety considerations.

MAXIMUM/MINIMUM pH IN OVERTREATMENT. Evaluators should determine the maximum and minimum possible pH, especially if the neutralization process precedes or is part of a biological treatment system, or will discharge to a POTW. Overdosing an acidic wastewater with caustic soda, for example, can produce a very high pH that may not meet treatment or discharge requirements. If this is problematic, another base should be considered. Magnesium hydroxide [$Mg(OH)_2$], for example, will not raise the pH significantly because it is insoluble at approximately pH 9.0 or higher.

EASE OF CHEMICAL HANDLING. Depending on the type and usage rates of the selected pH-control chemicals, these chemicals may be delivered in dry or liquid form. Dry forms include powdered and granular chemicals that must be wetted, mixed, and stored in liquid form. Dry chemicals may be shipped in bags (up to several hundred kilograms), which are typically manually emptied into chemical-mixing equipment, or in "supersacks" that must be hoisted to a rack for emptying into the conveying equipment. Liquid chemicals may be delivered in drums, totes, truckloads, or railcars.

The type and quantity of chemical selected determines the facilities required to receive, unload, store, and deliver it to the pH-control system. Other chemical handling and storage issues include safety, freeze protection, dust control, construction materials, and chemical-specific handling systems. For example, carbon dioxide is typically delivered by the truckload in liquid form and stored at low temperatures in a pressure vessel. A vaporizer is used to evaporate the carbon dioxide in gaseous form, and this gas may then be added to wastewater via a gas-diffusion system.

AVAILABILITY AND OTHER ISSUES. Availability, price volatility, and required grade are significant factors when evaluating pH-control chemicals. For example, if a chemical is manufactured nearby, its transportation costs will be less and, therefore, so will its unit costs. Also, neighboring facilities may be able to combine their wastewaters to neutralize the pH without significant chemical addition.

The most commonly used neutralization chemicals are described below; a more complete list is presented in Table 11.2. Table 11.3 provides information on bulk chemical properties, as well typical as handling and feeding requirements.

BASIC AGENTS. The following bases are typically used to neutralize acidic wastes.

Lime. Lime is typically used to neutralize acidic wastewater because it is widely available and relatively inexpensive. The types of lime and limestone materials used to neutralize acid wastes include

- High-calcium hydrated lime (slaked lime),
- Calcium oxide (quicklime or unslaked lime),
- Dolomitic quicklime,
- Dolomitic hydrate,
- High-calcium limestone,
- Dolomitic limestone,
- Calcium carbonate, and
- Spent calcium carbide waste (calcium hydroxide).

Each form has a different reaction time, which will affect the size of neutralization tanks and, therefore, capital costs. Some also have a significant percentage of inert materials, which add to the quantity and type of solids produced.

Lime compounds dissolve and react slowly; they need relatively long contact times and high mixing power levels to function effectively. Their principal disadvantages are solids and scale production (because of the formation of insoluble calcium salts), and lime dust, which is a nuisance and potential health concern. Solids must be removed via a clarifier or quiescent pond, dewatered, and then disposed. Scaling is rarely a problem when lime is neutralizing a strong acid to a pH less than 5. At pH levels between 5 and 9, the deposits may be either granular sludge or scale, depending on the wastewater characteristics, type of lime used, and whether solids are recirculated. At pH levels between 9 and 11, a hard scale may form that will cement itself to pH electrodes, valves, pipes, pumps, and weirs. It must be frequently removed to avoid fouling. Also, overtreatment with lime can raise the pH to as high as 12.5, which is a corrosivity hazard according to the Resource Conservation and Recovery Act (RCRA).

Table 11.2 Common alkaline and acid reagents (WEF, 1994).

Chemical	Formula	Equivalent Weight	Amount to neutralize 1 mg/L of acidity or alkalinity (mg/L as $CaCO_3$)
Calcium Carbonate	$CaCO_3$	50	1.00
Calcium Oxide	CaO	28	0.56
Calcium Hydroxide	$Ca(OH)_2$	37	0.74
Magnesium Oxide	MgO	20	0.40
Magnesium Hydroxide	$Mg(OH)_2$	29	0.58
Dolomitic Quicklime	$[(CaO)_{0.6}(MgO)_{0.4}]$	24.8	0.50
Dolomitic Hydrated Lime	$\{[Ca(OH)_2]_{0.6}[Mg(OH)_2]_{0.4}\}$	33.8	0.68
Sodium Hydroxide	$NaOH$	40	0.80
Sodium Carbonate	Na_2CO_3	53	1.06
Sodium Bicarbonate	$NaHCO_3$	84	1.68
Sulfuric Acid	H_2SO_4	49	0.98
Hydrochloric Acid	HCl	36	0.72
Nitric Acid	HNO_3	62	1.26
Carbonic Acid	H_2CO_3	31	0.62

TABLE 11.3 Summary of properties for common neutralization chemicals (WEF, 1994).

Property	**Calcium Carbonate ($CaCO_3$)**	**Calcium Hydroxide ($Ca(OH)_2$)**	**Calcium Oxide (CaO)**	**Sodium Carbonate (Na_2CO_3)**	**Sodium Hydroxide (NaOH)**	**Sulfuric Acid (H_2SO_4)**	**Hydrochloric Acid (HCl)**
Common Form	Powder, crushed	Powder, granules	Lump, pebble, ground	Powder	Liquid	Liquid	Liquid
Shipping Container	Bags, barrels, bulk	Bags, bulk	Bags, barrels, bulk	Bags, bulk	Drums, totes, bulk	Drums, totes, bulk	Drums, totes, bulk
Bulk Weight (lb/ft^3)	Powder: 48-71 Crushed: 70-100	25-50	40-70	34-62	74-100	106-114	64-74
Commercial Strength	NA	Typical 13%	75-99%; typical 90%	99.2%	20%, 50%, 98%	78%, 93%	27.9%, 31.45%, 35.2%
Water Solubility (lb/gal)	Nearly insoluble	Nearly insoluble	Nearly insoluble	0.58 at 32°F 1.04 at 50°F 1.79 at 68°F 3.33 at 86°F	Complete	Complete	Complete
Feeding Form	Dry slurry used in fixed beds	Dry or slurry	Dry or slurry	Dry, liquid	Liquid	Liquid	Liquid
Feeder Type	Volumetric pump	Volumetric metering pump	Dry volumetric, wet slurry	Volumetric feeder, metering pump	Metering pump	Metering pump	Metering pump
Accessory Equipment	Slurry tank	Slurry tank	Slurry tank, slaker	Dissolving tank	---	---	---
Suitable Handling Materials	Iron, steel	Iron, steel, plastic, rubber	Iron, steel, plastic, rubber	Iron, steel	Iron, steel, FRP, plastics	Kynar, teflon, stainless steel, some plastics	Hastelloy A, selected plastics

Limestone is typically one of the least expensive options for basic reagents. When used in beds through which the wastestream passes, it produces carbon dioxide, which tends to gas-bind the beds. When limestone is used to neutralize sulfuric acid wastes, a calcium sulfate coating will likely form on the bed material and must be removed via mechanical agitation. Limestone reaction times may be 1 hour or longer, depending on the quality and size of the stones, and the bed must be periodically replenished to maintain process effectiveness.

Caustic Soda. Sodium hydroxide (NaOH)—also called *caustic soda*—is available in both solid and liquid forms, but anhydrous NaOH is considered impractical in wastewater treatment applications because of safety concerns associated with its handling and dissolution. So, the following discussion pertains to liquid NaOH.

Caustic soda is typically expensive but offers numerous advantages in capital, operation, and maintenance costs compared to lime and other bases. It is a strong neutralizing agent and reacts rapidly, thereby reducing tankage requirements. It is also a "clean" chemical to store and handle, and generates significantly less solids than lime-based compounds. Also, the sodium salts formed via caustic soda are typically highly soluble, so solids sedimentation is often not required after pH adjustment.

Caustic soda typically is co-produced with chlorine and because the chlorine supply and demand varies by region, the price and availability of caustic soda can be volatile. Other disadvantages of caustic soda include health and safety concerns: it is harmful to lungs and unprotected skin, and it is a slipping hazard if spilled. Also, an overdose of caustic soda can rapidly raise a wastestream's pH to more than 12, which is a compliance concern because RCRA considers a pH of 12.5 or higher to be a corrosivity hazard.

Sodium Bicarbonate. A salt of weak carbonic acid (H_2CO_3), sodium bicarbonate ($NaHCO_3$)—also called *baking soda*—is a highly effective buffering agent. It is nearly pH neutral, so it is quite useful for adding either alkalinity or acidity, acting primarily as a buffering agent. It is particularly effective for pH control in anaerobic biological treatment systems.

Sodium Carbonate. Sodium carbonate (Na_2CO_3; soda ash) has fewer and less extreme handling precautions than caustic soda, and is less expensive than sodium bicarbonate. However, it typically is a less-effective neutralizing agent than either NaOH or $NaHCO_3$. Soda ash is a moderately fast-acting neutralizer but generates carbon dioxide, which may cause foaming problems. Because of its low solubility in water, soda ash is most economically fed in slurry form in the same manner as hydrated lime.

Magnesium Hydroxide. Magnesium hydroxide [$Mg(OH)_2$] is a weak base that is relatively safe to handle and—unlike lime and caustic soda—is endothermic when dissolved in water. The chemical is very basic but does not react as rapidly as lime or caustic soda. Its solubility is low at ambient temperatures and decreases as the temperature rises. It also becomes insoluble at a pH of approximately 9.0, so an overdose will not make the wasewater's pH excessively high. Magnesium hydroxide is gaining acceptance as a cost-effective alternative for neutralizing acidic streams, especially when dissolved metals must be removed. It typically produces a low-volume metal hydroxide sludge; however, this material can be more difficult to dewater than one generated via lime.

ACIDIC AGENTS. The following acids are typically used to neutralize alkaline wastewater.

Sulfuric Acid. Sulfuric acid (H_2SO_4) is the chemical most commonly used to neutralize alkaline wastewaters. It is economical and requires conventional materials for storage and feeding under most conditions, but special safety and materials-handling precautions are needed because of its corrosiveness. If the wastewater contains high concentrations of sodium or calcium, the reaction will also produce soluble sodium salts or insoluble calcium salts, respectively. Under anaerobic conditions, the sulfate ion (SO_4^{2-}) can be reduced to sulfide and then form hydrogen sulfide (H_2S)—a corrosive, dangerous gas that tends to accumulate in collection systems. Under aerobic conditions, sulfide can be biologically oxidized back to sulfate and then form weak solutions of sulfuric acid that may corrode concrete pipes.

Carbon Dioxide and Flue Gas. Compressed carbon dioxide (CO_2) gas has become fairly common for neutralizing alkaline wastewater. When dissolved in wastewater, CO_2 forms carbonic acid (H_2CO_3), a weak acid that reacts with alkaline wastes to lower the pH. Neutralization with CO_2 is most cost-effective when used to "fine tune" the wastewater's pH in a two- or three-stage neutralization process or when only minor pH adjustment is required.

Using flue gas to neutralize alkaline wastewater may be an economical method of CO_2 addition, depending on its availability. The flue gas typically contains about 14% CO_2, and the neutralization principles are the same as those for compressed CO_2 gas.

Other Acids. Other acids (e.g., hydrochloric, nitric, and phosphoric acid) can neutralize alkaline wastewater in certain situations, but they are typically more expensive and difficult to handle than H_2SO_4. Also, if the discharge permits have chloride, total nitrogen, or total phosphorus limits, these acids can create compliance issues.

BULK STORAGE AND HANDLING REQUIREMENTS. General material and bulk storage requirements for various neutralization chemicals are given below. Chemical suppliers, manufacturers, and trade associations should be consulted before selecting materials or designing storage and handling systems for pH-control chemicals.

Bulk quicklime (CaO) is stored in airtight concrete or steel bins whose outlets have at least a 60-degree slope. Hopper agitation is typically not required. Bulk lime can be conveyed by conventional bucket elevators and screw, belt, apron, drag-chain, or bulk conveyors made of mild steel. Pneumatic conveyors subject lime to air slaking, reducing particle size, so dust collectors should be provided on manually and pneumatically filled bins. Quicklime is typically added in a slurry form by slaking the lime into water and then pumping the slurry into the pH-control tank.

Quicklime typically is used on wastewater that needs large quantities of a basic chemical. Although it is less expensive than other basic chemicals, quicklime often requires significant maintenance because grit in the raw material creates excessive wear on valves, pumps, slakers, and other equipment. Also, it emits a significant amount of heat when mixed with water (exothermic reaction), which can create other operational and safety concerns.

The storage and handling requirements for hydrated lime [$Ca(OH)_2$] are the same as those for quicklime, except that the storage bin outlet should have hopper agitation. Also, the bin outlets should have nonflooding rotary feeders, and the hopper slopes should be at least 65 degrees. The slurry typically contains less undissolved grit than quicklime but still can cause excessive wear on valves, pumps, and other handling and storage equipment.

Liquid caustic soda (NaOH) can be stored at a 50% concentration (by weight) but will crystallize at 11.7° C (53° F), so the storage tanks should be indoors or else provided with heating and suitable insulation. If diluted to a 20% solution (by weight), it will crystallize at about −26° C (−15° F). (Consult the manufacturer for recommendations on diluting caustic soda solutions, because special handling and safety considerations are necessary.) Liquid caustic soda may be stored in drums, totes, or tanks large enough to accept bulk delivery by truck or rail. The storage vessel's capacity should equal about 1.5 times the largest expected bulk delivery (with an allowance for dilution water, if used) or a 2-week supply at the anticipated feed rate, whichever is larger. If storing a 50% solution of NaOH at temperatures between 24 and 60° C (75 and 140° F), the tank may be constructed of mild steel. If storing NaOH at more than 60° C (140° F), the vessel will require more elaborate materials (typically not recommended). Caustic soda tends to dissolve iron when stored in steel vessels for extended periods. If iron contamination must be avoided, the storage vessel may be made of 316 stainless steel, nickel alloys, plastics, and even rubber may be used (subject to temperature and solution limitations).

Soda ash (Na_2CO_3) typically is stored in steel bins and conveyed by steel pneumatic equipment provided with dust collectors. Bulk or bagged soda ash tends to absorb atmospheric carbon dioxide and water, converting into sodium bicarbonate (which is less active). The storage system typically consists of a tank, a means of slurrying the bulk chemical and transferring it to storage, and a means for reclaiming solution from the tank and replenishing the water. One of the most important storage requirements is maintaining the required operating temperature to prevent the formation of crystals, which are difficult to redissolve. The water used to operate the system should be preheated, and heating coils may be immersed in the bottom of the slurry tank. If the slurry tank is outdoors, insulation may be necessary. Stored soda ash is sometimes subject to arching, bridging, or "rat-holing"; to prevent this, electric or pneumatic vibrators should be mounted on the bottom of the bin (outside) just above the outlet. Slurries containing 50 to 60% total soda ash (by weight) can be pumped but require heat-loss prevention to avoid crystallization. Weak solutions (5 to 6% dissolved soda ash) can be handled just like water.

The storage and handling requirements for sodium bicarbonate ($NaHCO_3$) are similar to those for soda ash.

Magnesium hydroxide [$Mg(OH)_2$] is available as an aqueous slurry of agglomerated particles at 55 to 60% $Mg(OH)_2$. It is not particularly corrosive or difficult to handle, and typically is delivered by bulk tanker trucks. Its storage tanks typically are made of fiberglass-reinforced plastic (FRP), although other materials are also suitable. This slurry freezes at 0° C (32° F) and must be kept in mildly agitated storage. While the product should not be harmed by freezing, separation may occur and reslurrying may be difficult.

Mineral acids (sulfuric, hydrochloric, nitric) are typically stored as liquids in drums or totes provided by the chemical manufacturer. Bulk storage tanks are also common. Depending on the concentration, sulfuric acid can be stored in stainless steel, FRP, and other plastic vessels. Hydrochloric acid is typically stored in hard-rubber-lined steel tanks, FRP tanks, or various plastic tanks. Nitric acid typically requires low-carbon stainless steel tanks (Type 304 or better). The storage vessels do not require mixing. Metering pumps are typically used to deliver acids to the addition point for neutralization. The portion of the pump that contacts the reagent must be chemically inert to the acid (consult the manufacturer for recommendations).

Carbon dioxide is typically delivered in a refrigerated truck under pressure. Liquid carbon dioxide is also stored in a refrigerated, pressurized vessel. A vaporizer converts liquid CO_2 to the gaseous form, which is then diffused into the wastewater for neutralization.

DESIGN OF pH CONTROL SYSTEMS

A pH-control system should consistently adjust the wastewater's pH within acceptable permit or process-control limits. To do this, the system must:

- Add the proper amount of acid or base to the wastewater,
- Adequately mix the wastewater and the pH-control chemical(s),
- Provide enough time for the neutralization reaction to reach equilibrium or near-equilibrium conditions.

Nearly all wastewaters vary over time, so the pH-control system must be able to measure the wastewater's pH and control the amount of chemical added to reach the target pH. Designing pH-control systems is complicated because pH is a logarithmic function of the hydrogen ion concentration. For example, let's say that adding x amount of base to a strong acid solution with a pH of 2 will increase the solution's pH to 3. Then, to increase the pH to 4, only approximately 10% of the original dose (x) may be required. Only 1% of x will be needed to increase the pH to 5, and only approximately 0.1% of x is required to reach pH 6. Therefore, adjusting a wastestream from pH 2 to 7 can be a difficult control problem. A large quantity of base may be required before any measurable change in pH is produced, but as the pH increases, the rate of pH change also increases until the solution reaches an equivalence point, which depends on the wastewater's composition. Then, the rate of change decreases. To control pH precisely, an accurate and responsive control system is required.

Following are general design considerations for pH-control systems. (For more details on pH-control system design, see Chapter 14.)

GENERAL DESIGN CONSIDERATIONS. Neutralization-system designers must consider the effects of variations in wastewater flow rate, pH, and buffering capacity. An industrial wastewater's pH often varies significantly over time (minute to minute, day to day, and month to month). Some wastewaters (e.g., food-processing wastewater with both basic and acidic cleaning chemicals) can vary from 2.0 to 12.0 pH in a matter of minutes.

If a wastewater's pH varies significantly, an equalization process can reduce the necessity and size of the pH-control process. Equalization is often used in wastewater treatment to dampen variations in wastewater characteristics [e.g, flow, suspended solids, or biochemical oxygen demand (BOD)], and such equalization processes have relatively straightforward designs because these characteristics are typically conservative under normal conditions. However, pH is not a conservative substance, but a result of multiple complex chemical equilibria, which may change rapidly and significantly. A pH change of only two standard units (e.g., 2 to 4) represents a 100-fold change in the wastewater's hydrogen ion concentration. Other wastewater parameters rarely have changes of this magnitude. For more details on equalization, see Chapter 8.

Many industries generate both acidic and alkaline wastewaters. Others only generate acidic wastewater, but may have neighbors that generate alkaline wastewater. When acidic and alkaline wastes are generated simultaneously or at neighboring locations, combining them can be a cost-effective neutralization method. Each waste may need its own storage tank so the wastewaters can be blended at the proper ratios and slugs of acid or alkali can be avoided. Provisions should also be made to supplement the weaker wastestream, which may not be able to completely neutralize the stronger one.

Before blending wastestreams from multiple facilities, however, design engineers should evaluate their overall compatibility by reviewing related material safety data sheets, contacting chemical suppliers, and analyzing each flow. They should be particularly careful about blending a nonhazardous wastestream with a hazardous one, because any resulting solids must be handled and disposed as a hazardous waste in conformance with RCRA. Also, if one wastestream will need more treatment (e.g., biological treatment), combining the wastewaters may be undesirable because of the effects on downstream processes (sizing and other considerations).

BATCH AND CONTINUOUS FLOW SYSTEMS. The two main types of pH-control systems are batch and continuous-flow systems. The major differences between the two systems are the control systems used and the hydraulic control into and out of the pH-control vessel(s).

Batch pH Control. Batch pH-control processes are typically used at plants with intermittent or low volumes of wastewater. A maximum flow of 190 to 380 m^3/d (50 000 to 100 000 gpd) is often cited as applicable for batch control systems, though much larger batch-control systems have been successfully installed. Batch pH-control systems are typically simpler than continuous-flow systems and can be more reliable because each batch of wastewater can be adjusted to a target pH before being discharged.

Batch systems typically include multiple pH treatment vessels or a large equalization/holding tank upstream of a single batch tank (Figure 11.2). Because of the nature of the process, wastewater is typically pumped to the pH-control vessel. Control valves on the inlet side of the control tanks are used to determine which tank

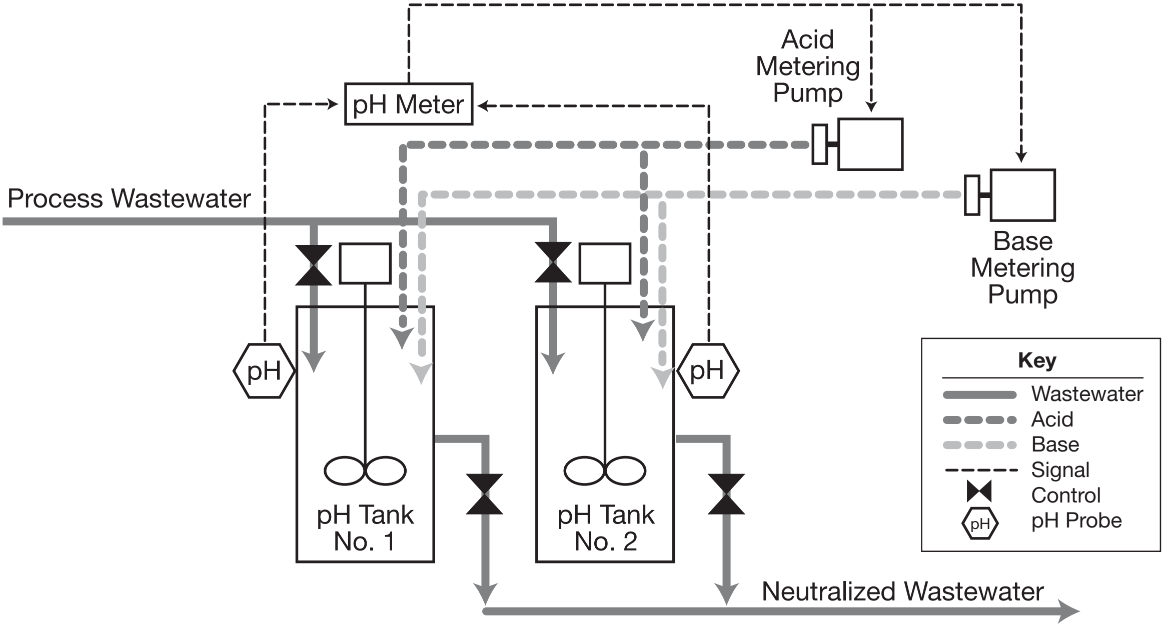

FIGURE 11.2 A batch pH control system schematic.

receives influent. Control valves on the tank outlets are used to discharge neutralized wastewater via gravity to downstream processes or a municipal collection system. A typical batch system design also includes tank level controls, pH-monitoring equipment, chemical-addition equipment, and mixing equipment in the batch tanks. Wastewater is pumped into one of the control tanks until it reaches a predetermined level. Depending on the raw wastewater's pH, the neutralizing chemical may be added during the filling period or after the tank is full. The neutralizing chemical is added until the target pH is reached. Once the target pH has been maintained for a period of time, the neutralized wastewater is discharged.

One of the main advantages of a batch pH control system is its simplicity, so the equipment and control systems should also be simple. Liquid control chemicals (e.g., sulfuric acid or caustic soda) typically are used for batch systems. Because the wastewater volumes are relatively low, the chemical use rate is typically low and chemical costs are rarely critical when selecting a chemical. The pH-control chemical typically is stored in a liquid-chemical storage tank, and electronic or motor-driven metering pumps deliver it to the batch neutralization tank.

Continuous-Flow pH Control. Continuous-flow pH control systems are typically used when the flow rate to be neutralized is more than about 190 to 380 m^3/d (50 000 to 100 000 gpd), though much smaller systems have been implemented. Continuous-flow systems typically require a more sophisticated pH-monitoring and -control system to consistently meet the effluent pH target.

Continuous-flow systems may only have one pH control vessel or may have two or three tanks operated in series (Figure 11.3). The number of tanks depends on the degree of pH adjustment required, the wastewater's buffering capacity, and the target pH range. For wastewater with average buffering capacity that only requires minimal pH adjustment, one tank may be enough. For widely variable wastewater, or wastewater requiring a large change in pH (e.g., from 2 to 7), multiple tanks are typically used. In this case, pH is grossly adjusted in the first tank and then "fine tuned" in the second and subsequent tanks to meet the target. Each tank will typically have an independent pH-monitoring and chemical-addition system.

The target pH level in each tank can be approximated via titration curve analyses (Figure 11.4). In the first tank, the wastewater's pH is adjusted to the point at which the wastewater's buffering capacity has been nearly exhausted, and adding more chemical would cause the pH to change rapidly. In the second tank, smaller amounts of pH-control chemical are added, until the target pH level is reached.

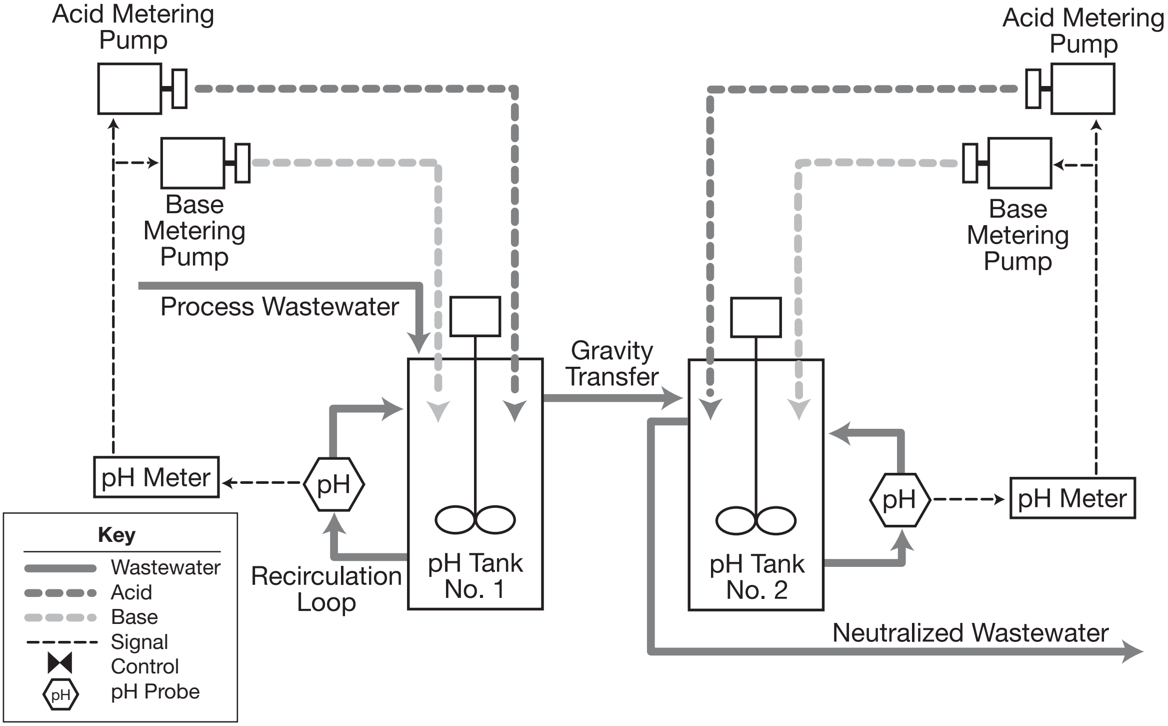

FIGURE 11.3 A continuous-flow pH control system schematic (two-stage).

Depending on the site and wastewater hydraulics, continuous-flow systems may be able to flow via gravity. More likely, however, a pumping station will be needed to lift wastewater to the first tank, and then wastewater can flow via gravity to the downstream tanks. Automatic control valves typically are unnecessary because the wastewater continuously flows in and out of the tanks.

The chemical storage and delivery systems may be similar to those used for batch-control systems. However, because continuous-flow systems are typically used for large wastewater flows, dry chemicals (and their associated mixing and delivery systems) may be less expensive than liquid ones.

HYDRAULIC DETENTION TIME. A pH-control system's hydraulic detention time is calculated as the volume of the pH-control vessel(s) divided by the influent flow rate. The required detention time is a function of the neutralization reaction rate

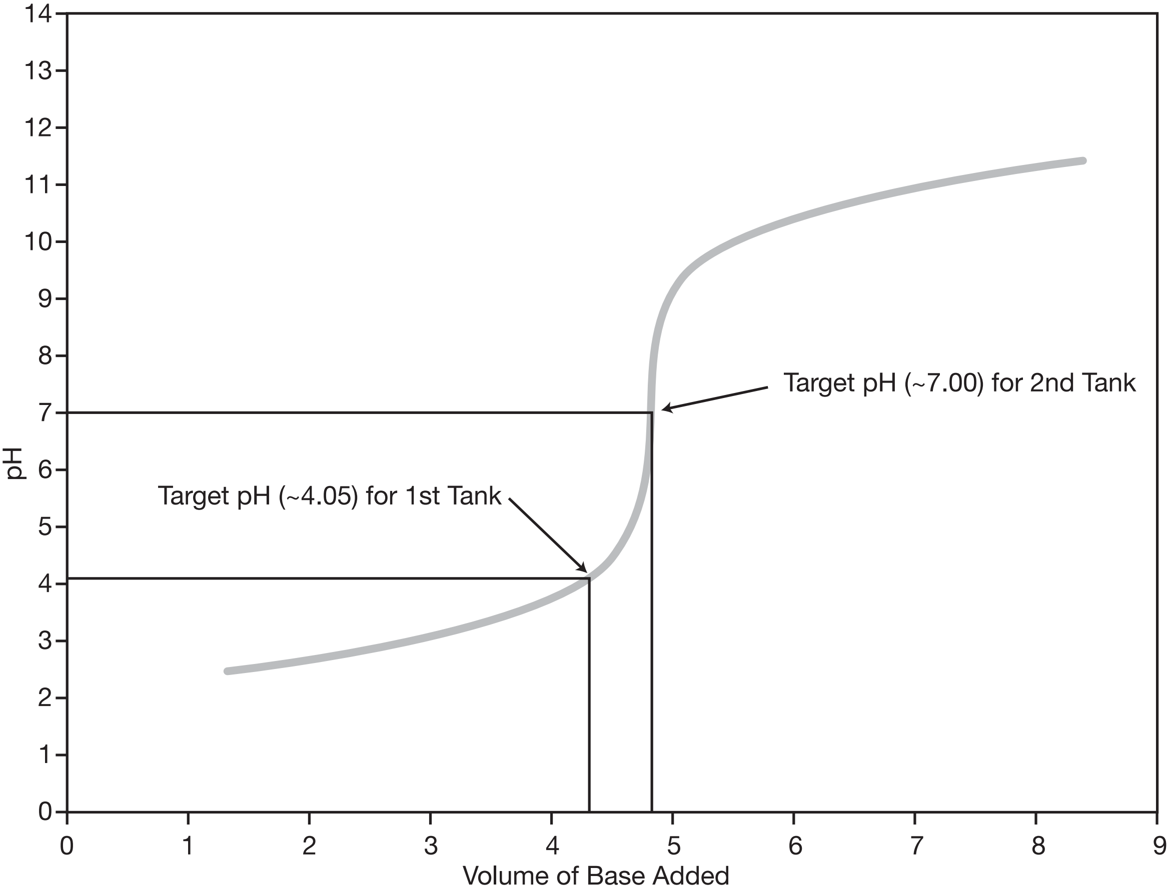

FIGURE 11.4 Two-stage pH control using titration curves.

and the type and intensity of mixing provided. So, the pH-control vessels must be large enough to effectively control the wastewater's pH under the highest anticipated flow rates and lowest (or highest) pH levels. Therefore, wastewater variability must be carefully determined before designing the system.

Minimum hydraulic detention times typically are set at 5 to 10 minutes less than worst-case conditions. Under average wastewater conditions, a hydraulic detention time of 15 to 30 minutes is common. For highly variable wastewater discharges, hydraulic detention times of 1 to 2 hours or more have been used.

The hydraulic detention time is also depends on the pH-control chemical used. Liquid chemicals typically should have at least 5 minutes to neutralize wastewater. Solid chemicals (including slurries) may need at least 10 minutes. If dolomitic lime is used, the required detention time is as much as 30 minutes.

SYSTEM GEOMETRY. For optimum mixing efficiency, a cylindrical reaction vessel's depth should be about equal to its diameter. A square tank should be approximately cubic (depth, width, and length should be equal). In continuous-flow systems, the inlet and outlet should be at opposite sides of the reaction vessel to reduce short-circuiting.

The reagent may be added at the reaction vessel inlet, to the influent before it enters the vessel, or to a sidestream-recirculation loop (if a pump-based mixing system is used). If a vertical-turbine mixing system is used in a cylindrical tank, two or more wall baffles should be added to the tank to avoid a whirlpool effect. The baffle width typically is one-twelfth to one-twentieth of the tank's width. (Square tanks provide for better mixing without needing baffles.)

MIXING REQUIREMENTS. Mixing must be provided in the neutralization tank(s) to reduce the required reaction time. Mechanical mixing is typical, although hydraulic mixing via recirculation pumps or air injection may be more desirable, depending on the tank layout, flow rate, etc. The required mixing energy depends on the chemical's reaction time, tank's hydraulic detention time, and the type of mixing provided (Figure 11.5) (Eckenfelder, 1989). The typical power requirement is about 0.04 to 0.08 kW/m^3 (0.2 to 0.4 hp/1000 gal).

Mixing should provide enough energy so the system's "dead time" is no more than 5% of the vessel's hydraulic retention time. *Dead time* is period between reagent addition and the first detectable change in the wastewater's pH. A short dead time is required so the control system can adjust the chemical feed rate based on current information.

OPERATIONAL CONSIDERATIONS

PROCESS CONTROL. The following is a general description of process-control issues for pH-control systems. (For a detailed discussion of process-control equipment and instrumentation, see Chapter 14.)

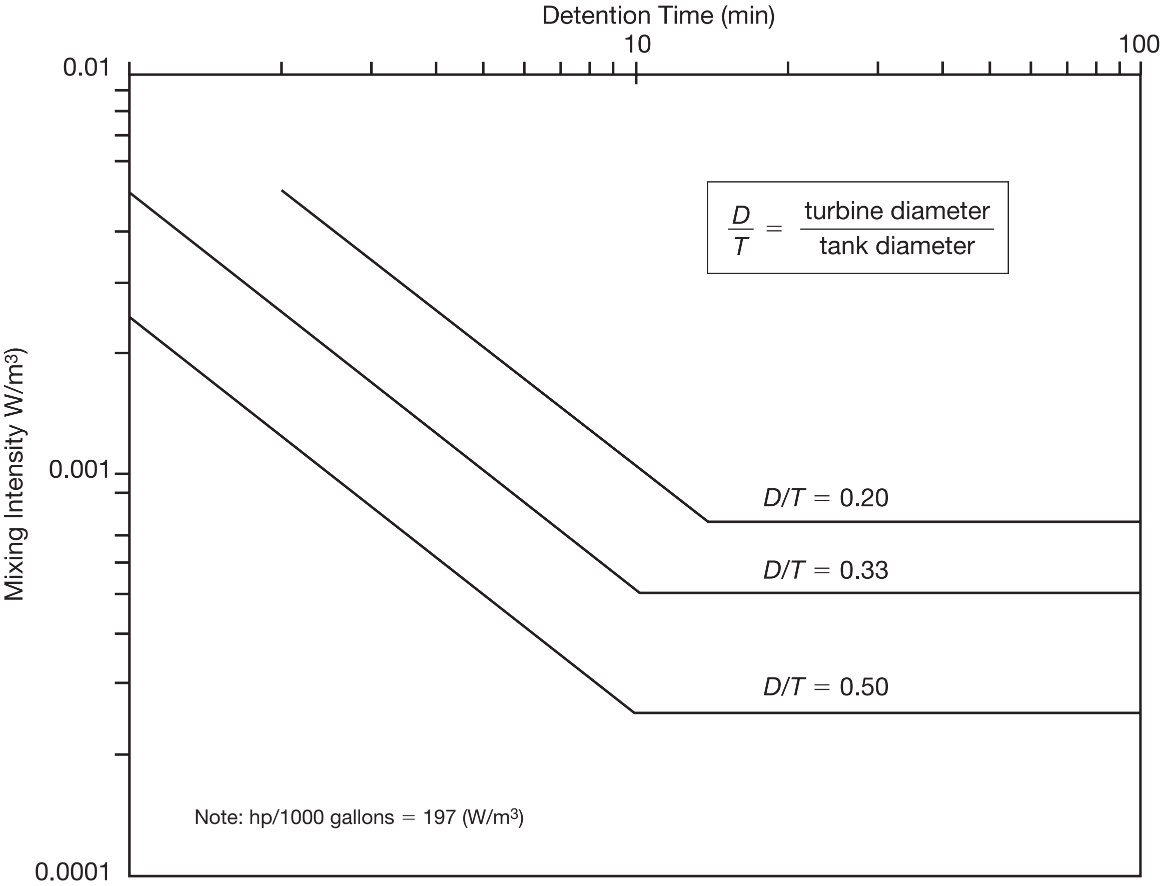

FIGURE 11.5 Mixing intensity versus detention time (Eckenfelder, W. W., Jr., *Industrial Water Pollution Control,* 2nd ed., copyright © 1989, McGraw-Hill: New York; reproduced with permission of The McGraw-Hill Companies).

Batch Systems. Batch pH-control systems typically use a simple pH monitoring and control system. Because the wastewater can be held in the batch tank until the target pH level is achieved, process control is typically less critical than it is in a continuous-flow system.

The pH probe is often mounted on an extendable arm and submerged into the batch tank from above. Alternatively, the pH probe may be mounted through the tank's sidewall with a special valve fitting so the probe can be removed, maintained, and calibrated without taking the tank out of service. The pH probe must be mounted so it is always under the tank's minimum water level to avoid drying out the probe's membrane.

The pH meter can be used to directly control the pH-addition equipment (metering pumps or valves) based on several control programs available from various manufacturers. Alternatively, the pH meter may transmit pH readings to a PLC, which controls the chemical-addition equipment. The selection of control equipment is typically an owner preference and depends on site-specific control requirements. When metering pumps are used, variable-speed drives may be used to increase chemical addition rates as the measured pH deviates further from the target control point, and vice versa. Once the target pH is reached, the wastewater should be held in the batch tank for 5 minutes or more before discharge to allow the pH to stabilize. Otherwise, an instantaneous pH reading at the target level could result in the release of wastewater that is outside the target pH range.

Continuous-Flow Systems. For continuous flow systems, accurate and responsive control systems are required because the wastewater is discharged continuously. The pH-control setpoint is typically required to be conservative, because even a short-term pH excursion could result in a violation or downstream process upset. For example, if an alkaline wastewater must be adjusted to a maximum pH of 9, the pH-control setpoint may need to be 8.5, 8.0, or even lower depending on the buffering capacity, pH variability, and control systems employed.

Because continuous flow systems typically use larger contact vessels, mounting the pH probe directly in the tank may be impractical and not representative of actual conditions throughout the tank. If so, the pH monitoring point should be as close as possible to the pH-control tank (e.g., in the tank's effluent line or in an external recirculation loop). The influent pH may also need monitoring to improve the chemical-addition equipment's response time. The exact process-control requirements will be dictated by the wastewater's characteristics and variability.

CORROSION. A major concern with pH-control systems is corrosion of equipment, structures, and piping. Because many pH-control chemicals are corrosive acids or bases, design engineers should select appropriate construction materials when designing the pretreatment system. Stainless steel, fiberglass, and various plastics are often used to minimize or eliminate corrosion. If concrete tanks are used, chemical-resistant coatings can help minimize corrosion from acids.

Operating the system at a higher or lower pH than is required for permit compliance is another way to reduce corrosion. For example, if the permit requires that an acidic wastewater be adjusted to a minimum pH of 5.5, the operators may choose to adjust the pH to 6.0 or 6.5 to reduce potential corrosion. This, of course, depends on the materials and pH-adjustment chemical involved. Another method to reduce corrosion is to select a pH-adjustment chemical that is less corrosive. For example, carbon dioxide is less corrosive than sulfuric acid under most circumstances.

SCALE. When supersaturated lime solutions are used to control pH, a common type of scale develops. It can form on mixers, pumps, piping, tanks, and instrumentation, decreasing the system's efficiency and accuracy. Scale buildup should be periodically cleaned via mechanical or chemical methods.

SOLIDS HANDLING. Although pH control is designed to adjust the concentration of hydrogen ions in wastewater, numerous competing reactions will also occur with chemical addition. Some reactions may produce precipitates (i.e., convert dissolved solids to suspended solids). The suspended solids formed either stay in suspension or settle, depending on the amount formed, the precipitates' weight, and the system's mixing intensity.

If downstream processes (or the POTW) can tolerate these byproducts, the easiest method is to discharge the solids with the pH-adjusted wastewater. However, solids tend to be problematic for downstream processes and collection systems, so they should be concentrated and removed for separate disposal.

Sedimentation is the most common method of solids removal. In a batch system, flexibility can be designed into the system to allow the pH control tank to serve as the sedimentation vessel. Solids are removed from the bottom of the batch tank after adequate time is provided for solids settling. For continuous-flow systems, a separate sedimentation tank is typically required. Alternate solids removal technologies include granular media filtration, cloth media filtration, and membrane filtration.

After removal, solids are often dewatered to remove free water and reduce the volume/mass for disposal. (For a detailed discussion of solids dewatering equipment, see Chapter 9.)

OPERATING COSTS. The operating costs for a pH control system include chemical, power (mixing and pumping), equipment cleaning and calibration, maintenance, labor, and for some installations, sludge handling. For many applications, chemical costs will be the most significant ongoing operating cost of the system, so careful consideration should be given to proper chemical selection, accurate pH monitoring, and chemical dose control.

Because industrial processes often change over time, wastewater characteristics may also change over time. Titration curves should be developed regularly to provide information for implementing changes to the pH control system. This can have a measurable effect on the cost of operating the control system. In addition, chemical costs can vary significantly over short periods of time. For example, caustic soda is typically produced as a byproduct of chlorine production. So as chlorine demand fluctuates, caustic soda costs will also vary. In such cases, it may be advantageous to switch to alternate neutralization chemicals.

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Chapter 12

Removal of Inorganic Constituents

(continued)

Inorganic constituents are naturally abundant. They enter groundwater and surface water via a variety of geochemical processes (e.g., soil leaching) and human activities (e.g., manufacturing, construction, agriculture, and transportation). High inorganic concentrations in industrial wastewaters are undesirable because they could adversely affect waterbodies, people, and publicly owned treatment works (POTW). The inorganic constituents of concern found in industrial wastewaters include heavy metals, cyanide, sulfides and nutrients (primarily nitrogen and phosphorus).

This chapter focuses on the treatment and removal of inorganics. (Organic forms of nitrogen and phosphorus are addressed in Chapter 13.)

EFFECTS ON MUNICIPAL WASTEWATER TREATMENT PLANTS

Heavy metals and cyanide can inhibit or kill microorganisms in biological systems, as well as make solids handling and disposal problematic. Sulfide causes odors, forms toxic gases, corrodes concrete and steel structures, and promotes filamentous bulking in activated sludge systems. Nutrients (e.g., nitrogen and phosphorus) could unduly increase the oxygen demand [nitrogenous oxygen demand (NOD)] at the POTW or hinder the POTW's ability to meet its nutrient limits. Ammonia may be toxic to the POTW's activated sludge and digestion systems.

These effects often determine industrial pretreatment standards.

METALS AND CYANIDE. The toxic properties of metals and cyanide can inhibit or kill microorganisms in municipal and industrial biological treatment systems. Biological systems can become acclimated to heavy metal concentrations that would typically be inhibitory (toxic). However, changes in pH may exacerbate the harmful effects of metals by changing the levels of dissolved metals, which the organisms physically or chemically absorb. A shift in pH from 8 to 7 can increase the solubility of most metals, especially metal-hydroxides, soluble oxides, or metals adsorbed to solids.

Heavy metals also accumulate in a reactor's solids, especially in activated sludge systems, and aerobic and anaerobic digesters. As the biologically degradable materials are oxidized or reduced, undissolved metals may remain and their concentrations will significantly increase as the solids are settled, thickened, and dewatered. This could lead to a POTW's ultimate failure to comply with biosolids regulations.

Municipalities limit heavy metals discharged to municipal POTWs as part of their comprehensive pretreatment program. Industrial dischargers to POTWs also must comply with state and federal categorical pretreatment regulations.

SULFIDES. Sulfides and other sulfur compounds are health and safety issues and corrosion problems in wastewater collection systems. Sulfur compounds can also present operational and biotoxicity problems to POTWs and industrial biological treatment systems, particularly in activated sludge processes and digestion processes.

Key sulfur compounds of interest in industrial wastewaters include hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and organic sulfur compounds such as mercaptans. Hydrogen sulfide affects collection systems and POTWs by corroding infrastructure and creating offensive odors. Hydrogen sulfide corrosion is especially manifested on concrete and steel pipe, particularly at manholes and at high points in forcemains. Hydrogen sulfide odors are detectable at concentrations of 0.01 to 0.30 ppm in air. The recommended National Institute for Occupational Safety and Health (NIOSH) exposure limit is 10 ppm for 10 minutes. Concentrations of 100 ppm are considered by NIOSH to be immediately dangerous to life or health (IDLH). Hydrogen sulfide is also explosive under certain circumstances.

Besides health and safety issues, excessive sulfides also promote the growth of filamentous bacteria in activated sludge processes. These filamentous bacteria can result in very slow settling (a condition called *bulking*) in activated sludge systems.

Soluble sulfides concentrating in anaerobic digesters have been found to be toxic to anaerobic and bacteria at concentrations of 200 mg/L, causing so-called "stuck" digesters and poor digestion performance (Parkin and Owen, 1986). Excessive hydrogen sulfide and sulfur dioxide gases in digesters create odor and corrosion problems, explosion hazards, and potential exposure to toxic gas.

PHOSPHORUS COMPOUNDS. Inorganic phosphorus compounds are major problems for POTWs and receiving streams, largely because phosphorus is a critical nutrient for plants and algae growth. Phosphorus compounds are typically found in wastewater from fertilizer manufacturers, soft drink manufacturers, milk and other beverage producers, pharmaceutical manufacturers, etc.

Excessive phosphorus can cause algae blooms, fish kills, and major taste and odor problems in drinking water supplies. Many POTWs are now required to remove phosphorus before discharging effluent to receiving waters, so municipalities may require industrial dischargers to remove excessive phosphorus before discharging their wastewaters to POTWs.

The forms of inorganic phosphorus addressed in this chapter are orthophosphate and polyphosphate. The orthophosphate ion (PO_4^{-3}) is the simplest form of phosphate. Polyphosphates (e.g., $P_2O_7^{-4}$) are often used in soaps, detergents, and other cleaning solutions. (For information on treating organic phosphorus compounds, see Chapter 13.)

NITROGEN COMPOUNDS. Like phosphorus, nitrogen compounds in industrial wastewater are problematic for POTWs and receiving streams because nitrogen promotes algae growth and ammonia-nitrogen significantly increase oxygen demand at POTWs and in receiving streams, due to biological nitrification. Nitrogen compounds are found in many industrial wastewaters (Table 12.1).

High ammonia levels in industrial wastewater may chelate heavy metals, preventing them from being easily removed via conventional treatment. Excessive nitrogen can cause algae blooms and fish kills, as well as major taste and odor problems in drinking water supplies. Many POTWs are now required to oxidize or remove nitrogen before discharging effluent to receiving waters, so municipalities are increasingly requiring industrial dischargers to remove excessive nitrogen before discharging their wastewaters to POTWs.

There are four primary forms of nitrogen in industrial wastewater: ammonia-nitrogen (NH_4^+–N), organic nitrogen (various forms), nitrite-nitrogen (NO_2^-–N), and nitrate-nitrogen (NO_3^-–N). The sum of ammonia-nitrogen and organic nitrogen concentrations is called *total Kjeldahl nitrogen* (TKN). Because organic nitrogen can be converted biologically to ammonia (a process called *ammonification*), TKN is often a better predictor of total nitrification potential than ammonia concentrations alone. Total Kjeldahl nitrogen is often used in biological design calculations.

Ammonia. Ammonia is found in many industrial wastestreams (e.g., feedlots, meat processing, metal-finishing and printed wire-board manufacturing, and refineries). Most forms of organic nitrogen can be hydrolyzed to ammonia via biological action. The rate of conversion from organic nitrogen to ammonia-nitrogen influences the subsequent effects of ammonia on the bacteria in a POTW or receiving stream.

The equilibrium of ammonia gas (NH_3) and ammonium ion (NH_4^+) in water is shown in the following reaction:

$$NH_4^+ + OH^- \leftrightarrow NH_3\uparrow + H_2O \tag{12.1}$$

This equilibrium reaction is strongly pH-dependent. Higher pH values (typically 10 or higher) favor the release of ammonia gas; lower values favor its dissolution in water.

Nitrite. Nitrite compounds are typically found in high concentrations in wastewater from dyestuff manufacturers, textile manufacturers, meat processors, metal coaters, the rubber industry, etc. They are often an intermediate oxidation state in the nitrification process. Further biological oxidation of nitrites results in the formation of nitrates.

Nitrate. Nitrate compounds are typically found in wastewater from pharmaceutical manufacturers, meat processors, pigment manufacturers, fertilizer producers, and explosives manufacturers. Nitrate compounds are also formed during biological nitrification. The principal concern about nitrates in wastewater is that they are a nutrient source for plants and algae. Excessive algae growth, in particular, can cause nuisance conditions in receiving waterbodies and taste and odor problems in drinking water sources.

Because virtually all nitrate compounds are soluble in water, precipitation is ineffective. The most common nitrate-removal methods are biological denitrification, ion exchange, land treatment of wastewater, and constructed wetlands. Biological nutrient removal is discussed in Chapter 13. Ion exchange is discussed below. Land application and constructed wetland systems are beyond the scope of this book [see Metcalf & Eddy (2003) and various U.S. EPA publications].

TYPICAL INDUSTRIES WITH INORGANIC COMPOUNDS

Table 12.1 lists inorganic constituents sometimes found in industrial wastewaters.

TYPICAL TREATMENT STRATEGIES AND PROCESSES

Treatment techniques for inorganic pollutants are varied, reflecting the range of inorganic compounds found in industrial wastewater. Because of the variety of sources involved, inorganic pollutants are often treated in individual, rather than combined,

TABLE 12.1 Typical industries with inorganics in wastewater.

	Ag	**As**	**Ba**	**B**	**Cd**	**CN**	**Cr**	**Cu**	**Fe**	**Pb**	**PO_4**	**Mn**	**Hg**	**Ni**	**N**	**Se**	**Zn**
Paint manufacture		X	X		X		X	X		X	X	X	X	X	X	X	X
Cosmetics/pharmaceuticals manufacture				X							X		X		X		X
Ink manufacture	X						X					X			X		
Animal-glue manufacture							X								X		
Tannery operations		X		X			X		X						X		
Carpet production				X	X											X	
Photographic supplies	X			X	X	X	X			X			X		X	X	
Textile manufacture					X			X	X						X	X	X
Pulp/paper/paperboard manufacture				X				X					X	X			X
Food/beverage processing	X								X		X				X		
Printing industry					X		X							X	X		X
Metal finishing	X			X	X	X	X	X	X	X				X	X		X
Battery manufacture	X	X			X			X		X		X		X			X
Pharmaceuticals						X				X	X		X				X
Jewelry manufacture	X							X							X		
Electrical/electronics manufacture			X					X					X		X	X	
Explosives manufacture			X							X			X		X		

wastestreams. This is particularly true of metal-finishing wastewaters containing cyanide, complexed metals, and hexavalent chromium.

Common treatment techniques for inorganic pollutants include:

- Neutralization-precipitation,
- Chemical reduction,
- Oxidation,
- Air and steam stripping,
- Ion exchange,

- Adsorption,
- Membrane filtration,
- Electrodialysis, and
- Evaporation.

NEUTRALIZATION-PRECIPITATION. In neutralization and precipitation, chemicals are used to adjust the wastewater's pH and combine with pollutants to create an insoluble compound (precipitant) that is removed from the wastewater via settling, and sometimes by filtration. This process typically removes most heavy metals, phosphates, and sulfides.

The chemicals used include iron salts (ferrous and ferric chloride and sulfates); aluminum salts (aluminum sulfate, polyaluminum chloride, and sodium aluminate); lime; sodium bicarbonate and sodium carbonate (soda ash); sodium hydroxide; and sulfide salts (e.g., ferrous sulfide). Jar and pilot testing best demonstrate which chemical will be most effective.

The removal of metals and phosphates by iron and aluminum salts is typically stoichiometric: higher pollutant concentrations require higher iron and aluminum doses to achieve the desired results. On the other hand, the removal of metals and phosphates by hydroxide precipitation (the mechanism for lime and sodium hydroxide) is typically pH-dependent. The reaction typically occurs at pH 7.5 to 10.6 [depending on the pollutant(s) being removed], so the effluent's pH often must be adjusted afterward. Moreover, when treating phosphates, hydroxide typically produces more solids than iron or aluminum salts.

In most neutralization-precipitation processes, the chemical is fed to the wastewater via chemical metering pumps or feeders. Chemical addition may be manually or automatically controlled based on wastewater flow, pH, or another process parameter. Normally, chemical precipitation requires a flash-mix and flocculation process before sedimentation. The resulting solids are then removed for further treatment. (For process design parameters and guidelines, see Chapter 11.)

Predicting Inorganic Compound Solubilities. In determining the applicability of precipitation to a particular inorganic pollutant, the solubility product of the ions must be calculated or known (Table 12.2).

Table 12.2 Simplified solubility chart (Kemmer, F. N., The Nalco Water Handbook, copyright © 1988, McGraw-Hill: New York; reproduced with permission of The McGraw-Hill Companies).

Anion→	F^-	Cl^-	Br^-	I^-	HCO_3^-	OH^-	NO_3^-	CO_3^{-2}	SO_4^{-2}	S^{-2}	CrO_4^{-2}	PO_4^{-3}
Cation ↓												
Na^+	S	S	S	S	S	S	S	S	S	S	S	S
K^+	S	S	S	S	S	S	S	S	S	S	S	S
NH_4^+	S	S	S	S	S	S	S	S	S	S	S	S
H^+	S	S	S	S	CO_2	H_2O	S	CO_2	S	H_2S	S	S
Ca^{+2}	I	S	S	S	SS	VSS	S	I	VSS	X	S	I
Mg^{+2}	VSS	S	S	S	S	I	S	VSS	S	X	S	I
Ba^{+2}	VSS	S	S	S	VSS	S	S	VSS	I	X	I	I
Sr^{+2}	VSS	S	S	S	VSS	SS	S	I	VSS	X	VSS	I
Zn^{+2}	S	S	S	S	VSS	I	S	I	S	I	VSS	I
Fe^{+2}	SS	S	S	S	SS	VSS	S	VSS	S	I	X	I
Fe^{+3}	SS	S	S	S	I	I	S	I	S	X	X	I
Al^{+3}	S	S	S	S	X	I	S	X	S	X	X	I
Ag^+	I	I	I	I	I	I	S	VSS	S	I	I	I
Pb^{+2}	VSS	S	SS	VSS	I	VSS	S	I	I	I	I	I
Hg^+	I	I	I	I	I	I	S	S	VSS	I	VSS	I
Hg^{+2}	SS	S	S	I	I	I	S	I	VSS	I	SS	I
Cu^{+2}	SS	S	S	VSS	I	I	S	I	S	I	I	I

S = soluble (> 5000 mg/L).
SS = slightly soluble (2000–5000 mg/L).
VSS = very slightly soluble (20–2000 mg/L).
I = insoluble (< 20 mg/L).
X = not a compound.

As an example, an industrial facility needs to remove copper and zinc from its wastewater. To determine whether a precipitation chemical could treat these heavy metals, refer to the cation list in Table 12.2 and note which combinations of cation and anion are insoluble (I) or very slightly soluble (VSS). For copper and zinc, both are insoluble when combined with hydroxide (OH), and carbonate (CO_3). So, lime [$Ca(OH)_2$], sodium hydroxide (NaOH), and soda ash (Na_2CO_3) should be considered.

The precise chemical dosage and optimum process performance depend upon a number of factors, such as:

- Wastewater pH,
- Other competing ions,
- The wastewater's alkalinity and buffering capacity,
- The amount of organic material present, and
- The mixing and flocculation intensity and detention time.

As a result, jar and pilot testing are strongly recommended before selecting a chemical. Daily jar testing may also be useful during operations to optimize dosing and performance.

Hydroxide Precipitation-Coagulation. Heavy metals typically are removed from wastewater via chemical precipitation as a metal hydroxide, followed by coagulation of the metal particles into larger, heavier, flocculated particles (floc), which are then separated from the water via sedimentation or flotation. This method has proven reliable and can be inexpensive and highly selective. A properly designed and operated process can typically reduce metal concentrations to 1 mg/L or less.

Heavy metals are typically dissolved under acid conditions and precipitated under alkaline conditions, so pH control is important. Sodium hydroxide (NaOH; caustic soda), calcium hydroxide [$Ca(OH)_2$; lime] or magnesium oxide [$Mg(OH)_2$; hydrated magnesium hydroxide] are typically added to wastewater to increase the pH and provide hydroxide ions. Excess hydroxide ions are needed to ensure that the precipitation reaction is complete.

The heavy metal ions in solution react with the hydroxide ions to form solid metal hydroxide particles:

$$M^{+2} + 2OH^{-} \rightarrow M(OH)_2 \downarrow \tag{12.2}$$

The pH at which a metal is least soluble (i.e., most likely to precipitate) is metal-specific (Figure 12.1). The "knee" of the curve is the point at which the metal is least soluble. However, this point is often not as precise as shown in Figure 12.1; it may span a wider pH range. Other factors that affect metal solubility include the presence of chelating agents, surfactants, other ions, temperature, etc.

The major challenge in metals precipitation is that many metal-finishing wastewaters contain numerous metals. The design engineer must then determine the pH at

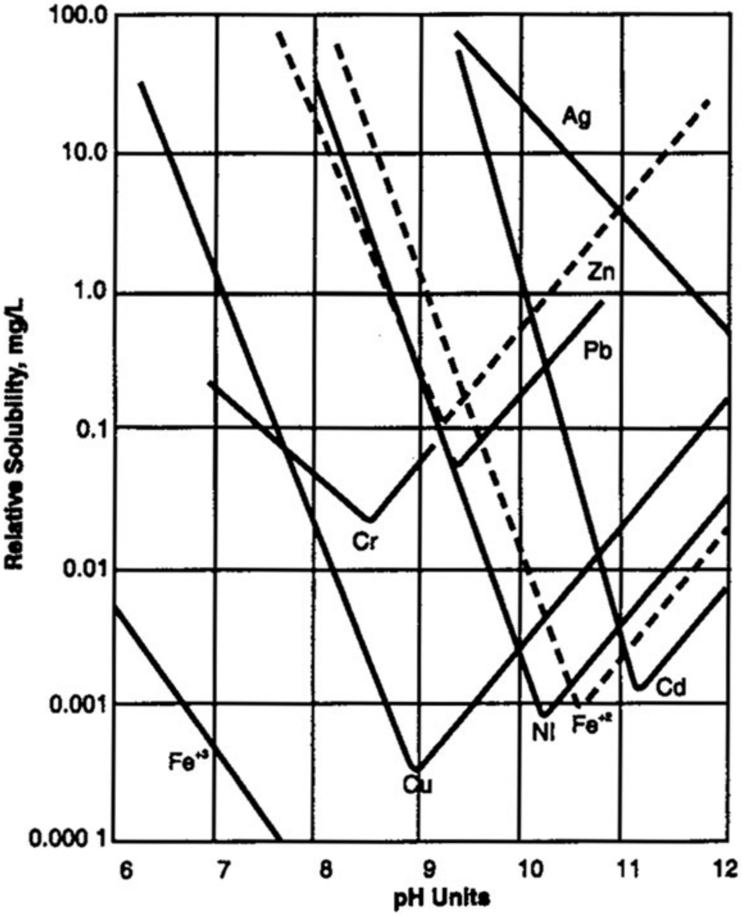

FIGURE 12.1 The relative solubility of selected metals versus pH (U.S. EPA, 1980).

which the most metals can be precipitated and removed. Also, the relative mix of metals in wastewater may change almost constantly, changing the optimum pH. Daily or hourly jar testing may be necessary to determine both the pH at which the most metals will precipitate and the probability that the effluent concentrations will meet regulatory limits. (Jar testing techniques are covered in more detail in Chapter 4.)

Once the metal hydroxides have precipitated, the tiny hydroxide particles must be coagulated into flocs. The heavier the flocs, the quicker they settle in a clarifier. Typically, hydroxide precipitates tend to be too fine to settle readily without a flocculent (polymer), which should be added to the wastewater before it enters the clarifier. After clarification (sedimentation), filtration will remove any remaining metal hydroxide particles. The wastewater pH may need to be adjusted before discharge to meet regulatory limits.

A key issue that is often overlooked in chemical addition is the quality of the chemicals themselves, particularly acids.. Acids and alkalis can contain heavy metals that can be problematic if the discharge limits are strict. So, the metal content of all reagents should be obtained and certified by the reagent supplier. Reagent-grade chemicals are available with very low levels of heavy metals present.

Iron and Aluminum Salt Precipitation-Coagulation. The iron and aluminum salts typically used to remove inorganic pollutants include ferrous and ferric chloride, ferrous and ferric sulfate, aluminum sulfate (alum), and polyaluminum chloride. They remove certain metals and other inorganics (e.g., phosphates) via precipitation. Depending on pH, hydroxides of aluminum and iron are also precipitated.

As with most chemical precipitation processes, the correct iron or aluminum salt and the optimal dose are selected after pilot-testing or bench-scale testing (see Chapter 4). Besides pollutant-removal effectiveness, the major considerations in selecting iron and aluminum salts include:

- The dosage and cost of the salt;
- The precipitate's settleability;
- The volume and nature of the solids produced;
- The pH of the resulting wastewater and the potential need for adjustment;
- Effluent iron or aluminum limits; and
- The temperature of the wastewater to be treated.

Sulfide Precipitation-Coagulation. When lower effluent metals concentrations are required, or when the metals are complexed with chelating agents (e.g., cyanide, EDTA, or ammonia), sulfide or carbonate precipitation may be an effective treatment method.

Table 12.3 compares the theoretical solubilities of various metal hydroxides, carbonates, and sulfides. Lower values indicate that the compound is less soluble and more likely to precipitate. The data show that metals are less soluble as sulfides or

Table 12.3 Theoretical solubilities of hydroxides, carbonates, and sulfides of selected metals in distilled water (U.S. EPA, 1983).

	Solubility of metal ion (mg/L)		
Metal	**As hydroxide**	**As carbonate**	**As sulfide**
Cadmium (Cd^{+2})	2.3×10^{-5}	1.0×10^{-4}	6.7×10^{-10}
Chromium (Cr^{+3})	8.4×10^{-4}	—	No precipitate
Cobalt (Co^{+2})	0.22	—	1.0×10^{-8}
Copper (Cu^{+2})	2.2×10^{-2}	—	5.8×10^{-18}
Iron (Fe^{+2})	0.89	—	3.4×10^{-5}
Lead (Pb^{+2})	2.1	7.0×10^{-3}	3.8×10^{-9}
Manganese (Mn^{+2})	1.2	—	2.1×10^{-3}
Mercury (Hg^{+2})	3.9×10^{-4}	3.9×10^{-2}	9.0×10^{-20}
Nickel (Ni^{+2})	6.9×10^{-3}	0.19	6.9×10^{-8}
Silver (Ag^{+})	13.3	0.21	7.4×10^{-12}
Tin (Sn^{+2})	1.1×10^{-4}	—	3.8×10^{-8}
Zinc (Zn^{+2})	1.1	7.0×10^{-4}	2.3×10^{-7}

carbonates than as hydroxides, particularly in the neutral and alkaline ranges. So, lower metal concentrations are theoretically possible with sulfide precipitation than with hydroxide precipitation.

Further, Figure 12.1 shows that metal hydroxides tend to re-dissolve as the pH rises, while metal sulfides become more insoluble and continue to precipitate. The heavy metal ions react with sulfide ions to form a metal sulfide precipitate:

$$M^{+2} + 2S^{-} \rightarrow MS_2 \downarrow \tag{12.3}$$

Two sulfide precipitation processes—insoluble and soluble—are used to precipitate heavy metals (Figure 12.2). Insoluble sulfide precipitation uses ferrous sulfide (FeS), while soluble sulfide precipitation uses a water-soluble reagent [e.g., sodium hydrosulfide ($NaSH \cdot 2HOH$) or sodium sulfide (Na_2S)]. The main advantage of insoluble sulfide precipitation is that because ferrous sulfide is relatively insoluble, hydrogen sulfide odor is typically minimal.

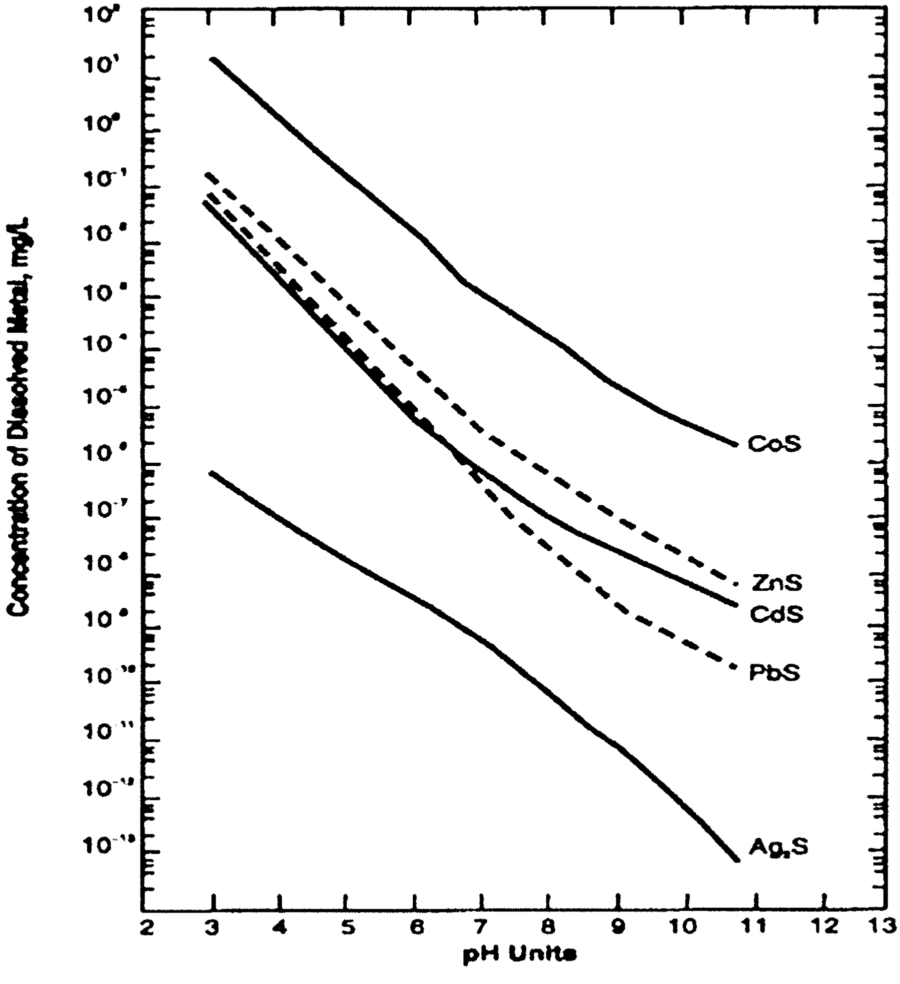

FIGURE 12.2 Theoretical metal sulfide solubility versus pH (U.S. EPA, 1983).

While theoretically more effective than hydroxide for precipitating metals, sulfide precipitation has a number of disadvantages:

- Excess sulfides can form hydrogen sulfide (H_2S), an odorous and toxic gas;
- Sulfide precipitation is typically more expensive than hydroxide precipitation;
- Sulfide treatment requires continuous operator attention to control-related toxicity hazards; and

- The solids formed are gelatinous, more voluminous, and more difficult to dewater than hydroxide sludges.

In practice, sulfide precipitation is often used to polish hydroxide precipitation effluent to minimize the sulfides required, sulfide sludge produced, and the hydrogen sulfide potential.

As with hydroxide precipitation, the optimum pH levels and chemical doses for sulfide precipitation should be determined via treatability and settling tests. Daily and hourly jar testing is also recommended.

Carbonate Precipitation-Coagulation. Like sulfide, carbonate precipitation can produce lower effluent metal concentrations than hydroxide, even in the presence of chelating agents. The chemicals involved are sodium carbonate (Na_2CO_3; also called soda ash) and sodium bicarbonate ($NaHCO_3$). Sodium bicarbonate is less effective than sodium carbonate at removing all metals from solution.

Carbonate precipitation has two advantages over hydroxide and sulfide precipitation:

1. The metals can be precipitated at pH 7 to 9, so the control system is simpler.
2. Carbonate neutralizes excess activity (i.e., it adds buffering capacity), potentially helping to meet discharge standards.

A bicarbonate-carbonate mixture can precipitate more metals than bicarbonate alone. Sodium bicarbonate can only raise the pH to about 8.3, which is not high enough to reduce some metals (e.g., nickel and cadmium) to typical pretreatment limits. The pH typically must be raised to 9.0+ to precipitate more metals, and combining carbonate with bicarbonate will do this.

The required pH and alkalinity can be tested and determined for the metals involved. The distributions of the three forms of carbonate (CO_3^{-2}, HCO_3^-, and H_2CO_3) remain the same for any pH level. Adding more carbonate can increase treatment efficiency by driving the equation's stoichiometry to the precipitate side. This is an advantage over hydroxide precipitation because overdosing hydroxide above a certain level (see Figure 12.1) will actually increase metal solubility.

Carbonate precipitation has two disadvantages:

1. The carbonate-metal reactions are slower, requiring larger flash-mix and flocculation units.
2. Most carbonate chemicals are available in dry form, requiring more handling and mixing steps.

Chelating Agents and Metals. Certain metal-finishing and printed wire-board manufacturing processes use substances called *chelating agents* or *complexing agents*. Chelating agents are used to maintain metals in solution over a wide range of pH values, enabling more uniform metal plating than by conventional electroplating. Such metals are often called *electroless metals.* Electroless copper and nickel are common forms of complexed metals used in the printed-circuit-board industry and other electroplating operations.

Chelating agents include ammonia, polyphosphates, nitrilo triacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), citrates, tartrates, cyanides, and gluconates. They bind with metals and prevent them from precipitating at normal alkaline pH values.

The metal-chelate complex typically must be broken before metals can be precipitated from wastewater. The metal-chelate bond can be broken by precipitating the metal from solution via a method that (unlike hydroxide precipitation) is relatively immune to chelating effects. Such methods include sulfide precipitation, iron coprecipitation (ferrous or ferric sulfate), carbamate precipitation, sodium borohydride, ion exchange, and water-insoluble starch xanthate (ISX) precipitation.

Alternatively, the bond can be broken by adjusting the pH to an extreme level (very low or very high, depending on the chelating agent). At these pH conditions, the complex dissociates, freeing the metal ion. A suitable cation (e.g., calcium) is then used to tie up the chelating agent so it cannot recombine with the metal ion when the solution is neutralized. This has proved to be an effective treatment method for some chelating agents.

To determine the most cost-effective technique for breaking the metal-chelate bond, consult the chelate manufacturer and then conduct bench- or pilot-scale testing to determine the dose and mixing parameters.

CHEMICAL CONVERSION. At metal-finishing facilities using hexavalent chrome or cyanide, two chemical treatments are used before the neutralization-precipitation step: cyanide destruction and hexavalent chromium reduction. Because of cost, these treatments are best performed only on the wastestreams that contain these constituents, rather than on the facility's entire wastewater flow.

Cyanide Destruction. Cyanide is used as a chelating agent in certain metal-finishing and other processes. It forms complexes with metals that prevent the metals from precipitating as hydroxides. Once the cyanide-metal bond is broken, however, the metal can precipitate under the appropriate pH conditions. Cyanide must be destroyed because it is toxic to microorganisms in biological treatment processes.

Before designing a treatment process, engineers should analyze cyanide-laden wastewater for two properties: total cyanide and the amount of cyanide amenable to chlorination. The cyanide that is amenable to chlorination is ultimately converted to carbon dioxide and nitrogen gas in a two-step process called *alkaline chlorination.*

Alkaline chlorination typically uses sodium hypochlorite (NaOCl) and caustic (NaOH) to break the cyanide bond under alkaline conditions, first by oxidizing cyanide to cyanaogen chloride (CNCl), then quickly to cyanate (CNO^-), and finally to carbon dioxide and nitrogen gas. The overall oxidation reaction is:

$$CN^- + NaOCl \rightarrow CNO^- + NaCl \tag{12.4}$$

Cyanogen oxidizes to carbon dioxide and nitrogen gas as follows:

$$2CNO^- + 3NaOCl + H_2O \rightarrow 2CO_2 + N_2 + 3NaCl + 2NaOH \tag{12.5}$$

The first step is converting cyanide (CN^-) to cyanate (CNO^-) with sodium hypochlorite at a pH 10.5 or higher. Caustic and sodium hypochlorite can also be used. This step takes about 30 to 45 minutes to complete at an ORP of at least 1+670 mV. More hypochlorite can be added to raise the ORP, if necessary.

Then, an acid is added to lower the pH to 8.5, so the cyanate will oxidize. More hypochlorite is added to raise the ORP to +790 mV. These conditions are maintained for 90 minutes to allow cyanate to completely oxidize to nitrogen gas and carbon dioxide.

The effluent may then be added to other wastestreams for further treatment, as required. Meanwhile, the amount of cyanide that is not amenable to chlorination should be complexed with iron, chromium, and nickel.

Other methods of cyanide destruction include ozone treatment, heat-pressure, electrolysis, and hydrogen peroxide.

Destruction of Cyanide Not Amenable to Chlorination. Certain cyanide complexes (e.g., iron-cyanide, chromium-cyanide, and nickel-cyanide complexes) are very stable and not readily destroyed via alkaline chlorination. Destroying them is more difficult. The following approaches have been proposed and used in limited cases:

- A proprietary chemical that binds with the iron-cyanide complex and settles out of the wastewater. Post-treatment pH adjustment is necessary, because the effluent will reportedly be alkaline (pH 10 to 12) (Shields, 2002).

- A photoactivation process involving ultraviolet light and hydrogen peroxide (U.S. Peroxide, 2007).
- Hydrogen peroxide addition, with a copper or zinc catalyst.
- Electrowinning to break the iron-cyanide bond, followed by conventional cyanide treatment to oxidize the free cyanide.
- Ion exchange (acid regeneration of the cation resin, however, may cause hydrogen cyanide to form before further pH adjustment).
- Membrane filtration (e.g., reverse osmosis) will separate the iron-cyanide complex from water, but concentrates the complex rather than destroying it.

Hexavalent Chromium Reduction. Hexavalent chromium (Cr^{+6}) is a form of the metal typically used in metal plating, dyestuffs, and corrosion inhibitors. It is typically present in metal-finishing wastewater in the dichromate form ($Cr_2O_7^{-2}$) or as chromic acid (H_2CrO_4). Hexavalent chromium is toxic to the microorganisms in POTWs' biological treatment systems and is not precipitated by conventional neutralization reactions, so it must be converted to a less toxic, more treatable form [usually trivalent chromium (Cr^{+3})].

Conventional treatment for hexavalent chromium involves reducing it to the trivalent form, then neutralizing and precipitating it as chromium hydroxide (Figure 12.3). Hexavalent chromium can be reduced via

- Sulfur dioxide (SO_2),
- Sodium sulfite (Na_2SO_3),
- Sodium bisulfite ($NaHSO_3$),
- Sodium metabisulfite ($Na_2S_2O_5$),
- Sodium thiosulfate ($Na_2S_2O_3$), or
- Ferrous sulfate ($FeSO_4$).

The process typically requires an oxidation-reduction potential (ORP) controller and a pH controller. Except for ferrous sulfate, sulfur compounds work most effectively in pH 2 to 3. Acid typically must be added to wastewater to reduce the pH to these levels. Then, the ORP level should be maintained at +250 mV or lower for approximately 30 minutes. When hexavalent chromium is reduced to the trivalent form, the water will change color from yellow to green.

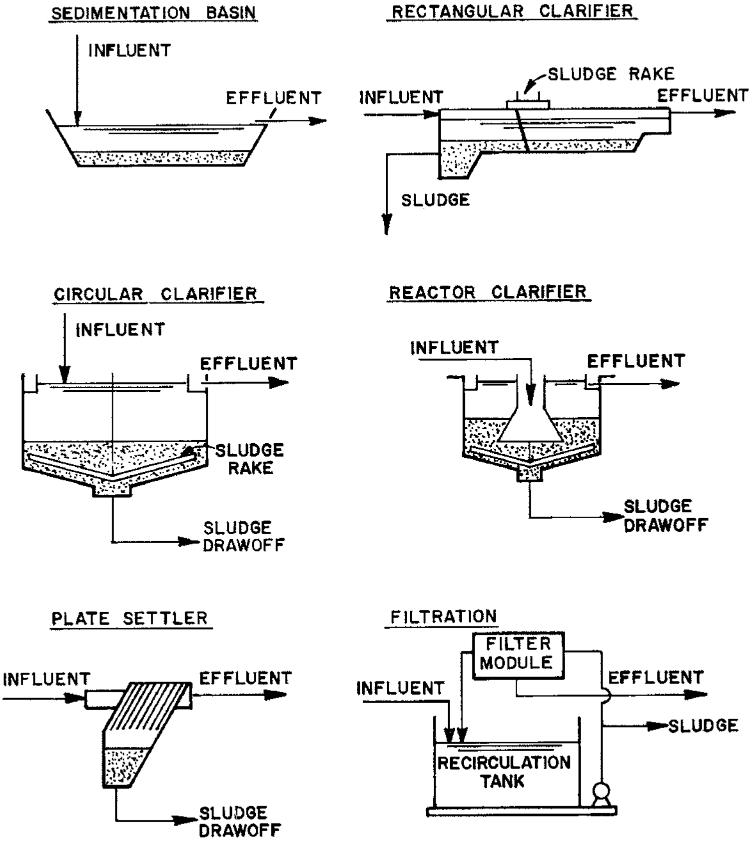

Figure 12.3 Schematics of various sedimentation options.

Ferrous sulfate can reduce hexavalent chromium to trivalent chromium within several minutes at pH 7.5 to 8.5. The amount of ferrous iron depends on the amount of oxidants (including dissolved oxygen) in the wastewater. One disadvantage of ferrous sulfate compared to other reducing agents is that it produces more solids.

After chromium reduction is complete, an alkali (lime or caustic) is added to return the solution to pH 7.5 to 8.5, the optimal range for trivalent chromium precipitation. The reactions occur as follows:

$$2H_2Cr_2O_7 + 3H_2SO_3 \rightarrow Cr_2(SO_4)_3 + 5H_2O \qquad (12.6)$$

$$Cr_2(SO_4)_3 + 6NaOH \rightarrow 2Cr(OH)_3 \downarrow + 3Na_2SO_4 \qquad (12.7)$$

Iron Coprecipitation. Iron coprecipitation is a process in which iron is used as a coagulant to remove metals from wastewater. Unlike other coagulants, which rely on the formation of metal hydroxides or sulfides at alkaline pH levels, iron binds strongly to metals at a range of pH values. Once bound to the metal(s), iron is readily precipitated at a pH range of 7.5 to 8.5.

The term *coprecipitation* refers to the fact that both iron and the metal are removed together. Unlike conventional neutralization/precipitation, which is dependent on pH and the metal being removed, iron coprecipitation relies on the solubility of iron rather than on a number of individual metal hydroxides or sulfides. Iron coprecipitation removes a number of metals in one step by binding them in an iron-metals matrix, which is then precipitated in a pH range of 7.5 to 8.5. Because the metal-removal mechanism is via occlusion in a strong iron-metal matrix, a number of different metals can be removed to low levels, typically below their solubility limits.

Both ferrous and ferric salts are used in iron coprecipitation. If a ferrous salt is used, another oxidation step is necessary to oxidize the ferrous iron to ferric, which is insoluble in the selected pH range. The metals are then removed as a ferric hydroxide metal complex. Ferrous iron can be oxidized via mechanical aeration or the addition of a chemical oxidant (e.g., chlorine, sodium hypochlorite, or hydrogen peroxide).

In addition to a range of heavy metals, iron coprecipitation will also remove the oxidized forms of arsenic and selenium, which will be discussed later in this chapter.

Sodium Borohydride Reduction. Sodium borohydride ($NaBH_4$), also known as sodium tetrahydroborate, is a strong reducing agent that allows some metals to be precipitated in elemental form. The wastewater must be acidified (pH 4 to 6) before sodium borohydride is added. The sodium borohydride solution contains caustic, which will raise the wastewater's pH (ideally to 5 to 7). After chemical addition, the wastewater is held at an ORP of −600 mV for 15 minutes.

The basic reactions for the process are:

$$8MX + NaBH_4 + 2\,H_2O \rightarrow 8M^0 + NaBO_2 + 8HX \tag{12.8}$$

$$NaBH_4 + 2\,H_2O \rightarrow NaBO_2 + 8H^+ \tag{12.9}$$

Where

M = a single valence metal, and
X = the anion (chloride, carbonate, etc.).

Sodium borohydride has been used to remove metals (e.g., silver, copper, and nickel) from chelated wastewater streams. The chemical may also be used to reduce mercury to elemental form so it can be removed from solution.

Sodium borohydride's main advantage is that it recovers precious or valuable metals for recycling. A major disadvantage is that the liquid must be removed from solids quickly, or else the metals tend to re-solubilize. Also, pH control is critical, because under acidic conditions, explosive hydrogen gas and possibly sodium oxide can form.

Sodium Dimethyldithiocarbamate. Sodium dimethyldithiocarbamate ($C_3H_6NnaS_2$; DTC) is another option for removing metals not easily removed via conventional methods. DTC is an organic sulfur compound that reduces metallic ions to elemental form, similar to sodium borohydride, so it may precipitate metals to very low concentrations. It is used to remove chelated metals with such chelating agents as ammonia, EDTA, sodium citrate, and sodium tartrate. It is also reportedly effective on manganese, molybdenum, sulfides, and tin (Schmelter, 2002). The chemical reportedly works best in a pH range of 6 to 9 (Youmans et al., 2002).

A less toxic, proprietary alternative to DTC, sodium polythiocarbonate (PTC), reportedly creates less sludge than DTC and other metal salts, has a lower dosage than DTC, and enables industries to pass whole effluent toxicity testing (Schmelter, 2002).

Carbamate generates less sludge than iron coprecipitation, but it is biotoxic and can generate dangerous carbon disulfide when mixed with water.

Arsenic, Selenium, and Mercury Removal. While most heavy metals are readily removed via the various technologies described above, arsenic, selenium, and mercury are special pretreatment challenges and are addressed separately in this section.

Arsenic. Arsenic is biotoxic, so it must be completely removed from wastewater before discharge to a POTW. Industrial sources of arsenic are primarily mine waste, wood preservatives, and semiconductor manufacturers. Arsenic occurs in industrial wastewater in two principal forms: arsenite (As^{+3}; $H_3AsO_3^-$) and arsenate (As^{+5}; $H_3AsO_4^-$).

Arsenite is not effectively removed via conventional chemical treatment, adsorption, or ion exchange in the normal pH range. It typically is oxidized to arsenate before further treatment. For this reason, design engineers must analyze the wastewater to determine which form of arsenic is present before developing a treatment strategy. Oxidation of arsenite to arsenate may be accomplished using chlorine, sodium hypochlorite, ozone, potassium permanganate, and hydrogen peroxide.

After oxidation, arsenate is removed by a variety of means including:

- Chemical addition (lime, iron, and aluminum salts);
- Adsorption using special media;
- Ion exchange (when sulfates are less than 120 mg/L, and total dissolved solids are low);
- Activated alumina (pH 5.5 to 6.0), and
- Membrane filtration ((U.S. EPA 2000b; U.S. EPA 2000c),

Iron coprecipitation requires less pretreatment to be effective than the other technologies mentioned. While also effective, the other treatment technologies must be preceded by settling or filtration (Table 12.4). In all cases, pilot testing is recommended before final implementation.

Table 12.4 is a summary of arsenate removal technologies that have proved effective in full-scale applications, along with recommended dosages, design parameters, and comments on features and disadvantages of the methods.

Selenium. Selenium is biotoxic, so it must be removed from wastewater before discharge to a POTW. Industrial sources of selenium are primarily copper, molybdenum, zinc, sulfur, and uranium mines; flue gas dust; electric power plants; oil refineries; and iron and steel manufacturers.

Inorganic selenium occurs in four oxidation states:

1. Colloidal elemental selenium (Se^0);
2. Biselenite (Hse^{-1});
3. Selenite [Se(IV); $HSeO_4^{-1}$ and SeO_3^{-2}]; and
4. Selenate [Se(VI); SeO_4^{-2}].

Selenium also exists in organic compounds. Inorganic forms of selenite and selenate are the primary forms of concern in industrial wastewater, as both are readily soluble in water.

The reduced selenite form Se (IV) is more readily removed by conventional chemical means, particularly with iron salts. Iron selenite is extremely insoluble, therefore is a preferred method for removing selenium.

TABLE 12.4 Summary of arsenic treatment technologies (adapted from U.S. EPA, 2000b; 2000c).

Technology	Dosage/design*	pH	Required pretreatment	Comments
Iron salts	30 mg/L	5.5–8.0	None	• >95% removal • Better arsenic removal than alum
Aluminum salts	30 mg/L	5.0–7.0	pH adjustment	
Lime	Varies	10.5–12.0	Post-treatment pH reduction required	• Can remove As(III) and As(V) at elevated pH • Significant sludge generated
Adsorption	Bed depth = 3–4 ft 6–8 gpm/sq ft	6.0–8.0	Settling and filtration	• Media not regenerated on site Disposal required at bed exhaustion
Ion exchange	Bed depth = 3–4 ft 10–15 gpm/sq ft	8.0–9.0	Settling and filtration	• Significant effects of high sulfate (> 120 mg/L) and TDS • Avoid iron salts to prevent fouling • High arsenic regenerant requires treatment and disposal
Activated alumina	Bed depth = 2.5–4.0 ft EBCT = 10–15 minutes	5.5–6.0	Settling and filtration	• Significant effects of high sulfate (> 120 mg/L) and TDS • Regeneration may be inefficient and require more frequent media replacement • High arsenic regenerant requires treatment and disposal
Reverse osmosis	100–200 psi	6.5–7.5	Settling and filtration	• Likely to be more costly than other processes • High arsenic reject water requires treatment and disposal

*ft × 0.3048 = m; gpm/sq ft × 2.444 = $m^3/m^2{\cdot}h$; psi × 6.895 kPa.

Iron selenate [Se(VI)] is much more soluble than iron selenite, particularly if significant amounts of sulfates are present. So, selenate must be reduced to selenite before further treatment. For this reason, design engineers must analyze the wastewater to determine which form of selenium is present before developing a treatment strategy.

Selenate can be reduced to selenite or elemental selenium via elemental iron and certain biological treatment processes (Twidwell et al., 1999; U.S. EPA, 2001b). Chemical reduction of selenate is inhibited by sulfates and nitrates, which tend to combine with an iron reducing agent before selenate does.

Selenite removal methods include:

- Iron salts (pH 6.5 to 8.0);
- Ion exchange with special media (when sulfates are less than 120 mg/L, and total dissolved solids are low);
- Activated alumina (pH 3.0 to 8.0), and
- Reverse osmosis.

Activated carbon treatment is not effective in removing either form of selenium (Twidwell et al., 1999).

Mercury. Mercury is one of the most strictly regulated elements; it must be completely removed from wastewater before it is discharged to a POTW. Industrial sources of mercury include metal-finishing and printed circuit board manufacturers, refineries, pharmaceutical manufacturers, mercury mines, landfill leachate, and incinerator scrubber water. Mercury is also found in the dental amalgam used to fill teeth, and dental offices are typically required to recover the mercury onsite.

Mercury occurs in industrial wastewater in three principal inorganic forms: elemental mercury (Hg^0), mercury I (Hg^{+1}), and mercury II (Hg^{+2}). Some of the more common mercury salts are mercuric chloride ($HgCl_2$), mercurous chloride (Hg_2Cl_2), mercuric nitrate [$Hg(NO_3)_2$], mercuric sulfide (HgS), and mercuric sulfate ($HgSO_4$). These compounds' solubility range from negligible (e.g., Hg_2Cl_2 and HgS), to very soluble [e.g., $HgCl_2$ and $Hg(NO_3)_2$].

Mercury can also occur in organic forms, the most notorious being methylmercury, the source of the environmental disaster in Minamata, Japan. Methylmercury is typically formed as a result of anaerobic microbial activity in highly organic sediments containing mercury. It is not typically found in industrial wastewaters.

Mercury removal methods include coprecipitation (iron and aluminum salts), sulfide precipitation using sodium sulfide, carbon adsorption using special sulfur-impregnated media, ion exchange, membrane filtration, and mercury reduction to elemental mercury. An analysis of these technologies revealed that coprecipitation, ion exchange, and impregnated carbon produced the lowest effluent mercury concentrations (U.S. EPA, 1997).

Chemical treatments for mercury either reduce ionic mercury to insoluble elemental mercury for mercury recovery, or precipitate it as an insoluble mercury salt. In the case of mercury reduction, reagents (e.g., sodium borohydride) are used. One major advantage of the reduction technique is that the mercury can be recovered and most of the solids are reused. A disadvantage is that effluent mercury levels are higher with chemical reduction than with precipitation (U.S. EPA, 1997).

Ion exchange and activated carbon treatment for mercury must be preceded by sedimentation and filtration. Also, to maximize mercury removal, an oxidant should be added to the wastewater before ion exchange or activated carbon treatment to ensure that all mercury is in the ionic, rather than the reduced, form. Again, pilot testing is recommended before final implementation.

Summary of Chemical Treatment Methods. Each chemical treatment scheme has its advantages and disadvantages. Table 12.5 summarizes the advantages and disadvantages of chemicals that are used most often in metals removal.

SOLIDS SEPARATION PROCESSES. There are a number of ways to separate solids (produced during precipitation–coagulation) from wastewater. Following are the methods typically used to remove inorganic solids (Figure 12.4).

Sedimentation Pond. A sedimentation pond or lagoon is typically a rectangular basin in the ground that is either made of concrete or lined with an impervious material such as clay. They are typically sized based on the sludge generation rate (as calculated in the treatability study) to hold accumulated solids for a number of months or years. The basins should have multiple cells, so solids can be removed from one cell while the others remain in operation.

Because they require large areas of land, their use is limited in many industries. Also, hydroxide sludge is hydrophilic and does not thicken easily over time. Another disadvantage of long solids storage is the possibility that metals will re-dissolve into the water.

TABLE 12.5 Advantages and disadvantages of common treatment chemicals.

Treatment	Advantages	Disadvantages
Hydroxide precipitation—lime	Least expensive Can coprecipitate high concentrations of sulfate ions Fewer safety issues Imparts a buffering capacity on wastewater Reliable treatment	Dusty, slow to dissolve, and must be made into a slurry Slurry must be pumped and can obstruct piping More sludge and is fluffier and difficult to handle Not effective in presence of chelating agents
Hydroxide precipitation—sodium hydroxide	Liquid that does not need to be mixed in storage Readily dissolves Does not clog piping—less maintenance than lime Does not need to be hydrated Sulfate in waste stream can interfere with reaction	Hydroxides reprecipitate if pH changes More expensive than lime No buffering capacity imparted on wastewater More sludge and is fluffier and difficult to handle Sodium hydroxide gels at 10° C (50° F) or less
Hydroxide precipitation—magnesium oxide	Forms particulate precipitant Better sludge handling than other hydroxide precipitants Less sludge volume than lime Lower freezing point than sodium hydroxide	Hydroxides re-precipitate if pH changes More expensive than lime Slurry must be pumped and mixed during storage
Sulfide precipitation	Coprecipitates other ions Removes to extremely low concentrations Removes metals at pH = 7–9 Can remove hexavalent chromium without reduction Less interferences with chelating agents	Generates toxic fumes Generates odorous H_2S gas More expensive than hydroxide precipitation Sludge often doesn't settle as well as lime, alum, and iron salts
Carbonate precipitation	Imparts a significant buffering capacity on wastewater Adding more carbonate increases precipitations Precipitant remains over a normal pH range	Does not precipitate all metals
Iron coprecipitation	Removes many metals in same step at pH 7–8.5 Achieves very low metals in effluent	May impart color to the water

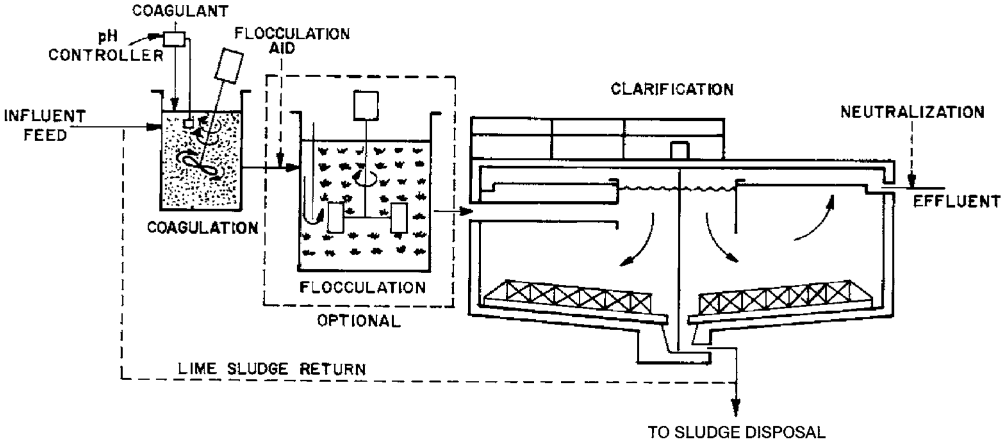

FIGURE 12.4 A schematic of a typical chemical feed system.

Conventional Clarifier. A conventional clarifier is a continuous-feed unit designed to remove precipitated solids from wastewater and thicken them for further treatment. Clarifiers may be rectangular, or circular with concave, cone-shaped bottoms. Circular units are equipped with electrical, rotating rakes that gather settled solids to the lowest point of the cone for draw-off. A rectangular clarifier or sedimentation basin may be equipped with a traveling sludge collector, which continuously scrapes the solids to a hopper.

Circular clarifiers typically remove solids more effectively than rectangular ones because they are less prone to short-circuiting. However, rectangular units are more space-efficient and may be less costly because of common-wall construction.

The clarifier size is based on the design overflow rate (hydraulic loading per unit area) for the effective surface area. Settled solids are periodically transferred to a holding tank or lagoon, where they sometimes thicken further. A holding tank designed for solids filtration or mechanical dewatering is called a *solids thickener.* It is similar to a clarifier but sized based on the detention time before dewatering.

Solids Contact Clarifier. A solids contact clarifier is similar to a conventional clarifier but has a central, inverted cone near the top (Figure 12.4). This type of clarifier is often used when the influent has a high solids concentration, or if the chosen coagulant (polymer) will generate large amounts of solids. The influent cone is intended to flocculate incoming solids.

The polymer and pH-adjusted wastewater enter the clarifier through the top of the cone. Inside the cone, the floc forms, enlarges, and begins to settle. Rather than being drawn off continuously, the solids are allowed to accumulate in the bottom of the cone. This thick layer of solids, called a *sludge blanket*, serves as a nucleus for the floc and a filter for smaller floc particles. The water flows through the blanket and up over the weir around the top of the clarifier. In some solids contact units, mechanical flocculators are installed in the influent cone.

Inclined-Plate Clarifier. An inclined-plate clarifier (IPC) is a deep, rectangular tank equipped with several parallel plates slanted at an angle (often 45 to 55 degrees) and spaced 1 to 2 in. (25 to 50 mm) apart. The pH-adjusted, polymer-treated wastewater flows upward through the plates. Floc particles settle onto the plates and slide down into the unit's solids-holding area.

The advantage of the parallel plates is that the flocs have a shorter settling distance, and are removed more effectively than in conventional units. Another significant advantage of an inclined-plate clarifier for industrial uses is that its "footprint" is much smaller than that of conventional clarifiers (it is taller, however, than conventional units). Because of its relatively compact size, the unit may be manufactured elsewhere and delivered to the site for installation.

Under heavy solids loadings, operating problems may develop, causing solids to "bridge" across the tank and become difficult to remove. This problem is compounded if polymer use is excessive.

Angled plates may also be installed in existing conventional clarifiers to increase the overall surface area and create more settling capacity if higher flows are anticipated. However, tank hydraulics should be checked to ensure that flooding will not occur at the new flow rate.

Dissolved Air Flotation. In systems where the precipitated solids are light and space is limited, dissolved air flotation (DAF) units may be used for solids separation. High-rate DAF units with inclined plates have the smallest footprint. (For DAF system design data, see Chapter 9.)

Dissolved-air flotation should be pilot-tested before implementation to ensure that the solids can be floated.

Filtration Systems. Because most chemical systems make soluble pollutants (e.g., heavy metals) insoluble, removing precipitated solids becomes a key to meeting discharge standards. When pretreatment standards are strict, sedimentation alone may not provide enough solids removal.

Filtration systems are often used to supplement sedimentation. In addition, the performance of chemical addition is often enhanced by having two chemical addition points: one before sedimentation and one located between sedimentation and filtration. If solids levels are expected to be low, filtration may be used instead of sedimentation. (For more information on filtration systems, see Chapter 9.)

PRETREATMENT PROCESSES FOR NUTRIENTS.

Pretreatment processes for nutrients (principally nitrogen and phosphorus) include physical-chemical and biological processes. Regulators increasingly require POTWs to remove nutrients from their discharges to control algae growth and oxygen demand in waterbodies. As a result, industries with high nutrient levels in their wastewater may be forced to pretreat for nutrients before discharging to a POTW or directly to a receiving water.

Phosphorus Removal.

Conventional phosphorus-removal methods include biological nutrient removal (BNR) and neutralization-precipitation. Industries typically use neutralization-precipitation to remove phosphorus when the pretreatment regulations limit phosphorus discharges. The chemicals used to remove phosphorus are the same as those used to remove heavy metals: iron salts (e.g., ferric and ferrous chloride, and ferrous and ferric sulfate); aluminum salts (e.g., alum, sodium aluminate, and polyaluminum chloride); and lime. (For information on using BNR to remove phosphorus, see Chapter 13.)

Iron and Aluminum Salts. Iron and aluminum salts precipitate orthophosphate (PO_4^{-3}) as follows (simplified reaction):

$$M^{+3} + \mathrm{PO4}^{-3} \rightarrow M\,\mathrm{PO}_4\downarrow \qquad (12.10)$$

Where M is the aluminum or ferric ion.

This reaction is stoichiometric: the amount of iron or aluminum needed depends on the amount of phosphorus in the wastewater. In fact, other competing reactions (with metals, carbonates, hydroxides, etc.) increase the actual chemical requirements, so more chemical typically will be needed than is predicted by stoichiometry alone.

Table 12.6 summarizes municipal experience with phosphorus precipitation. (Municipal wastewater typically contains 3 to 8 mg/L of total phosphorus.) The

TABLE 12.6 Comparison of typical metal salt doses for phosphorus removal (adapted from U.S. EPA 1987a; 1987b).

Metal salt	Dose (mg/L, as metal)	Ratio of metal ion:phosphorus (lb/lb*)
Ferrous chloride	9–15	3–4
Ferric chloride	10–15	4–5
Ferrous sulfate	8–15	2–5
Ferric sulfate	5–15	2–5
Alum (aluminum sulfate)	10–20	2–4

*lb × 0.4536 = kg.

metal doses shown in Table 12.6 are intended as a starting point for industrial flows and are probably lower than industrial requirements, given the number of competing ions likely to be present in industrial wastewaters. Also, the final dose will depend on the level of phosphorus removal required. Jar testing is necessary to determine the optimal chemical and dose.

A general schematic of chemical treatment systems is shown in Figure 12.5. For design parameters for chemical feed, flash mix, flocculation, and sedimentation facilities, see Chapter 9.

Lime. The term *lime* can refer to quicklime (CaO) or hydrated lime [$Ca(OH)_2$]. To be used in water, quicklime must first be *slaked*—a process in which quicklime is hydrated to create hydrated lime. The slaking process is dusty, messy, and releases significant heat. It is typically used at large POTWs, where the demand for lime is larger than that of most industrial pretreatment systems. So, this section focuses on hydrated lime for industrial applications.

Unlike aluminum and iron, which precipitate phosphate directly, lime reacts with the alkalinity in wastewater to form calcium carbonate ($CaCO_3$). When enough lime is added to increase the wastewater's pH to 10 or higher, the excess calcium reacts with phosphate to form calcium hydroxyapatite, an insoluble calcium phosphate salt that is then settled out of the wastewater. The wastewater's pH must then be lowered for further treatment and discharge.

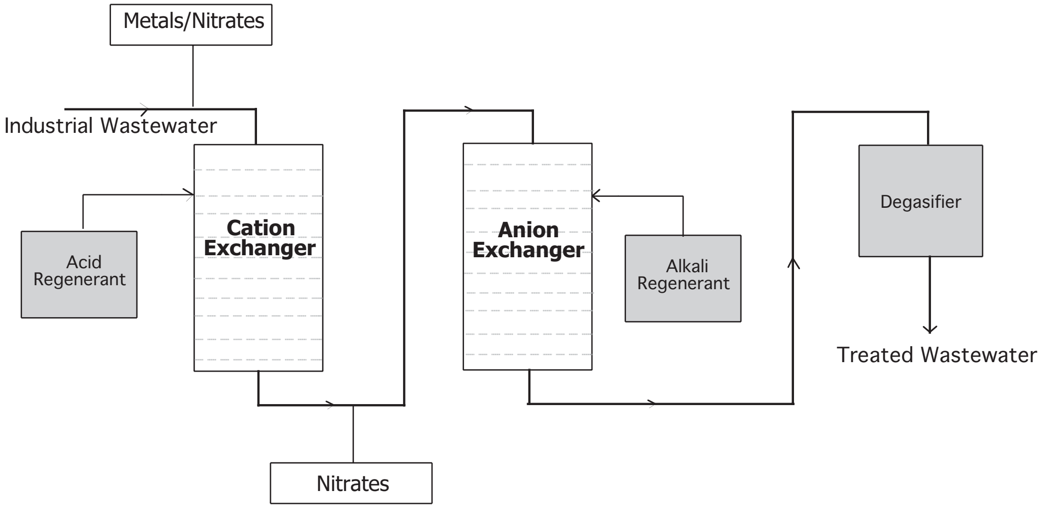

FIGURE 12.5 A process diagram of a typical ion-exchange system.

When comparing lime to aluminum and iron, design engineers must consider the following:

- Removing phosphorus with lime creates far more sludge than aluminum or iron salts;
- Lime is typically messier to handle and more maintenance-intensive;
- The unit cost of lime is less than that of aluminum and iron salts, which may justify the amount of lime needed;
- Removing phosphorus with lime is a function of pH that is largely independent of phosphorus concentration, making lime an attractive option if phosphorus concentrations are high.

Nitrogen Removal. Federal and state regulators are increasingly limiting nitrogen discharges from POTWs to manage nutrient levels in rivers and lakes. As a result, POTWs are beginning to add nutrient limits to their industrial pretreatment requirements. The following are typical technologies used to remove nitrogen in POTWs and industrial discharges.

Air/Steam Stripping of Ammonia. The ammonia-ammonium equilibrium relationship has been used to strip ammonia from water in stripping towers. Ammonia-nitrogen exists as either the ammonium ion (NH_4^+) or ammonia gas (NH_3), depending on the solution's pH. In water, this relationship is:

$$NH_4OH \leftrightarrow NH_3\uparrow + H_2O \tag{12.11}$$

Raising the wastestream's pH to between 10.8 and 11.5 drives the reaction to release ammonia gas. The air rising through the tower facilitates the removal of ammonia vapor from water. The stripping process is further improved if warm air or steam is used to strip the ammonia.

While successful in removing ammonia from wastewater, air or steam stripping has generally been abandoned because of the need for pH adjustment, the creation of cross-media (air) pollution and possible need for air permits, odors, scaling in the stripping towers, and freezing in cold weather. Air or steam stripping may be indicated if pH levels are already elevated, waste steam or warm water is available, and ammonia levels are less than 100 mg/L.

(For more information on air and steam stripping systems, see U.S. EPA, 2000d).

Ion Exchange. Ion exchange has been used to remove ammonia, nitrite, and nitrate. Ammonia is often removed by a naturally occurring zeolite material called *clinoptilolite,* although synthetic media are also used. Other ion exchange media are specific to nitrite and nitrate removal. (The ion exchange process is addressed in more detail later in this chapter.)

Ion exchange needs less space to remove nitrogen compounds than biological treatment processes and achieves low effluent nitrogen concentrations. However, operating costs are significant, particularly with high levels of contaminant, and for media with very specific ion removal. Also, significant pretreatment is required to remove suspended solids and competing ions such as iron and aluminum prior to ion exchange. Regeneration of the beds and treatment/disposal of the spent regenerant are also significant costs.

When selecting and designing ion exchange systems, engineers should consult resin manufacturers and conduct pilot tests to determine the full-scale design parameters and estimate capital and operating costs more accurately.

Breakpoint Chlorination of Ammonia. In the breakpoint chlorination process, chlorine is added to wastewater to chemically oxidize ammonium ions to various products (primarily nitrogen gas):

$$NH_4 + HOCl \rightarrow 0.5\,N_2\uparrow + 2.5\,H^- + 1.5\,Cl^- + 0.5\,H_2O \qquad (12.12)$$

Enough chlorine is added to react with all of the oxidizable substances and form free chlorine residual. Many complex reactions are involved, and the success of the process depends on proper application of the chemical and design techniques. Under proper operating conditions, 95 to 99% of the ammonia-nitrogen in wastewater can be converted to nitrogen gas. The type of reaction and the extent of its predominance depend on certain process variables (e.g., pH, temperature, contact time, and the initial chlorine:ammonia-nitrogen ratio).

Like air stripping, breakpoint chlorination is a well-established technology for removing ammonia, particularly if ammonia removal is only needed seasonally. However, breakpoint chlorination is not commonly used, particularly if ammonia concentrations are high (say, more than 15 to 20 mg/L). The theoretical chlorine:ammonia ratio is 7.6 to 1 (by weight), though competing reactions with organics in the wastewater make the actual ratio significantly higher, raising costs and other concerns with high chlorine doses. The concerns include:

- The production of free chlorine residual that typically must be removed before discharge to a POTW or receiving water;
- The potential production of nitrogen trichloride (NCl_3) gas, which is both toxic and explosive;
- The potential formation of disinfection byproducts (e.g., chloroform and bromoform);
- The increase of total dissolved solids, which could create further discharge concerns;
- Corrosion of steel surfaces by the hydrochloric acid produced in the reaction.

If breakpoint chlorination is selected as the preferred option for ammonia removal, a number of steps should be taken during design to address these concerns. First, pretreatment must reduce high concentrations of inorganic or organic compounds (e.g., sulfides, sulfites, thiosulfites, ferrous ions, phenols, amino acids, proteins, and carbohydrates) before the breakpoint chlorination process. These compounds can exert a large additional chlorine demand.

Enough hydraulic or mechanical energy must be provided to ensure rapid and thorough blending of the chlorine solution, pH-adjustment chemical, and wastewater. Adequate mixing ensures process consistency, a prerequisite for the feedback instrumentation used to control the process. After the chemicals are mixed, the reaction is rapid. A 1-minute contact period is enough for full-scale applications. The contact basin should be designed to produce plug-flow conditions as much as possible.

To minimize the formation of nitrogen trichloride, the process pH must be controlled near 7.0. The pH-adjustment chemical should be added to the chlorine solution *before* the solution is added to the process. Effective mixing of the chemicals is important because a disproportionate mixture of chlorine solution and pH-adjustment chemical may result in pockets of liquid in the breakpoint reaction zone that are not at the desired pH. If the breakpoint reaction occurs in these pockets, excessive concentrations of nitrogen trichloride result. Because nitrogen trichloride cannot be completely prevented, sufficient ventilation must be provided if the reaction basin is enclosed.

The process generates acidity via the hydrolysis of chlorine gas in solution and the oxidation of ammonia. Approximately 15 mg/L of alkalinity is consumed per milligram per liter of ammonia oxidized. So, if the ammonia concentration is significant, the alkalinity must be substantial to provide buffering capacity and maintain the pH.

Biological Nitrification of Ammonia. Ammonia is typically removed from wastewater via biological nitrification according to the following two-step reaction:

$$NH_4^+ + 1.5O_2 + 2HCO_3^- \rightarrow NO_2^- + 2H_2CO_3 + H_2O \tag{12.13}$$

$$NO_2^- + 0.5O_2 \rightarrow NO_3^- \tag{12.14}$$

The first step is accomplished in a biological treatment step by *Nitrosomonas* bacteria, the second by *Nitrobacter* bacteria. The process nominally requires 2 kg (4.6 lb) of oxygen or more per 1 kg (2.2 lb) of ammonia nitrified. The process also destroys alkalinity that must be replaced in the process to avoid lowering pH to levels that would inhibit nitrification (typically, less than 6.5).

In a stream, the oxygen used by the nitrification process is referred to as *nitrogenous oxygen demand* (NOD). If nitrification occurs in a stream, significant oxygen deficits may result from NOD. As a result, nitrification may be required for pretreatment, or in the POTW if the stream is oxygen-limited. Also, high ammonia concentrations may cause toxicity concerns for sensitive macroinvertebrates (e.g., water fleas, shrimp, and trout). (For more details on designing biological nitrification facilities, see Chapter 13.)

Biological Denitrification. The nitrification process results in the end formation of the nitrate ion. Like ammonia, nitrate is a nutrient for the growth of plants and algae, so the nitrification process does not remove nutrients, only oxygen demand (NOD).

If nutrient (nitrate) removal is also a discharge requirement, any ammonia present must first be nitrified to nitrate, and the nitrates then converted to nitrogen gas in a process known as *biological denitrification.* Below is the simplified denitrification reaction:

$$2\,NO_3^- + 3C \rightarrow N_2\uparrow + 3CO_2 \tag{12.15}$$

The biological denitrification reaction occurs under anoxic conditions, meaning at a dissolved oxygen concentration of 0.3 to 0.7 mg/L. The denitrifying bacteria also require a carbon source. In separate nitrification-denitrification systems, this carbon source is often methanol, which is added as a function of the nitrate present.

However, the nitrification-denitrification process is often combined into a biological nutrient removal (BNR) process that facilitates both reactions: first, the nitrification reaction producing nitrates, and then the denitrification reaction converting the formed nitrates to nitrogen gas. Carbon for the denitrification process is typically provided by the influent, unless the wastewater is carbon-deficient. (For more details on the design of biological denitrification facilities, see Chapter 13.)

OTHER TECHNOLOGIES

A significant disadvantage of the neutralization/precipitation process in conventional metal-finishing industries is that the facility uses a number of plating lines with different metals and batch dumps, so the wastestreams can vary significantly. Even if the wastestreams are equalized, finding an optimum pH for treatment is difficult and may change occasionally. In addition, the large quantities of hazardous materials (metals) involved make conventional neutralization processes less desirable than other technologies that produce less solids.

Given these factors and the rising cost of potable water, many metal finishers (both platers and printed-circuit-board manufacturers) have turned to other treatment technologies (e.g., ion exchange, activated carbon, membrane filtration, electrodialysis, and evaporation) with higher metal removal rates and lower solids volumes. These technologies also produce reusable water, thereby reducing a facility's need for potable water. Most of these technologies are widely used to remove or recover metals in locations where recovered material benefits are high or local pretreatment standards are strict.

ION EXCHANGE. In the ion exchange process, a resin exchanges certain of its ions (e.g., sodium or hydrogen) for other ions with a similar electrostatic charge (e.g., metals dissolved in wastewater). Ion exchange can remove both cations (e.g., metals) and anions (e.g., nitrates and sulfates) from wastewater.

Figure 12.6 is a simplified schematic of an ion exchange process intended to remove heavy metals and nitrates. In the example, the positively charged metal ions are exchanged with hydrogen or sodium ions in the cation exchange column(s) and removed, leaving the anionic nitrate ions in the waste stream. The negatively charged nitrate ions are then exchanged for hydroxyl (OH-) ions in the anion exchange column.

When all or most of the resin's ions have been exchanged, it must be taken off-line and regenerated. Cation exchange resins are typically regenerated by soaking them in an acid solution, which removes the metals and replaces them with hydrogen ions. Anion exchange resins are regenerated by soaking them in an alkali

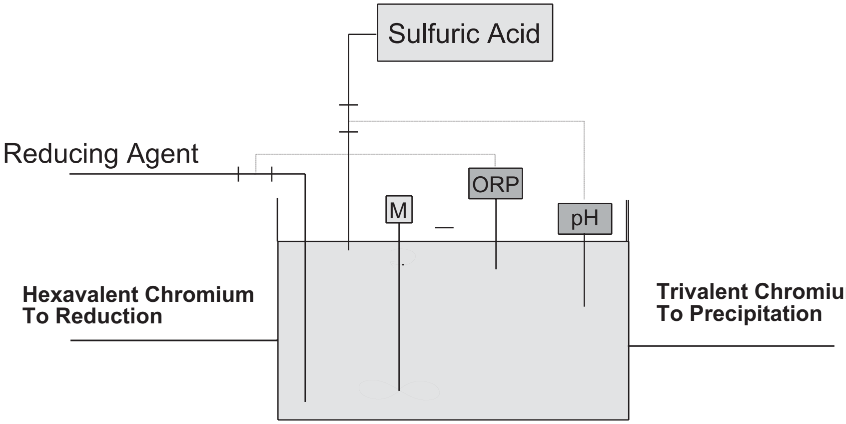

FIGURE 12.6 A schematic of a typical hexavalent chrome reduction system.

(e.g., sodium hydroxide), which removes the metals and replaces them with hydroxyl ions.

Increasingly, ion exchange resins are designed to target specific pollutants to improve pollutant removal efficiency while reducing regeneration requirements.

Pretreatment. Suspended solids, FOG, organics, and high levels of total dissolved solids can interfere with ion exchange performance, increasing resin cleaning and regeneration/replacement frequency. Pretreatment is typically required upstream of an ion exchange system. Typically, sedimentation and/or filtration are used to remove suspended solids and FOG before ion exchange. Granular activated carbon treatment is used to remove high levels of organics before ion exchange. High levels of dissolved solids may require more ion exchange units to guarantee the desired removal efficiencies for chosen pollutants.

General Design Approach. Ion exchange systems must be pilot-tested before implementation to determine the effects of competing ions and other interferences. Resin manufacturers typically perform or help with such testing. They can recommend specific resins, wastewater pH levels, regenerants, and specific pretreatment requirements that will optimize system performance.

When designing ion exchange columns, the general hydraulic loading rate is approximately 235 to 350 $m^3/m^2 \cdot d$ (4 to 6 gpm/sq ft). Resin bed depths are typically 0.9 to 1.8 m (3 to 6 ft). The resins are chosen based on the various ions present; design engineers should coordinate with the resin manufacturer to determine the optimal resin, projected performance, and expected regeneration rates.

Metals. Ion exchange is often used to recover precious metals (e.g., gold, silver, and platinum). Many photographic labs recover silver by passing the film-developing wastewater through ion-exchange columns and collecting the silver in the regenerating solution. Ion exchange also removes ionic mercury effectively.

Three types of resin are typically used for metals removal: a strong acid cation resin, a weak basic anion resin, and a strong basic anion resin (for cyanide and fluoride removal). For this treatment process to be effective, design engineers must understand the "order" in which metals are removed (Table 12.7)—particularly if the wastewater contains a number of metals. The cations and anions at the top of the table are removed preferentially to those below them in the table. The number of bed volumes treated before regeneration may be determined by the concentration of ions located above the ion desired for removal.

Table 12.7 Order of cation and anion removal by ion exchange in order of decreasing preference.

Preference	Cation	Anion
↘	Barium	Phosphate
	Lead	Selenate
	Calcium	Carbonate
	Nickel	Arsenate
	Cadmium	Selenite
	Copper	Arsenite
	Zinc	Sulfate
	Magnesium	Nitrate
	Potassium	Bisulfite
	Ammonia Sodium	Chloride
	Hydrogen	Cyanide
		Bicarbonate
		Hydroxide
		Fluoride

Arsenic. Inorganic arsenic occurs in the arsenite and arsenate forms. Before considering treatment for arsenic, the wastewater should be tested to determine which forms are present and in what quantities.

Arsenite is not readily removed by ion exchange. However, it can be oxidized by chlorine or other oxidants into arsenate, which is then removed by ion exchange. Strongly basic anion exchange resins readily remove arsenate. They are regenerated with sodium salts. Newer ion exchange products eliminate the need for regeneration, but require periodic resin replacement and proper disposal of the spent media.

If the wastewater contains iron and sulfates as well as arsenic, the resin's exchange load will increase—as will its regeneration frequency.

Selenium. The most common forms of selenium in water are selenite and selenate. Selenate (Se^{+6}) is much easier to remove via ion exchange than selenite (Se^{+4}). Before choosing a treatment approach, design engineers should determine which selenium form(s) are present and in what quantities. An oxidant (e.g., chlorine, sodium hypochlorite, or hydrogen peroxide) may be used to convert selenite to selenate before the ion exchange process.

Strongly basic anion exchange resins are typically used to remove selenate. However, iron and sulfates will increase the resin's exchange load, so if they are present in the wastewater, a different resin may be needed to focus on selenate removal.

Ammonia. Ion exchange systems treat ammonia effectively. The choice of resin depends on the other cations and anions in the wastewater that may interfere. Many ion exchange systems designed for ammonia use clinoptilolite, a naturally occurring zeolite that is highly selective for the ammonium ion. It is regenerated with salt or caustic soda. Caustic soda strips ammonia easily, and the solution can be reused.

The optimum operating pH range is between 6 and 7, but ammonia removal is effective when the pH is between 4 and 8. Outside of this range, however, the ammonia exchange capacity drops and ammonia leakage increases, leading to breakthrough. When the pH is above 9, the ammonium ion volatilizes, becoming ammonia gas, which is not removed via ion exchange.

Ammonia is also removed by strong-acid cation exchange resins. These resins exchange sodium for the ammonium ions and are regenerated via a strong acid.

Nitrate. Virtually all nitrates are soluble (Table 12.2) and cannot be treated via neutralization or precipitation, but they can be removed via ion exchange. A strong-base anion resin is typically used; however, it will attract sulfates even more readily than nitrates (Table 12.7). This can be a capacity problem for nitrate removal if sulfate levels are high, so more selective nitrate resins should be used when this is the case. Both resins are regenerated with sodium or calcium salts.

Radioactive Materials. Ion exchange systems remove radioactive materials (e.g., uranium, radium, actinium, thorium, and protactinium) from wastewater effectively. However, removing and transporting spent radioactive media from the site may require special security precautions, or may be the resin manufacturer's responsibility.

Column Regeneration. Ion exchange columns are regenerated by first draining the column of wastewater. Then the resin is agitated by compressed air, backwashed with potable water, and drained. Once backwashing is completed, cation resins are soaked in an acid solution (8 to 10% by volume concentration) to regenerate them, while anion resins are soaked in a caustic solution (4% concentration). Then, the chemicals are drained, potable water is added, and rinsing continues until the proper pH is attained (pH 3 to 4 in cation column effluent, pH 10 to 11 in anion column effluent). The column is then ready for service.

All water and chemicals used in the regeneration process must be treated for metals removal.

ADSORPTION. *Adsorption* is the adhesion of substances to the surface of a solid. Following are brief descriptions of various adsorbents and their ability to treat inorganic compounds.

Activated Carbon. Activated carbon has long been used to remove organic substances from wastewater, but its use in treating inorganic compounds—particularly metals—is not well-demonstrated. Some metals removal occurs in activated carbon systems, but the removal efficiency is typically low and unpredictable. Activated carbon does remove free and combined chlorine residual successfully, but dechlorinating agents (e.g., sulfur dioxide and other reducing agents) probably do this more cost-effectively. (For more details on the design of granular activated carbon systems, see Chapter 13.)

Activated Alumina. Made by treating aluminum ore so it becomes porous and highly adsorptive, activated alumina removes arsenic, beryllium, fluoride, selenium, and thallium from wastewater. It works best at a pH range of 5.5 to 6.0.

The two most common uses of activated alumina in industrial facilities are fluoride and arsenic removal.

Fluoride. Fluoride is used in the production process at glass manufacturers, aluminum and steel processors, pesticide and fertilizer producers, and semiconductor manufacturers. The traditional fluoride-removal method—lime addition followed by precipitation of calcium fluoride—may not meet today’s pretreatment standards. Activated alumina is a viable alternative.

When treating fluoride, the activated alumina should first be soaked with a dilute alum solution. This greatly improves fluoride removal. Bicarbonate can interfere with fluoride removal, so either the wastewater should be pretreated to remove bicarbonate or the capacity of the activated alumina columns should be down-rated.

Activated alumina media is regenerated in a two-step process: it is treated with an alkali (e.g., sodium hydroxide), followed by an acid rinse.

Table 12.8 Comparison of activated alumina design data for two U.S. EPA treatment plants (U.S. EPA, 2000b).

Parameter*	Plant C	Plant D
Flow rate (gpm)	14	20
Cartridge filter size (μ)	30	20
Alumina loading rate (gpm/sq ft)	5.0	3.2
Alumina EBCT (min)	4.3	7.5
Time to replace media (months)	27	19

*gpm × 3.785 L/m; gpm/sq ft × 2.444 = $m^3/m^2 \cdot h$.

Arsenic. According to long-term research, activated alumina can cut both arsenite and arsenate concentrations to well below 10 μg/L, the Safe Drinking Water Act standard (U.S. EPA, 2000b). The two plants studied had slightly different hydraulic loading data but similar arsenic results (Table 12.8). Their empty bed contact times (EBCTs) also varied. The empty bed contact time is computed by calculating the volume of the media (rather than the vessel) and dividing it by the flow rate. Both plants used cartridge filtration as a pretreatment step and removed spent media rather than regenerating it. Based on these full-scale studies, a hydraulic loading rate of 235 to 350 $m^3/m^2 \cdot d$ (4 to 6 gpm/sq ft) and an EBCT of 7.5 to 10 minutes seem to be conservative values for activated alumina process design.

MEMBRANE FILTRATION. Membrane filtration is used primarily in the metal-finishing industry to remove metal ions and other dissolved ions to produce reusable water. Membrane filters are classified based on pore size. The two types used to remove dissolved cations and anions from industrial wastewater are reverse osmosis and nanofiltration.

Membrane filtration is not strictly a pretreatment process because the quality of its effluent is far better than most POTWs require or drinking water plants produce. The effluent is typically reused as rinse water in the plating line.

The high capital and operating costs of such systems can be justified when the POTW's pretreatment metals requirements are stringent, potable water costs are high, or the plating operation requires very high quality water.

However, scaling is a problem, particularly when calcium carbonate, barium and calcium sulfates, and silicates are present. Generally, sulfuric acid is used to control carbonate scaling. A polyacrylic acid antiscalant is used to control sulfate scaling. Silica scaling can be controlled by adding a specific silica antiscalant, reducing the membrane's hydraulic load, increasing the pH to 8.5 or higher, increasing the water temperature, or pretreating influent with a water softener.

Reverse Osmosis. Reverse osmosis (RO) membranes have the smallest pore size (<0.002 μm) used in liquid-liquid separation (Figure 12.7). They allow water to pass through and retain the solute (e.g., salts, metal ions, and certain organics). The salts become concentrated and are discharged as a concentrated brine, often to an electrodialysis or electrowinning process.

Pretreatment for reverse osmosis typically consists of cartridge or bag filtration, as well as chemical treatment to prevent membrane scaling. Post-treatment could include alkali addition to make the water less corrosive and readjust the pH to acceptable levels for reuse.

Because of the membrane's fine pores, high operating pressures (690 to 2410 kPa [100 to 350 psi]) are required to separate metal ions from water, making electricity a major operating cost. The higher the salt concentration to be removed, the higher the operating costs will be.

Another costly component of the reverse osmosis process is membrane replacement. Even with anti-fouling measures, the membranes must be replaced approximately every 5 years throughout the life of the asset.

A variation on reverse osmosis is "loose reverse osmosis," which has lower pressure requirements and less salt rejection. This option's operating pressures are about half of those for reverse osmosis. This may be an acceptable alternative if complete removal of metal salts is unnecessary.

Nanofiltration. Nanofiltration (NF) is a lower-cost alternative to reverse osmosis, but its effluent has a higher TDS content. A nanofiltration membrane's pore size is less than 0.001 to 0.01 μm. It allows water, single valence ions (e.g., fluorides, sodium, and potassium chloride), and nitrates to pass through, while retaining multiple valence ions (e.g., sulfates and phosphates). The salts become concentrated and are discharged as a concentrated brine.

The nanofiltration membrane operates at lower pressures than reverse osmosis, resulting in lower operating costs. The operating pressures are about one-third to one-half of those required for reverse osmosis. Nanofiltration membranes must be replaced approximately every 5 years.

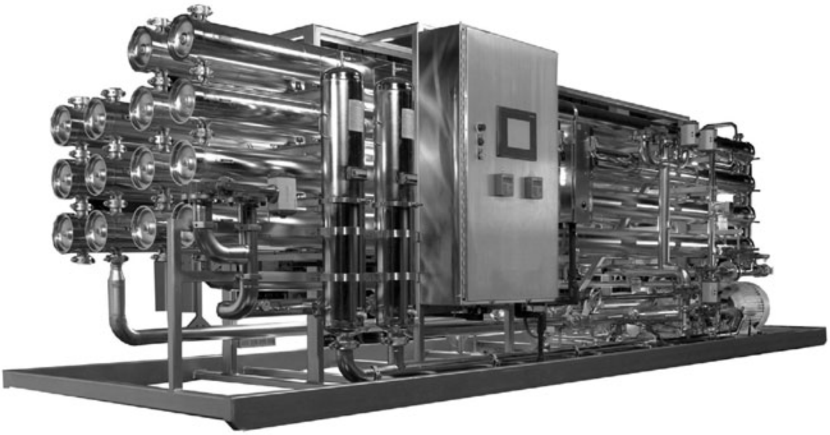

FIGURE 12.7 An example of a typical reverse osmosis unit (courtesy of GE Water & Process Technologies).

ELECTRODIALYSIS. Electrodialysis is typically used to recover precious metals (e.g., gold, silver, and platinum). The process uses small amounts of direct-current electricity to drive dissociated ions through a charged membrane. These membranes are typically arranged in stacks with an electrode placed between them. Wastewater containing both cations and anions is introduced between the membranes. Cations migrate toward the negative anode, while anions migrate toward the positive cathode. Cations and anions pass through cation- and anion-permeable membranes, respectively. Alternate cells contain either de-ionized water or concentrated metals.

Electrodialysis can be operated in either a batch or continuous mode. These units usually remove 40 to 60% of the salts in wastewater. Membrane fouling and scaling are potential problems. Pretreatment (e.g., chemical treatment, sedimentation or filtration, and even carbon adsorption) may be necessary.

EVAPORATION. Evaporation can recover useful byproducts from a solution or concentrated wastes (e.g., membrane reject water) before further treatment and disposal. Some evaporation processes may also recover a pure solvent from solution.

During evaporation, a solution is concentrated when a portion of the solvent, typically water, is vaporized, leaving behind a concentrated liquid containing virtually all of the dissolved solids, or solute, from the original feed water. The evaporation rate decreases as the solution becomes more concentrated.

Evaporation may occur naturally in solar evaporation ponds or mechanically via a commercial unit. The air emissions potential must be evaluated, because the evaporator may volatilize volatile organic compounds.

Evaporation Ponds. In areas where the annual evaporation rate exceeds the annual precipitation rate, solar evaporation ponds may be used to handle small or problem wastestreams. A solar evaporation pond is an open holding pond or lagoon that depends solely on climatic conditions (e.g., precipitation, temperature, humidity, pan evaporation rate, and wind velocity) to effect the evaporation of a solvent (typically water) from a wastewater solution.

Ponds must be sized to handle maximum wastewater flows, as well as the solids accumulation resulting from evaporation. If available, the 5-year average evaporation rate and precipitation rate are used. To size the required pond(s), a monthly mass balance is prepared:

$$\text{Net inflow (wastewater + precipitation)} - \text{net outflow (evaporation + leachate)} \tag{12.16}$$

The formula is calculated for each month, beginning with zero flow in the pond. At the end of each month, the quantity retained in the pond is used to begin the next month. The pond is large enough if, at the end of 12 months (each month having differing evaporation and precipitation rates), the pond is empty again.

The analysis is iterative: if the pond is not empty, the pond area must be made larger to increase the evaporation rate, and the analysis is performed again.

An impervious pond liner, underground leachate collection system, and leak-monitoring system typically are required. Provisions must be made to periodically remove accumulations of solids for disposal, and to inspect and repair the pond liner. Because the evaporation rate decreases as a liquid becomes more concentrated, conventional pan evaporation data should be used with an appropriate safety factor when sizing evaporation ponds.

Mechanical Evaporators. Mechanical evaporators effectively concentrate or remove salts, heavy metals, and other hazardous materials from solution. The evaporation process is driven by heat transferred from a condensing steam to a lower-temperature solution across a metallic heat-transfer surface. The absorbed heat causes the solvent to vaporize and the solute to concentrate. The resulting vapor may be vented to the atmosphere (if free of volatile compounds) or condensed for reuse.

Other methods of heating the water to promote vaporization include the use of hot oil, electric gas, fuel oil, waste heat from existing processes, and heat pumps. Because evaporation is an energy- and capital-intensive treatment process, an evaporation system must be carefully selected and designed for each application.

Evaporators have been used successfully in many industrial applications, including:

- Heavy metal and chelated metal plating wastestreams;
- Emulsified oil streams;
- Highly soluble biochemical oxygen demand (sugar) streams;
- Nonvolatile aqueous organic or inorganic streams (e.g., dyes, acids, and bases); and
- Process streams requiring some level of dewatering (e.g., food processing).

Evaporators may be an attractive alternative because they can concentrate and recover valuable materials for reuse without chemical addition. If proper construction materials are used, evaporators can treat virtually any combination of metals or nonvolatile organics at any metal concentration. In many metal-finishing and -processing applications, evaporators are used to achieve zero liquid discharge of rinsewater from the various manufacturing and coating processes.

Evaporation has a number of advantages over conventional physical-chemical treatment processes. One of the most significant advantages is that it produces high-quality distillate (typically <10 mg/L of total dissolved solids) that typically is reused in a manufacturing process.

Mechanical evaporation requires considerable quantities of energy, so design engineers must consider various energy alternatives to select the most efficient type of evaporator.

In an ideal system, 1 kg of condensing steam will evaporate 1 kg of water from the solution, so its steam efficiency (economy) is 1:1. A simple evaporator system has one evaporation chamber (effect) and is said to have an "economy of one." Evaporator economy can be increased by increasing the number of effects. A multiple-effect evaporator uses the vapor from the previous effect as the steam source for each subsequent effect, which boils at a slightly lower pressure and temperature (Figure 12.8). Each additional effect increases the evaporator's energy efficiency. For example, a double-effect evaporator requires about 50% of the steam required by a single-effect

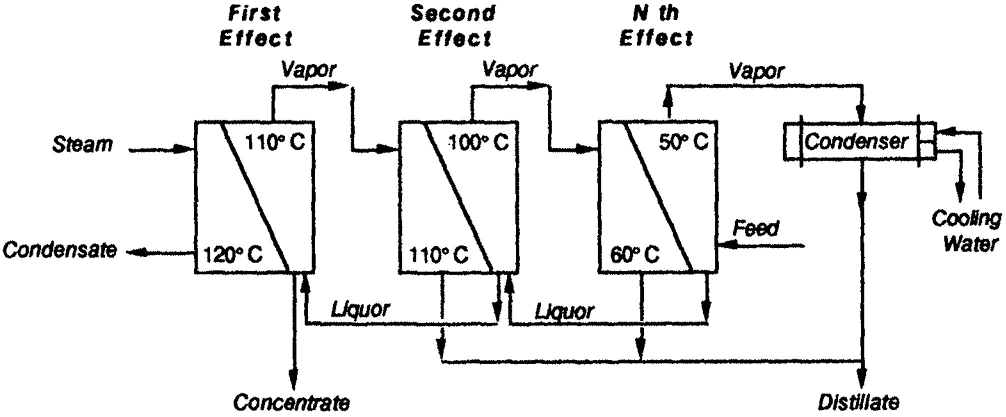

FIGURE 12.8 A schematic of a multiple-effect evaporator.

unit and is said to have an economy of 2. The number of effects can be increased until the capital cost of the next effect exceeds the energy savings.

Vapor compression is another proven technique to reduce energy requirements. In a vapor compression system (Figure 12.9), vapor discharged from the evaporator chamber is compressed to the required pressure and temperature in the evaporator's heat exchanger. Mechanical compressors (e.g., positive-displacement, centrifugal, or axial) are the most frequently used vapor-compression method. An evaporator system using mechanical vapor compression will need an outside steam source only to initiate unit operations. A small boiler or resistance heater in the evaporator feed tank typically can supply this steam source.

When available, waste steam or heat from other process streams may also be used to lower evaporation costs. Hot process fluids can be pumped through the heating tubes instead of steam, recovering heat and transferring it to the fluid to be evaporated.

Mechanical evaporators typically are categorized according to the arrangements of their heat transfer surfaces and the methods they use to impart energy (heat) to the solution. The typical evaporator categories are vertical-tube falling film, spray film, horizontal-tube spray film, forced circulation, and a combination of types.

Vertical-Tube Falling Film. In vertical-tube falling film evaporators (Figure 12.10), recirculating liquor (process fluids) is introduced at the top of a vertical tube bundle and falls in a thin film down the inside of the tubes. The liquor absorbs heat

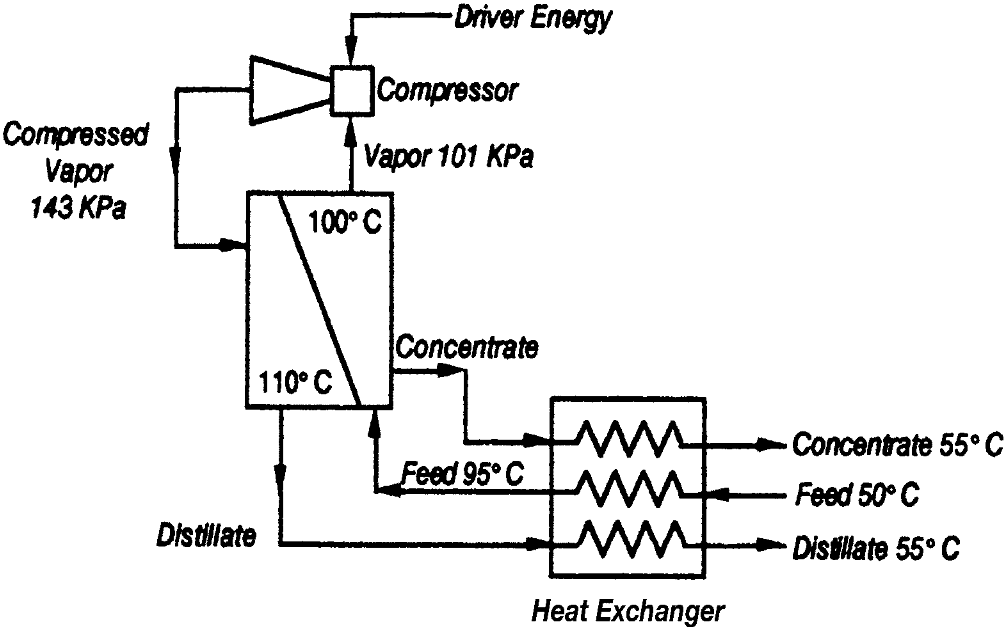

FIGURE 12.9 A schematic of a vapor-compression evaporator.

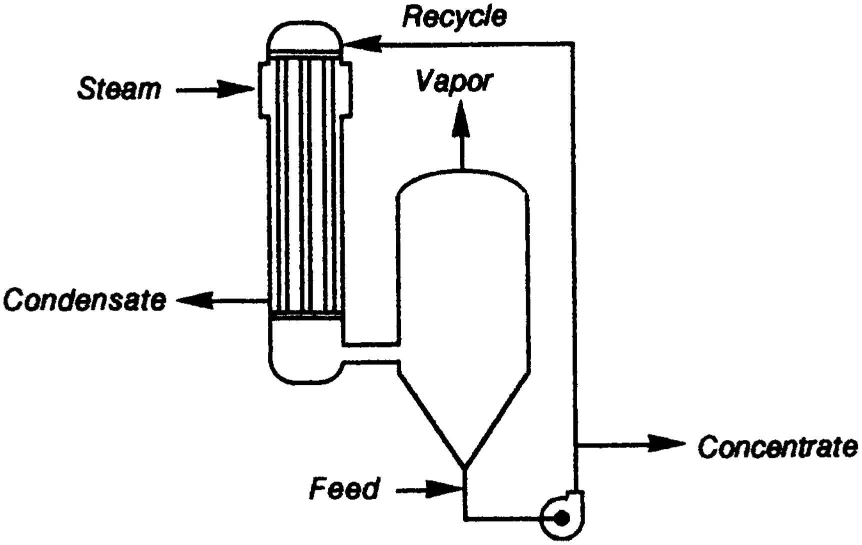

FIGURE 12.10 A schematic of a falling film evaporator.

from steam condensing on the outside of the tubes, and the water in the liquor is vaporized. The vapor and liquor are then separated at the bottom of the tubes.

Vertical-tube falling film evaporators are typically used on higher viscosity liquors and to concentrate heat-sensitive solutions that require low residence times.

Horizontal-Tube Spray Film. In a horizontal tube spray film evaporator (Figure 12.11), recirculating liquor is heated and sprayed over the outside of a horizontal tube bundle, which is carrying low-pressure steam and condensed water vapor inside the tubes. Vapor from the evaporator chamber can be used as steam in a subsequent effect or mechanically compressed and reused as the heating medium for the stage in which it was generated. Scale on the outside of the tubes can be periodically removed via chemical cleaning.

These units can be used indoors or in areas with low headroom.

Forced Circulation. In a forced-circulation evaporator, recirculating liquor (process wastewater) is pumped through a heat exchanger under pressure to prevent boiling and subsequent scale formation in the tubes (Figure 12.12). The wastewater then enters a separator chamber operating at a slightly lower pressure or partial vacuum, where water flash evaporates and insoluble crystals form in the liquid.

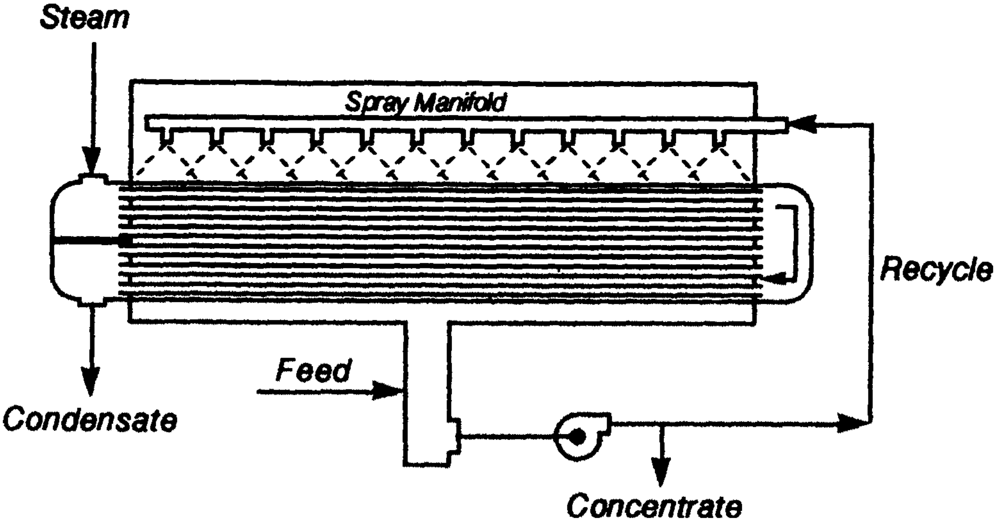

Figure 12.11 A schematic of a horizontal-tube spray film evaporator.

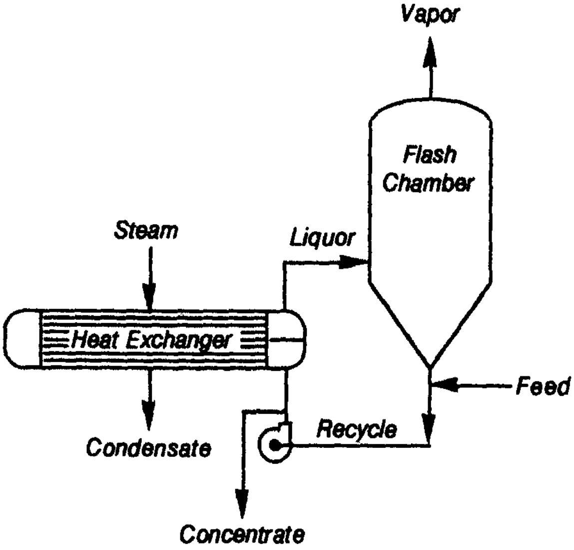

FIGURE 12.12 A schematic of a forced-circulation evaporator.

Forced-circulation evaporators (crystallizers) are often used at facilities that have large amounts of suspended solids or need high solids concentrations or crystallizing. Their energy costs typically are higher because of the high recirculation rates required.

Combined Systems. Sometimes evaporators can be combined with other types of evaporators or with other treatment processes to reduce capital and operating costs or meet specific treatment objectives. One fairly common arrangement uses a falling-film evaporator followed by a forced-circulation crystallizer. In this scheme, an evaporator initially concentrates the wastewater to 20 to 30% solids, and a crystallizer further concentrates it into a solid. Energy costs may be reduced by using the evaporator's vent steam to operate the crystallizer.

"Hybrid" systems are being considered in an increasing number of zero-liquid-discharge applications. A hybrid system consists of an evaporator or evaporator/crystallizer preceded by a reverse osmosis or electrodialysis unit. In this arrangement, the preconcentrator's concentrate (reject) is the evaporator's influent.

Although a hybrid system may be more complex, it should significantly reduce the size of the evaporator and, therefore, the overall energy requirement. However, some wastewaters, especially those with high scaling tendencies, may not be candidates for hybrid systems.

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Chapter 13

Removal of Organic Constituents

(continued)

This chapter discusses the biological, chemical, and physical treatment technologies used to treat the organics in industrial wastewater. Sometimes several technologies will be needed to meet federal, state, and local requirements.

BIOLOGICAL TREATMENT PROCESSES

Biological treatment processes are typically used to treat industrial wastestreams with a significant biodegradable fraction. Industries where biological treatment is typically used include the food processing industry, meat/poultry industries, feedlots, beverage industry, certain organic chemical manufacturing, etc. Biological processes may also be used to destroy hazardous organics, convert them into more benign colloidal and soluble forms, stabilize organic sludges, and remove nutrients (e.g., nitrogen and phosphorus) from wastewater.

A biological treatment may be considered a "conversion" process if it converts soluble wastes (e.g., soluble organics or BOD) into solids (e.g., biomass or sludge). When selecting a biological treatment process, design engineers must consider the energy-synthesis relationships because they affect many practical concerns (e.g., sludge production, operating costs, and treatment speed). For example, aerobic processes are typically rapid but produce a lot of sludge, while anaerobic processes are slower but produce far less sludge. Attached-growth systems can handle higher waste loads, but mass-transfer limitations are important design considerations.

Biological treatment processes rely on microorganisms (e.g., bacteria, protozoa, and rotifers). Protozoa and other organisms indicate that the bioreactor is functioning well and providing a satisfactory degree of treatment.

Biological treatment systems may be classified based on the distribution of microorganisms in the reactor (i.e., suspended-growth, attached-growth, and hybrid) or based on the environment in the reactor (i.e., aerobic, anoxic, and anaerobic) (Table 13.1).

ENERGY-SYNTHESIS RELATIONSHIPS. Biological treatment is a conversion process. The energy released while oxidizing easily biodegradable fractions of organics in wastewater is used for cell synthesis (sludge production) and maintenance (metabolism). The typical fractions of reducing equivalents (energy released while oxidizing organics) used for cell synthesis and maintenance are summarized in Table 13.2. Energy-synthesis relationships directly influence several practical aspects of industrial wastewater treatment (e.g., estimation of sludge quantity and treatment costs, the need for nutrients, and operating costs related to aeration and other process-specific systems).

TREATMENT ORGANISMS. The organisms found in wastewater treatment systems include viruses, bacteria, fungi, protozoa, and rotifers. Public health and disinfection requirements monitor virus populations. Fungi or algae can treat certain hazardous wastes. Protozoa and rotifers are found in many biological treatment processes (e.g., activated sludge process) and typically indicate a polished degree of treatment.

TABLE 13.1 Bioreactor systems used in industrial waste treatment.

System	Description
Activated sludge process	Suspended-growth systems with recycle; typically used in aerobic treatment of industrial wastewater. Process variations include nitrification and combinations with nutrient-removal reactor configurations.
Sequencing batch reactor	Four- or five-stage process that may be used for a variety of industrial wastewaters, with the advantages of faster removal rates observed with batch processes combined with an efficient solids-removal mechanism.
Aerobic lagoons	Aerated lagoons may be classified into three groups: facultative, aerobic flow-through without recycle, and aerobic flow-through with recycle. The design principles of aerated lagoons follow activated sludge process design to a large extent. Aerated lagoons with recycle have SRTs of the order of 20–30 days. Nitrification is likely in aerated lagoons with recycle, particularly in warm climates.
Facultative lagoons	Facultative ponds and lagoons have aerobic and anaerobic layers that are separated by thermal stratification. Facultative ponds depend on algal generation of oxygen to keep the top layer aerobic.
Anaerobic lagoons	Capable of handling high organic loading rates, used in pretreatment of slaughterhouse waste, meat-packing waste, feedlots, dairy waste, etc.
Trickling filters	Plastic media filters are used to treat industrial wastewaters. Filters may be used for rouging filters or a polishing step after a secondary process (e.g., the activated sludge process).
Rotating biological contactors	May be used for polishing operations; not typically used for industrial wastewater treatment.
Expanded bed reactors	Plastic media or coarse sand, suspended in a reactor via sufficient hydraulic head, provides the attachment surface for microorganisms.
Fluidized bed reactors	Plastic media or sand is suspended in a reactor via a high hydraulic head. The mass transfer rate and treatment rate of organic waste is higher than for expanded bed reactors.
Anaerobic filters	Biofilm-based systems that can withstand high organic loading rates to treat high-strength industrial wastewater.
Anaerobic contact	Suspended-growth systems with sludge recycle to achieve higher solids retention times; applicable for food-processing industry wastes.
Submerged media Anaerobic reactors	The media on which the microorganisms attach and grow is completely submerged; the specific surface area is significantly greater than rotating biological contactors or trickling filters.

System	Description
Integrated fixed-film activated sludge systems	Fixed-film media are placed in the activated sludge basin to add the advantages of fixed-film processes to the activated sludge process.
Membrane bioreactors	Membrane-type systems and systems that encapsulate microorganisms. Examples include MBBE.
Upflow anaerobic sludge blanket	Anaerobic granules form dense settling flocs and a blanket in the bottom half of the reactor. Wastewater is fed from the bottom, and a high degree of contact is achieved between the waste organics and the microorganisms. The system can handle high organic loads and high influent suspended solids. Granulation is often a key factor and requires seeding from an established system.
Thermophilic aerobic process	Thermophilic aerobic treatment systems can produce rapid destruction of organics at a relatively low biological solids production level. Examples of such systems include Advanced Fluidized Composting which uses either thermophilic aerobic or thermophilic anaerobic treatment, solids separation, and chemical treatment of the residual solids.
Thermophilic anaerobic process	Thermophilic anaerobic treatment systems have been used to treat organic wastes from the food industry.
Oxic/anoxic process	The oxic/anoxic process is a recent development for nitrogen removal from industrial waste streams and uses a two-step alternate oxic-anoxic treatment sections with separate biomass.

TABLE 13.2 Energy-synthesis relationships for common biological treatment processes.

Type of biological treatment process	Percent to synthesis	Percent to energy
Typical aerobic treatment		
High-rate aerobic treatment: SRT[a] < 2 days; F:M[b]>1	30–67%	33–70%
Conventional aerobic treatment: SRT 3–10 days; F:M 0.2–0.5	≈50%	≈50%
Low-rate aerobic treatment: SRT > 20 days; F:M < 0.1	20–30%	70–80%
Typical anaerobic treatment	5–10%	80–95%

[a] SRT = Solids retention time.

[b] F:M = Food-to-microorganism ratio.

Bacteria are responsible for most of the biological treatment of industrial wastewater. The average elemental composition of bacteria is widely accepted to be $C_5H_7O_2N$ (molecular weight ≈113 g/mole). Bergey's Manual provides a detailed description of various bacterial species, some of which are important in industrial waste treatment (Bergey's Manual, 1984). The bacteria vary in size (between 0.5 and 10 μm) and weight (typically on the order of 1 picogram).

The bacteria's surface properties are important in influencing solids-liquid separation in clarifiers. The bacteria's cell envelope may be a diffuse layer (slime) or a consolidated layer (capsule). It is typically made of a homogeneous polysaccharide occasionally containing proteins. Slimes are composed of exopolymers formed inside the cell; they are not known to have a metabolic role. Biopolymers, which also form slimes, have an important role in wastewater treatment, flocculation, sorption, and related issues in solids-liquid separation. Surface properties also affect the design and operation of attached-growth systems. For example, the bacterial capsule (glycocalyx) is 100 to 200 nm thick, consolidated, organized, and typically more discrete than the slime layer. This structure helps form the biofilm in attached-growth reactors. Knowledge of the surface properties will help engineers efficiently design process modifications and develop new biological treatment technologies.

Other organelles of bacteria (e.g., polyhydroxybutyrate granules) store carbon and nutrients. Volutin granules store phosphate.

MICROBIAL GROWTH KINETICS. A typical microbial growth curve may be divided into several phases (e.g., lag, exponential, declining growth, stationary, and endogenous decay) (Figure 13.1). Depending on the design, the biological treatment process may be operated at the exponential phase (e.g., high-rate activated sludge process), the stationary-endogenous phase (e.g., conventional activated sludge process), or the endogenous phase (e.g., extended activated sludge process). The operating phase directly affects the biodegradation rate, the extent of biodegradation, the quantity of sludge produced, and the sludge's settling characteristics. Depending on the food-to-microorganism (F:M) ratio, a biological treatment process can be designed to operate in different phases. If the F:M ratio is high, used as a preliminary treatment for high strength wastes, exponential growth phase is in effect. The metabolism rate is high, but the sludge produced has poor settling characteristics. The settling tank does not remove solids efficiently, and the effluent contains solids and unused organic matter. This is not desirable from a design standpoint. If the F:M ratio is low, used for situations where the waste strength is moderate and when a

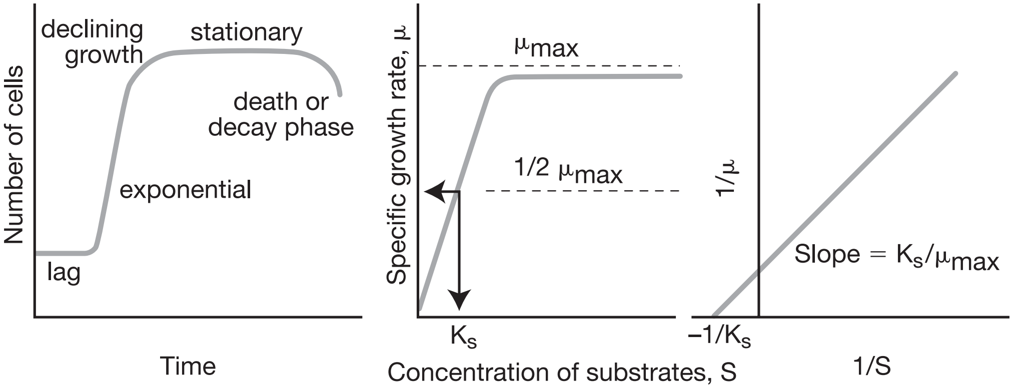


FIGURE 13.1 A graphical depiction of the microbial growth curve.

low-solids effluent is required, the operating regime is the declining-growth or endogenous-growth phase. Although the metabolism rate is low, the organics are nearly completely metabolized and the sludge has good settling characteristics.

Mass balance equations can be set up for any reactor configuration for microbial (bacterial) growth and substrate use (BOD exertion) (see Metcalf and Eddy, 2003). Changes in influent BOD will affect the BOD exertion rate, which will in turn influence the microbial growth rate. The yield coefficient is indicative of the expected sludge production. The substrate-use-rate constant is indicative of the BOD exertion rate or the organic contaminant removal rate and helps estimate the required treatment time. Process parameters [e.g., solids retention time (SRT), recycle ratio (if applicable), and effluent quality] may be calculated from the coupled mass balance equations.

FACTORS AFFECTING BIOLOGICAL TREATMENT PROCESSES. Biological treatment systems will be better designed if the following factors are considered carefully. Site-specific factors should also be considered during design. Also, if industrial waste treatment systems are underperforming, the underlying causes may be identified more easily if the following factors are considered.

Carbon Source. A carbon source is essential for maintaining cell growth and metabolism. In most treatment processes, the source of carbon is the organics in the wastewater. For certain processes (e.g., nitrification), an inorganic carbon source may be needed.

Nutrients and Growth Factors. Table 13.3 lists common macronutrients and micronutrients. Macronutrients (e.g., nitrogen and phosphorus) are needed so microorganisms can function properly. Small quantities of micronutrients (e.g., molybdenum) are critical in determining many biological reaction rates. For example, nickel is a trace nutrient for anaerobic processes (Speece, 1983). Growth factors (e.g., certain amino acids) promote proper microbial growth and floc formation.

TABLE 13.3 Nutrient requirements.

Group	Percent of dry cell weight
Major elements	
Carbon	45–55%
Oxygen	16–22%
Nitrogen	12–16%
Hydrogen	7–10%
Phosphorus	2–5%
Sulfur	0.8–1.5%
Potassium	0.8–1.5%
Sodium	0.5–2%
Magnesium	0.4–0.7%
Calcium	0.4–0.7%
Chlorine	0.4–0.7%
Iron	0.1–0.4%
Micronutrients and trace nutrients	
Zinc	<0.1%
Manganese	<0.1%
Molybdenum	<0.1%
Selenium	<0.1%
Cobalt	<0.1%
Copper	<0.1%
Tungsten	<0.1%
Nickel	<0.1%
Silicon	<0.1%
Growth factors	
Vitamins	<0.1%
Amino acids	<0.1%

References: WEF (1994), Bitton, (1994), Speece (1983).

A waste characterization study may determine that an industrial waste is often deficient in required macronutrients and micronutrients. If so, amendments are necessary to ensure that the biological treatment system functions properly. For example, a BOD:N:P ratio of 100:5:1 is often suggested as a guide for adding supplemental nitrogen and phosphorus. The proper ratio depends on the type of wastewater, the solids retention time, and the basin temperature; it is typically determined via trial and error.

Energy Source or Electron Donor. All biological reactions ultimately depend on an external source of energy to provide the driving force. It may be the carbon source for CBOD removal (heterotrophic reactions) or an inorganic chemical source (chemoautotrophic or chemolithotrophic) for nitrification.

Electron Acceptor. All biological reactions need a final electron acceptor to complete the oxidation-reduction process. Common electron acceptors include oxygen (in aerobic reactors), nitrate (in anoxic reactors), and carbon dioxide (in anaerobic reactors). If a treatment process does not have enough of the proper electron acceptor, biological reactions can be severely inhibited.

Temperature. Most biological reactions occur within a limited temperature range because the organisms' enzyme systems are adapted to that range. Biological treatment operations can typically be successful when operating within any organism's temperature range, but will assuredly fail if operated at temperatures outside their ranges.

Most industrial waste treatment processes operate in the mesophilic range. However, thermophilic treatment is gaining popularity in a variety of reactor configurations (e.g., anaerobic filters, sequencing batch reactors, and upflow sludge blanket reactors). For example, Lettinga et al. (1997) reports on developments such as the "Expanded Granular Sludge Bed" (EGSB) and the "Staged Multi-Phase Anaerobic" (MPSA) reactor systems, which can provide good removal efficiencies at higher organic loading rates for extreme conditions such as high temperatures and for inhibitory organic compounds. A thermophilic-mesophilic two-stage SBR system removed 26% to 50% more solids from diary wastewater than a mesophilic-mesophilic two-stage SBR (Dugba et al., 1997). No fecal coliforms were observed in the thermophilic-mesophilic system, compared with only a 2-log reduction in the mesophilic-mesophilic system.

pH. Most organisms can grow in environments in the range of pH 6 to 9. Some microorganisms (e.g., fungi) can survive at pH 5.5 and a little lower. However, fungi are rarely used in industrial waste treatment, although white rot fungus (*Phanerochaete chrysosporium*) can treat hazardous wastes containing polycyclic aromatic compounds (Bumpus, 1989).

Toxic Substances. Toxic substances in the industrial wastestream may reduce the rate of biological reactions. If the concentration is high enough, the biological reaction can stop completely.

Shock Loading. Slugs (shock loads) of organics, heavy metals, and inorganics can be toxic to biological treatment organisms. Accidental discharges of toxic substances may also cause severe problems. Plug-flow systems are particularly susceptible to shock loads.

Salinity. Biological processes can treat high-salinity industrial wastewaters. Ucisik and Henze (2004) reported that SBRs denitrified fertilizer industry waste containing 96.7 mg/L of chloride, although the high salinity decreased the denitrification rate. Smythe et al. (1997) noted that conventional activated sludge systems could tolerate up to 5% w/w salt, anaerobic systems could tolerate up 1.5% w/w salt, and fluidized beds and SBRs could handle up to 10% w/w salt. An acclimated culture in a fixed-film reactor with an organic loading rate of 1.00 g COD/L·d removed 87% of COD and 99% of total organic carbon (TOC) from fish-processing wastes containing 30 g/L of salinity (Gharsallah et al., 2002).

Solids Retention Time. In wastewater treatment systems, the rate of the slowest microbiological reaction often governs the overall rate. All bacteria need a minimum doubling time to reproduce (θ_c^{lim}).

Biological treatment systems also need to be designed so solids (bacteria) do not wash out prematurely. This is the minimum washout time (θ_c^{min}), which depends on the growth kinetic parameters [yield coefficient (Y), specific substrate use rate (k), and bacterial decay rate (b)] and the influent organic/BOD concentration. Treatment systems should operate at a solids retention time (θ_c) that is well in excess of θ_c^{min}.

The solids retention time (SRT) is one of the most important variables in biological treatment design and operations; it can affect a wide range of parameters [e.g., the food-to-microorganism (F:M) ratio, the effluent organic/BOD concentration, sludge production, solids loading on the secondary clarifier, and the effluent solids concentration]. If the SRT in an aerobic treatment process is less than 2 days, for example, the process will operate in the exponential growth phase, the F:M ratio will be high (>1), the process will produce a lot of sludge, and the clarifier may lose solids because of the sludge's poor settling properties. So, effluent quality will be poor (high solids content). If the SRT is between 10 and 20 days, the process will operate in the endogenous decay phase, the F:M ratio will be low (<1), the process will produce less sludge, and the sludge will have superior settling qualities. However, the higher SRT process will cost more to operate (particularly for aeration) than the lower SRT process.

Solids retention time also is important to achieve treatment goals. If nitrification is a treatment goal, for example, a longer SRT is essential.

Mixing (Reactor Design). Mixing is needed to distribute the electron acceptor (e.g., oxygen in aerobic treatment processes), energy source, nutrients, etc. so microorganisms have easy access to them. Also, completely mixed systems can handle toxic shock loads better than plug-flow systems. In some systems (e.g., chlorine disinfection systems), mixing may need to be minimal to provide extended contact between a wastewater constituent and a treatment chemical.

DESIGN APPROACHES. To design effective biological treatment systems, engineers should take into account biological reaction kinetics, bacterial-growth and pollutant-removal rates, and process-control parameters (e.g., solids retention time [θ_c] and hydraulic retention time [θ]). A rational design approach would include the development of a materials-balance equation taking into account inputs (e.g., oxygen and nutrients for an activated sludge process design); outputs (e.g., sludge, methane for anaerobic sludge treatment); and other factors affecting biological treatment processes.

The kinetics and yield coefficient data needed to design a biological treatment process may be obtained from the literature, laboratory experiments, and a thermodynamics-based approach. Collecting data from the literature typically requires less time and money than conducting laboratory experiments. However, a large amount of literature must be reviewed, and reviewers may not find information about all the constituents in a given industrial wastewater. Collecting data via laboratory experiments can fill the literature data gaps. Laboratory analyses also directly determine the relevant kinetic parameters for the facility, which is important because industrial wastewater constituents tend to be site-specific. Meanwhile, biokinetic parameters can be developed a priori using thermodynamics and energy-flow considerations.

This approach uses biological stoichiometry (see Sawyer et al., 2003; Rittmann and McCarty, 2001).

In practice, data from the literature, past case studies, laboratory analyses, and the engineer's knowledge base are used. Even when using the thermodynamics approach, the design engineer must consult data from the literature and augment the work with laboratory experiments. Table 13.4 provides a summary of typical values of the cell generation time ($\theta_c{}^{\lim} = \frac{1}{Yk - b}$), as well as theoretical values for the yield coefficient and specific substrate use rate constant for biological treatment processes. This data may be useful to provide some background information and help in the preliminary calculations of the design variables and quantities for aerobic and anaerobic treatment. Using the biological stoichiometry approach (Sawyer et al., 2003), similar data could be developed for biological treatment of industrial wastes where little or no prior case-study information is available.

TREATMENT TECHNOLOGIES. Following are various biological technologies used to treat industrial wastewater. Depending on wastewater characteristics and treatment objectives, one or more of these methods may be needed. (For more information, see Grady et al., 1999; Metcalf and Eddy, 2003; Pavlostathis and Giraldo-Gomez, 1991; and WEF, 2007.)

Activated Sludge Process. The activated sludge process is one of the most common biological processes used in both municipal and industrial wastewater treatment. Several variations of the activated sludge process may be used for industrial wastewater treatment, including variations in how the sludge is wasted. In a typical activated sludge process (Figure 13.2), the aeration tank and the secondary clarifier must be designed as one integral system because changes in aeration tank variables will affect clarifier operations, and vice versa. (For details on clarifier design, including operational control measures, see Keinath, 1985; Metcalf and Eddy, 2003; and WEF, 2006.)

Changes in industrial wastewater influent will also change effluent quality, particularly with respect to solids. If the change in influent characteristics is permanent, a state point analysis may be needed to determine the effects on effluent solids and the biomass in the aeration tank.

Eckenfelder (2000) notes the treatment performance of activated sludge systems in the coke, tannery, protein processing, pharmaceutical, organic chemicals,

Table 13.4 Typical values for θ_c^{lim}, Y, and k for biological treatment processes.

	θ_c^{lim}	Y	k
Aerobic processes			
Organic removal	0.1–0.2	$0.45\ \frac{\text{g bact}}{\text{g COD}}$	$22\ \frac{\text{g COD}}{\text{g bact-day}}$
Nitrification	1.5	$0.36\ \frac{\text{g bact}}{\text{gN}}$	$2.0\ \frac{\text{g N}}{\text{g bact-day}}$
S^{2-} to SO_4^{2-}	0.6	$0.59\ \frac{\text{g bact}}{\text{g S}}$	$2.5\ \frac{\text{g S}}{\text{g bact-day}}$
$Fe^{2}+$ to Fe^{3+} (pH $\approx$ 2.7)	2.2	$0.0075\ \frac{\text{g bact}}{\text{g Fe}}$	$60.0\ \frac{\text{g Fe}}{\text{g bact-day}}$
H_2 oxid to H_2O	0.5	$0.36\ \frac{\text{g bact}}{\text{g H}_2}$	$1.3\ \frac{\text{g H}_2}{\text{g bact-day}}$
Anaerobic processes			
Denitrification	0.2	$0.35\ \frac{\text{g bact}}{\text{g COD}}$	$14.0\ \frac{\text{g COD}}{\text{g bact-day}}$
SO_4^{2-} to S^{2-}	1.0	$0.10\ \frac{\text{g bact}}{\text{g COD}}$	$9.3\ \frac{\text{g COD}}{\text{g bact-day}}$
Methane fermentation			
Fats	3.8	$0.031\ \frac{\text{g bact}}{\text{g COD}}$	$8.4\ \frac{\text{g COD}}{\text{g bact-day}}$
Proteins	3.8	$0.081\ \frac{\text{g bact}}{\text{g COD}}$	$8.4\ \frac{\text{g COD}}{\text{g bact-day}}$
Carbohydrates	3.8	$0.23\ \frac{\text{g bact}}{\text{g COD}}$	$8.4\ \frac{\text{g COD}}{\text{g bact-day}}$
Sewage sludge	3.8	$0.081\ \frac{\text{g bact}}{\text{g COD}}$	$8.4\ \frac{\text{g COD}}{\text{g bact-day}}$

References: McCarty (1969); Sawyer *et al.* (2003).

and paper industries. BOD and COD loading and wastewater temperatures are site-specific. The F:M ratio ranges from 0.05 per day for protein-processing wastewater to 0.57 per day for vegetable oil. The solids retention time ranges from 5.2 days for paper mill wastewater to 20 days for tannery wastewater. Other parameters [e.g., MLVSS, hydraulic retention time (HRT), sludge volume index (SVI), and zone settling velocity] depend on wastewater characteristics and quantities.

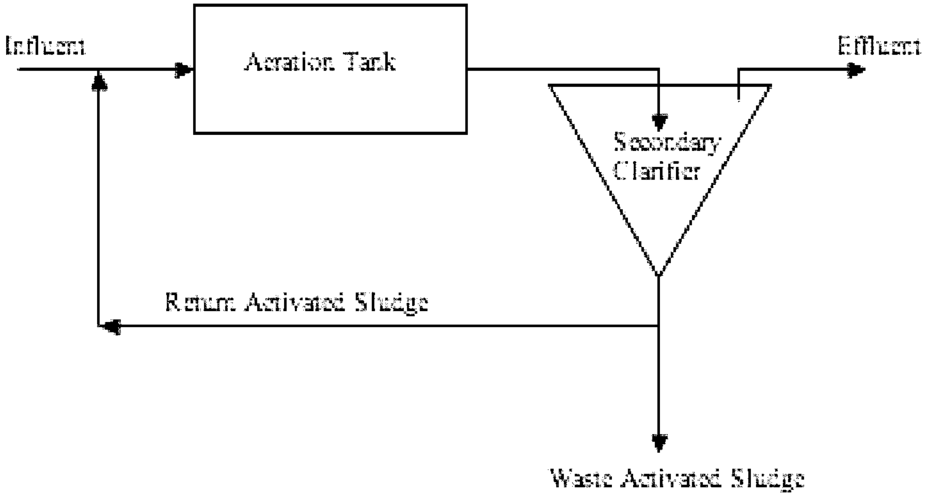


Figure 13.2 A schematic of the activated sludge process.

Microbiology. Activated sludge flocs contain bacteria, organics, and inorganics (Bitton, 1994). Floc size ranges from <1 to 1000 μm or more, and viable bacteria make up approximately 5 to 20% (Parker et al., 1971; U.S. EPA, 1987; Weddle and Jenkins, 1971). Although it is assumed that there is enough oxygen throughout the aeration tank, the oxygen distribution within the activated sludge is subject to mass-transfer limitations. The surface of the floc is aerobic, but an anoxic zone exists inside and there is a small anaerobic zone at the center (Weimin et al., 1987).

The microlife in activated sludge floc typically includes:

- Bacteria (e.g., *Zooglea, Pseudomonas, Flavobacterium, Alcaligenes, Bacillus, Achromobacter, Corynebacterium, Comomonas, Brevibacterium,* and *Acinetobacter*);
- Filamentous organisms (e.g., *Sphaerotilus, Beggiatoa,* and *Vitreoscilla*);
- Autotrophic bacteria (e.g., nitrifiers [*Nitrosomonas* and *Nitrobacter*] and phototrophic bacteria [*Rhodospirrilaceae*]);
- Protozoa (e.g., ciliates, flagellates, and *Rhizopoda*); and
- Rotifers (e.g., *Bdelloidea, Monogononta, Lecane* sp., *Notommato* sp., *Philodina* sp., and *Habrotrocha* sp.).

The total aerobic bacterial count in activated sludge is approximately 10^8 colony-forming units (CFU) per milligram of sludge. *Comomonas* and *Pseudomonas* predominate. Many of the bacteria, including *Zooglea* and many *Pseudomonas* species, can produce an exocellular biopolymer that surrounds the cell.

The term *ecological succession of microorganisms in activated sludge* refers to a mixed community of bacteria, *Sarcodina* and halophytic protozoa, holozoic mastogophera, free-swimming ciliates, stalked ciliates, and rotifers in proportions indicative of an optimal activated sludge process. With this in mind, the activated sludge floc may be examined via phase contrast microscopy to determine potential reasons for process upsets and poorly settling sludge.

Problems in Solids-Liquid Separation. Solids-liquid separation is a major issue in industrial wastewater treatment. A balanced mix of filamentous and floc-forming microorganisms is essential to produce sludge with good settling properties (Bitton, 1994; Eckenfelder, 2000). When activated sludge microorganisms oxidize organics, a polysaccharide slime layer is produced that attracts both activated sludge organisms and flagellates. The efficiency of solids-liquid separation is influenced by wastewater composition, the microbiology and structure of activated sludge flocs, nutrient-deficient industrial wastes, shock loads of organics, poor oxygen transfer, and toxic substances.

The sludge volume index (SVI), measured in milliliters per gram of sludge, is a useful indicator of a sludge's settling properties. It is determined by placing a mixed-liquor sample in a 1- to 2-L cylinder and measuring the volume and corresponding mixed-liquor suspended solids (MLSS) concentration after 30 minutes:

$$\mathrm{SVI} = \frac{\text{Volume of settled sludge} \times 1000}{\text{MLSS}}$$

If the SVI is between 50 and 150, the sludge will settle reasonably well. A sludge volume index greater than 150 is typically associated with excessive filamentous growth (Parker et al., 2001).

Other issues may result in a poor-settling sludge. For example, foaming can be the result of surfactants that have not been biodegraded, rising sludge, and excessive growth of *Actinomycetes.* The microorganisms identified in foams include *Nocardia amarae, N. rhodochrous, N. asteroids, N. caviae, N. pinensis, Sptretomyces* spp., *Microthrix parvicella, Micromonospora,* and *Rhodococcus* spp. Potential mechanisms of foam production include gas bubbles within flocs, hydrophobic nature of the foam that the bacteria transport to the surface, biosurfactants, and long retention times and warm temperatures. Foams may be controlled by chlorinating the return activated sludge (RAS), increasing sludge wasting, using anoxic biological selectors, reducing airflow rate to the aeration tank, reducing oil and grease levels, adding anaerobic digester supernatant (which is toxic to *Nocardia*), and using physical-chemical methods (e.g., sprays, anti-foam agents or iron salts).

Proper solids-liquid separation depends on a balance of both floc-formers and filamentous organisms. Excessive growth of filamentous organisms can result in filamentous bulking. Filamentous microorganisms can be used as a diagnostic tool to indicate process upsets. They have a high surface-area-to-volume ratio, allowing them to survive and predominate when DO (*S. natans* and *Thiothrix*), F:M ratio, and nutrients are low. High-carbohydrate industrial wastes are susceptible to filamentous bulking, as are high sulfide (*Beggiatoa* sp. and *Thiothrix* sp.) and low pH (*fungi*) conditions. Controlling process conditions and variables (e.g., dissolved oxygen, pH, nutrients, and sludge age) can promote a well-settling sludge. Anoxic selectors can be used to control *S. natans* and *Nostocoida lumicola*, and anaerobic selectors can be used to suppress *S. natans.*

Nonfilamentous bulking is the result of nutrient deficiency (Jenkins, Richards, and Daigger, 2004). Under nutrient-deficient conditions, several genera of bacteria can produce excessive quantities of exocellular polymer. Identifying and addressing the specific nutrient deficiency can correct the problem.

Dispersed growth could cause poor-quality sludge; the most likely reasons are high BOD loading, oxygen-transfer limitations, or toxicity. Pinpoint flocs, essentially the disruption of larger flocs into tiny fragments, may be caused by a low density of filamentous organisms. Rising sludge may be the result of an excessively long detention time in the secondary clarifier. The detention time leads to denitrification in the clarifier, causing settled flocs to rise to the surface with the nitrogen gas.

Fungi (e.g., *Geotrichum, Penicillium, Cephalosporium, Cladosporium,* and *Alternaria*) are typically not found in flocs in abundance, except when the reactor environment is acidic, toxic, and nitrogen-deficient. They indicate potential reasons for process upsets (e.g., bulking). Sludge bulking may also result from an abundance of *Geotrichum candidum* under low pH conditions because of acid wastes.

Process Design. Figure 13.3 provides a flowchart of the overall design strategy for activated sludge systems. (Specific cases will require slight modifications.) Design engineers should begin by characterizing the waste and flowrates and determining the land requirements and geological considerations for site selection. Then they should address land use, environmental impact assessments (EIA), environmental impact statements (EIS), economic and manpower considerations, and transportation needs analysis. Next, engineers must determine the treatment goals, safety factors,

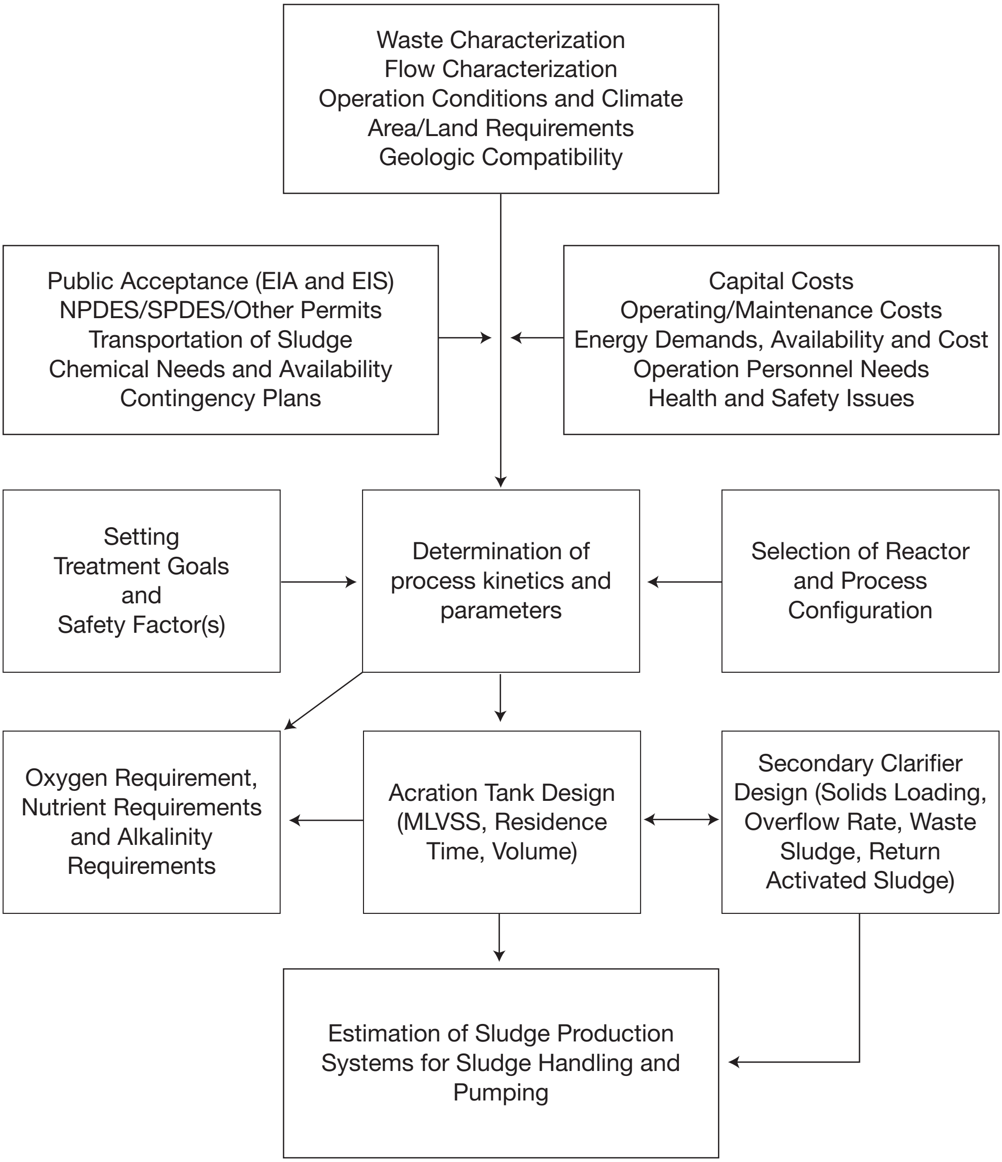


FIGURE 13.3 A design approach for biological treatment of industrial wastewater treatment.

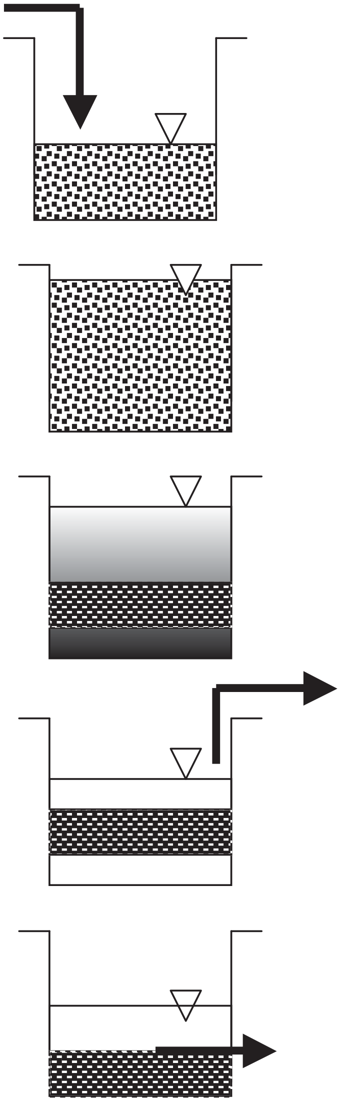
and solids retention time, as well as calculate the organic loading rate. The selection or measurement of kinetic parameters and choice of process modification(s) follows. Depending on the process modification, the design equations may be identified or developed via a materials balance approach. Then, engineers can select a solids concentration in the aeration basin and calculate the hydraulic residence time and volume in the aeration tank. Using literature, experimental data, or stoichiometry, they then can estimate the oxygen requirements, nutrient requirements [particularly for nutrient-deficient wastewaters (e.g., carbohydrate wastes)], and alkalinity requirements.

The solids-liquid separation process must be an integral part of the design. Engineers should determine return activated sludge and waste activated sludge concentrations and quantities. The process design calculations would yield sludge production quantities, which may then be used to design appropriate hydraulics to handle the sludge.

Finally, pilot-scale studies would help design engineers verify the design at a smaller scale. Although pilot-scale studies may be expensive, they are frequently necessary for industrial facilities, where wastewater constituents or treatment systems are site-specific.

Sequencing Batch Reactors. Sequencing batch reactors (SBRs) are essentially fill-and-draw reactors that remove BOD, nutrients (e.g., nitrogen or phosphorus), and organic contaminants from wastewater. They differ from conventional activated systems in that equalization, reaction, and clarification all occur in one tank via a time-controlled sequence (U.S. EPA, 1999). Sequencing batch reactors have been used since the mid-1980s and are becoming popular for industrial wastewater treatment because they need less space, can handle wide fluctuations in wasteloads, and adapt to various process applications and environmental conditions (e.g., high and low temperatures; high salinity; and aerobic, anoxic, and anaerobic conditions). For example, they have been used to treat industrial wastes at very low temperatures (Dague et al., 1998). A continuous flow version—the intermittent-cycle extended-aeration system (ICEAS)—is also available (U.S. EPA, 1999).

Sequencing batch reactors have been used to treat wastes from many industries (e.g., chemical, petrochemical, beverage, dairy, fish-processing, food-processing, pharmaceutical, pulp and paper, textile, and tobacco) (AquaSBR, 1999; Eckenfelder, 2000). Most SBRs have four or five stages of operation: fill, react, settle, draw, and idle (Figure 13.4). (Some do not use the idle stage.) The fill stage may be static, mixed, or aerated. Sludge is typically wasted in the react phase to ensure uniform



FILL: Add waste influent
% of cycle time = 25
% of max volume = 25 to 100
Operation = Air is ON/OFF

REACT: Reaction phase
% of cycle time = 35
% of max volume = 100
Operation = Air is ON/CYCLE

CLARIFY: Separate solids-liquids
% of cycle time = 20
% of max volume = 100
Operation = Air is OFF

DECANT: Remove effluent
% of cycle time = 15
% of max volume = 100 to 35
Operation = Air is OFF

IDLE or WASTE SLUDGE: Remove the sludge (Optional step)
% of cycle time = 5
% of max volume = 35 to 25
Operation = Air is ON/OFF

FIGURE 13.4 Illustrations of the steps in sequencing batch reactor operations.

effluent solids quality, but many sludge wasting options are possible to meet site-specific needs.

Because the SBR is a batch process, a batch-based design approach should be used. Applying the mass balance equation for a substrate "S" and bacteria "X," a kinetics-based design approach may be developed (Eckenfelder, 2000; Metcalf and Eddy, 2003). A typical SBR design approach consists of the following steps (AquaSBR, 1995; U.S. EPA, 1999; Metcalf and Eddy, 2003):

- Characterize the wastewater [e.g., design flow, maximum daily BOD_5 loading, TSS loading, pH, alkalinity, wastewater temperature, total Kjeldahl nitrogen (TKN), ammonia-nitrogen, and total phosphorus].
- Determine the effluent goals and safety factors, and resolve regulatory issues and permits. (At this stage, design engineers typically consult SBR manufacturers for a recommended design based on the key parameters outlined in the following steps.)
- Select the number of SBR tanks, the duration of each stage, the duration of the entire treatment cycle, and the number of cycles per day.
- Select the MLSS concentration, determine the fill volume (relative to tank volume), determine the decant depths, and determine the SBR tank volume (based on decant depths).
- For nitrification needs, determine the SRT, determine the TKN the will undergo nitrification, calculate the nitrifier biomass concentration, and check whether the aeration time will be sufficient.
- Determine the decant pumping rate, alkalinity requirements, oxygen requirements, and oxygen transfer rate.
- Estimate the sludge production.
- Calculate F:M and BOD volumetric loading.

The key design variables for SBRs are summarized in Table 13.5. The design should include at least two parallel SBRs so operations can continue when one unit is taken out of service for maintenance. For carbohydrate-rich wastestreams, nitrogen and phosphorus may be needed to achieve an acceptable degree of treatment and good solids-liquid separation. Trace metal nutrients (e.g., iron, cobalt, and nickel) may also be needed if their concentrations in the waste stream are low.

Table 13.5 Key design variables for sequencing batch reactor processes (AquaSBR®, 1995).

LOW LOAD		
Design variable	**Municipal waste**	**Industrial waste**
Food-to-microorganism ratio	0.05–0.1 d^{-1}	0.05–0.1 d^{-1}
Treatment cycle duration	4.8-6.0 hours	4.8–48 hours
Typically low water level mixed-liquor suspended solids	4000–4500 mg/L	4000–6000 mg/L
Hydraulic retention time	18–24 hour	Varies with waste characteristics and site-specific factors
Freeboard depth	Depends on expected surfactants in wastewater	Depends on expected surfactants in wastewater
CONVENTIONAL LOAD		
Design variable	**Municipal waste**	**Industrial waste**
Food-to-microorganism ratio	0.15–0.40 d-1	0.15–0.60 day-1
Treatment cycle duration	4.0 hours	4.0–24 hours
Typically low water level mixed-liquor suspended solids	2000–2500 mg/L	2000–4000 mg/L
Hydraulic retention time	6–14 hour	Varies with waste characteristics and site-specific factors
Freeboard depth	Depends on expected surfactants in wastewater	Depends on expected surfactants in wastewater

Lagoons. These variations of the activated sludge process may be appropriate for small flows or industrial facilities whose objective is to reduce the wastewater's strength before discharging it to a publicly owned treatment works (POTW). There are basically three types of lagoons: aerated lagoons, facultative ponds, and anaerobic lagoons. Aerated lagoons may be further subdivided into three categories: facultative, aerobic flow-through without recycle, and aerobic flow-through with recycle. Aerated lagoon designs are similar to activated sludge process designs, except for the inlet and outlet structures, and other peripherals.

Table 13.6 provides a summary of design parameters for stabilization ponds and lagoons (WEF, 2007).

Facultative Ponds. Facultative ponds and lagoons have aerobic and anaerobic layers that are separated via thermal stratification. They depend on algal generation of oxygen to keep the top layer aerobic. With depths up to 2.5 m and no mixing mechanisms (other than wind), facultative ponds may be more attractive in warmer climates.

Suspended solids in a facultative lagoon depend on the amount of power imparted via mixing. Solids undergo anaerobic degradation (including solubilization of particulate), which leads to feedback of soluble BOD into the upper aerobic layers. Feedback systems can be modeled using classical mathematical modeling techniques (Chapra, 1997). Nutrient addition typically is not necessary because nitrogen and phosphorus are released into the aqueous phase by anaerobic processes at the bottom of the lagoon.

Facultative ponds are not appropriate for several types of wastewaters—especially dye-laden ones (because light cannot penetrate colored effluents) (Eckenfelder, 2000). However, they can remove 80% of BOD from meat and poultry industry wastewater (81 kg BOD/ha·d), 87% of BOD from chemical industry wastewater (176 kg BOD/ha·d), 80% of BOD from paper industry wastewater (118 kg BOD/ha·d), 76% of BOD from petroleum industry wastewater (31 kg BOD/ha·d), and 80% from dairy industry wastewater (25 kg BOD/ha·d) (Eckenfelder, 2000). The facultative pond's area and detention time are industry-specific and also depend on the BOD loading rates. The pond typically is 0.5 to 2.5 m deep. (For more detail, see Eckenfelder, 2000.)

The use of facultative lagoons is diminishing because of the lack of a rational design approach (Metcalf and Eddy, 2003).

Table 13.6 Typical design parameters for stabilization ponds and lagoons.

	Type of pond					
Parameter	**Aerobic (low-rate)**	**Aerobic (high-rate)**	**Aerobic maturation**	**Aerobic-anaerobic-facultative**	**Anaerobic pond**	**Aerated lagoon**
Flow regime	Intermittently mixed	Intermittently mixed	Intermittently mixed	Intermittently mixed	Intermittently mixed	Completely mixed
Pond size (ha)	<4.0, multiple units	0.2–0.8	0.8–4.0, multiple units	0.8–4.0, multiple units	0.2–0.8, multiple units	0.8–4.0, multiple units
Operation	Series or parallel	Series	Series or parallel	Series or parallel	Series	Series or parallel
Detention time (day)	10–40	4–6	5–20	5–30	20–50	3–10
Depth (m)	0.9–1.2	0.3–0.4	0.9–1.2	1.6–2.8	2.8–5.6	1.8–6
pH	6.5–10.5	6.5–10.5	6.5–10.5	6.5–8.5	6.5–7.2	6.5–8.0
Temperature range (°C)	0–30	5–30	0–30	0–50	6–50	0–30
Optimal temp. (°C)	20	20	20	20	30	20
Typical BOD_5 loading (kg/ha/d)	67–135	90–180	17	56–202	224–560	—
BOD removal (%)	80–95%	80–95%	60–85%	80–95%	50–85%	80–95%
Principal conversion products	Algae, CO_2, bacteria	Algae, CO_2, bacteria	Algae, CO_2, bacteria	Algae, CH_4, CO_2, bacteria	CH_4, CO_2, bacteria	CO_2, bacteria
Algal concentration (mg/L)	40–100	100–260	5–10	5–20	0–5	—
Effluent suspended solids (mg/L)	80–140	150–300	10–30	40–60	80–160	80–250

Aerobic Ponds. Aerobic ponds can remove 80% of BOD from meat and poultry industry wastewater (510 kg BOD/ha·d), 51% of BOD from canning industry wastewater (159 kg BOD/ha·d), 89% of BOD from chemical industry wastewater (22 kg BOD/ha·d), and 50% of BOD from paper industry wastewater (140 kg BOD/ha·d) (Eckenfelder, 2000). The aerobic pond's area and detention time are industry-specific and also depend on the BOD loading rates. The pond typically is 1.4 to 3.0 m deep. (For more detail, see Eckenfelder, 2000.)

Combined Aerobic-Anaerobic Ponds. Combined aerobic-anaerobic ponds can remove 94% of BOD from meat and poultry industry wastewater (250 kg BOD/ha·d), 91% of BOD from canning industry wastewater (250 kg BOD/ha·d), and 94% of BOD from paper industry wastewater (11 kg BOD/ha·d) (Eckenfelder, 2000). The combined pond's area and detention time are industry-specific and also depend on the BOD loading rates. The pond typically is 1.6 to 2.2 m deep. (For more detail, see Eckenfelder, 2000.)

Anaerobic Lagoons. Anaerobic lagoons can handle very strong wastes; in fact, they are typically designed so the waste strength will make the entire pond anaerobic (Eckenfelder, 2000). Anaerobic lagoons are used extensively to treat wastewaters with very high BOD and organic loading rates (generated by meat processors, slaughterhouses, feedlots, and other food industries). A high degree of treatment is possible if the lagoon is followed by an aerobic treatment process.

Anaerobic lagoon design is similar to that of anaerobic digesters. The surface-area-to-volume ratio should be minimized to control heat loss and exposure to the atmosphere. A floating cover may be appropriate if low ambient temperatures are expected.

Fixed-Film Technologies. Biofilms are relatively thin layers of microorganisms that attach to and grow on surfaces (Figure 13.5). The layer is a few hundred microns thick, with aerobic zones near the wastewater and anaerobic zones near the solid surface. A biofilm develops on a surface via the following five steps (Characklis and Wilderer, 1989):

- Surface conditioning;
- Transport of microorganisms to the conditioned surface;
- Adsorption of the microorganisms to the solid surface via reversible or irreversible sorption;

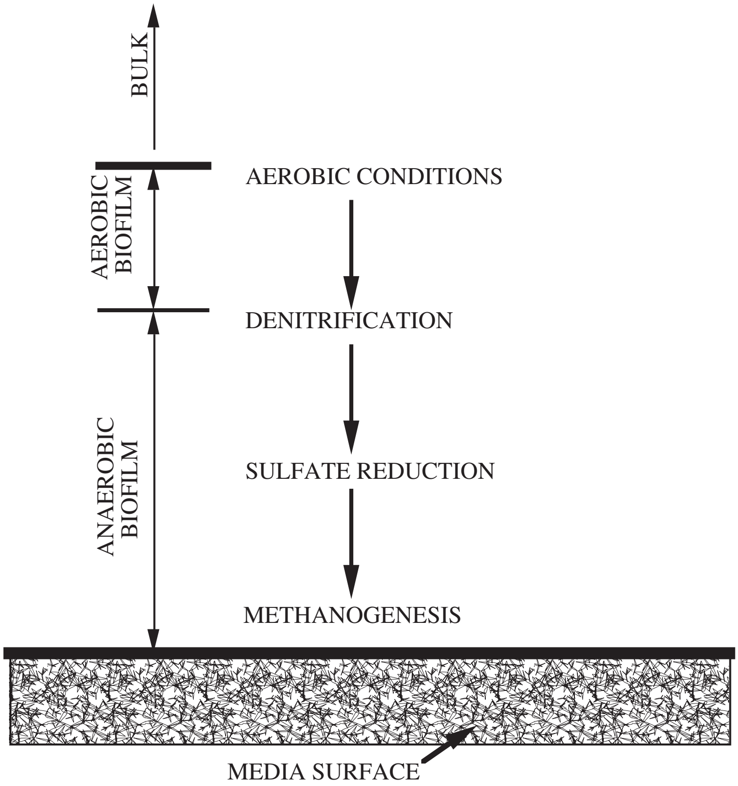


FIGURE 13.5 An illustration of the aerobic and anaerobic processes in biofilms (developed from Characklis and Wilderer, 1989).

- Biofilm accumulation, growth, and microbial succession; and
- Biofilm detachment from the media surface because of the shear force of the wastewater against the biofilm.

Based on a materials balance approach, Rittmann and McCarty (2001) developed an equation for the thickness of a biofilm at steady state (when the bacteria growth and decay rates are equal):

$$S_{\min} = K_s\left[\frac{b}{(Y)(k) - b}\right] \tag{13.1}$$

It is difficult to obtain a relationship between S, the kinetics parameters (Y, k, K_S, and b), and the solids retention time (θ_C). The problem is the simultaneous transport of electron donors and acceptors into the biofilm, and the transport of products out of it. The effect of product gases' diffusion on profiles of substrates and other chemical species also affects reactor performance. (For more detail on design using this kinetics and mass-balance based approach, see Rittmann and McCarty, 2001.)

Biofilm-based technologies include trickling filters, rotating biological contactors (RBCs), expanded bed reactors, and fluidized bed reactors. Several empirical models are available to design biofilm reactors, particularly for plastic media, which are widely used to treat industrial wastes.

Trickling Filters. Conventional trickling filters are cylindrical towers that are typically about 15 to 30 m in diameter and about 12 to 15 m deep. The tower is filled with media (stone or plastic), and wastewater enters at the top (for a gravity downflow trickling filter) via a sprinkler or other distribution system that spans the tower. Biofilm grows on the media during startup. Then, as wastewater flows past the media during operations, bacteria in the biofilm ("slime" layer) consume the organics (BOD). Aeration may be added if the wastewater is expected to be strong. The biofilm will increase over time until it becomes too thick to maintain, and the wastewater flowing past shears off some of it. The shorn pieces collect at the bottom of the tank and are periodically removed as waste activated sludge.

Trickling filters may be used as a "roughing filter" to treat high-strength wastes, followed by another treatment step (e.g., activated sludge). They may be used as a "polishing filter" after secondary treatment (e.g., activated sludge). Or they may be used as the only secondary treatment process (i.e., instead of an activated sludge process) if the treated wastewater will be discharged to a POTW.

Several design equations are available for packed plastic-media trickling filters, based mostly on mass balance principles and empirical methods to determine relationships between parameters (Table 13.7). In general, plastic media filters may be up to 12 m deep and have hydraulic loading rates up to 0.003 $m^3/m^2 \cdot s$. Media-specific design parameters may be obtained from the manufacturer. Design engineers typically use design curves provided by trickling filter manufacturers or suppliers, after they have characterized the waste and determined the treatment goals. (For loading rates and design parameters for selected plastic media, see Eckenfelder, 2000. For design equations for stone media filters, see Viessman and Hammer, 1998.)

Rotating Biological Contactors. Rotating biological contactors consist of plastic media fixed on a rotating shaft, which is housed in a tank through which wastewater flows. During startup, the plastic media are gradually colonized with bacteria. Once

TABLE 13.7 Summary of design equations used for plastic media filters.

Source	Equation
Velz (1948)	$\frac{dS}{dz} = -kz$ k = first-order decay constant, m^{-1}; z = filter depth, m
Howland (1958)	$t = \frac{CD}{\left[\frac{Q}{A}\right]^n}$ t = liquid contact time, min; D = packing depth, m; Q = flowrate in $\frac{L}{min}$; A = cross-sectional area, m^2; C = constant for the packing; n = hydraulic constant for packing. Note: "C" and "n" are determined from pilot plant data. Balakrishnan et al. (1969) reported values of "C" of 1.9 and "n" of 0.43 (without biofilm) and "C" of 11 and "n" of 0.045 (with biofilm)
Schulze (1960)	$\frac{S_e}{S_o} = e^{\left[-\frac{kD}{Q^n}\right]}$ S_o = influent BOD, $\frac{mg\,BOD}{L}$; S_e = settled effluent BOD, $\frac{mg\,BOD}{L}$ D = packing depth, m; k = experimentally determined rate constant, day^{-1} n = constant for packing = 0.67; Q = hydraulic rate in $\frac{m^3}{m^2 - day}$
Germain (1966)	$\frac{S_e}{S_o} = e^{\left[-\frac{kD}{Q^n}\right]}$ S_o = influent BOD, $\frac{mg\,BOD}{L}$; S_e = settled effluent BOD, $\frac{mg\,BOD}{L}$ D = packing depth, m; k = WW treatment & packing coefficient, $\frac{\left[\frac{L}{s}\right]^{0.5}}{m^2}$ n = constant for packing = 0.5; Q = hydraulic rate in $\frac{L}{m^2 - s}$

(continued on next page)

TABLE 13.7 *(Continued)*

Source	Equation
Modified Velz Equation	$\frac{S_e}{S_o} = \frac{1}{(R+1)\exp\left\{\frac{k_{20} A_s D \theta^{T-20}}{[q(R+1)]^n}\right\} - R}$ S_o = influent BOD, $\frac{\text{mg BOD}}{\text{L}}$; S_e = settled effluent BOD, $\frac{\text{mg BOD}}{\text{L}}$ R = recirculation ratio D = packing depth, m; k_{20} = filter treatability constant, $\frac{\left[\frac{L}{s}\right]^{0.5}}{m^2}$ n = constant for packing = 0.5; q = hydraulic rate in $\frac{L}{m^2\text{-}s}$; θ = temp correction factor Ref: Eckenfelder (1963), Eckenfelder & Barnhart (1963)

Correction for depth and volumetric loading in value of "k" in the modified Velz equation (WEF 2000)

$$\frac{k_2}{k_1} = \left[\frac{D_1}{D_2}\right]^{0.5} \left[\frac{S_1}{S_2}\right]^{0.5}$$

k_1 = k value for a 6.1 m deep filter at 150 $\frac{\text{mg BOD}}{\text{L}}$; k_2 = corrected k value for site specific conditions

D_1 = 6.1 m; D_2 = site-specific packing depth; S1 = 150 $\frac{\text{mg BOD}}{\text{L}}$; S_2 = site-specific value

Note: values for "k_1" for different industrial wastes are provided in Metcalf & Eddy (2003)

a biofilm has built up, treatment operations begin. When the media is above the water line, oxygen diffuses from the air into the biofilm. When the media is underwater, the bacteria in the biofilm oxidize the organics in the wastewater. The rotation provides some shearing force on the surface of the plastic media. The biofilm will increase over time until it becomes too thick to maintain, and the rotation force shears off some of it. The shorn pieces collect at the bottom of the tank and are periodically removed as waste activated sludge.

Design of rotating biological contactors for industrial wastewater treatment typically requires pilot-plant studies (Eckenfelder, 2000). For industrial wastewaters with relatively stable influent strengths, Eckenfelder (2000) suggests using the following design equation:

$$\frac{Q}{A}[S_0 - S] = kS \tag{13.2}$$

Where
Q = flowrate (m^3/s);
A = surface area available for biofilm attachment (m^2);
S_0 = influent substrate concentration (kg/m^3);
S = effluent substrate concentration (kg/m^3); and
k = reaction rate constant (s/m) that is waste-, microorganism-, and media-specific.

For industrial wastewaters with a highly variable influent strength, Eckenfelder (2000) suggests using the following design equation:

$$\frac{Q}{A}[S_0 - S] = K\frac{S}{S_0} \tag{13.3}$$

Where
Q = flowrate (m^3/s);
A = surface area available for biofilm attachment (m^2);
S_0 = influent substrate concentration (kg/m^3);
S = effluent substrate concentration (kg/m^3); and
K = modified reaction rate constant ($kg/s \cdot m^2$) that depends on waste-, microorganism-, and media characteristics.

The performance of "*n*" stages of RBCs in series can be described by an equation similar to the one developed for a series of aerated lagoons (Eckenfelder, 2000):

$$\frac{S}{S_0} = \frac{1}{\left\{1 + k\frac{A}{Q}\right\}^n} \tag{13.4}$$

For multiple-stage systems, the loading and oxygen requirements for each stage must be checked as well.

Submerged Media Attached-Growth Reactors. Submerged media attached-growth (SMAG) reactors (e.g., packed-bed reactors and fluidized-bed reactors) are becoming increasingly important in industrial wastewater treatment applications, partly because they can be adapted for various environmental and process conditions (aerobic, anoxic, or anaerobic) and partly because they may be designed as modular units. Fluidized beds have been used to treat wastes from chemical processors, refineries, petroleum bulk-storage terminals, and tank-bottom treatment facilities. They also have been used as a polishing step to further remove toxics and ammonia. Packed bed reactors have been used for treatment of high-strength wastewaters, including citrus waste and kraft mill effluent.

In fluidized-bed reactors, hydraulic head is used to suspend the media throughout the reactor (Table 13.8). In packed-bed reactors, the superficial velocities are relatively small and the media are not suspended. Expanded-bed reactors are a type of fluidized-bed reactor in which the media are not fully suspended to occupy the entire reactor depth.

The media are denser than the wastewater (Rittmann and McCarty, 2001). Table 13.9 lists examples of media used for packed and fluidized beds (Grady et al., 1999). Because the media are completely submerged, the specific surface area is significantly larger than that in RBCs or trickling filters (Grady et al., 1999; Rittmann and McCarty, 2001).

Mass transfer occurs between the wastewater and the biofilm, and organic wastes are oxidized in the biofilm. The biofilm thickness can be selected by using an appropriate fluid flow to adjust for shear. In general, expanded beds have thinner biofilms than packed ones, as well as higher waste velocities across the biofilm. Other factors (e.g., temperature, dissolved solids, and presence of toxic substances) also influence the biofilm's thickness and the microorganisms' activity in the biofilm.

The design of fixed-bed reactors may be summarized as follows (Grady et al., 1999):

- Characterize the waste, develop treatment goals, and resolve regulatory and permitting issues. (After this stage, design engineers would consult fixed-bed manufacturers to complete the reactor design using manufacturer-supplied data.)
- Select the media.
- Select the recycle rate, and calculate the total hydraulic loading rate.

TABLE 13.8 Submerged attached growth processes (Grady et al., 1999; Rittmann and McCarty, 2001).

Feature	Downflow packed bed (DFPB)	Upflow packed bed (UFPB)	Fluidized bed (FBBR)	Combined suspended and attached growth (CSAG)
Application	Industrial waste treatment; organics removal; nitrification; denitrification	Industrial waste treatment; organics removal; nitrification; denitrification	Aerobic treatment of low BOD wastewater; toxic organics; nitrification; denitrification	Combined organics/nitrogen/phosphorus removal; anaerobic treatment of industrial wastewater
Oxidation of organics	Efficient	Efficient	Efficient	Efficient
O_2 transfer	High	High	High	Not applicable
Denitrification	Possible	Possible	Possible	Possible
Filtration capability	Less efficient than UFPB	High	None	None
Separate solids-liquids separation process	Not needed	Not needed	Not needed	Required
Established process design basis	Well established	Well established	Well established	Not well established
Volumetric loading rate	Lower than FBBR	Lower than FBBR	High	Higher than other suspended growth systems but lower than packed and fluidized beds
Full-scale experience	High	High (but less than DFPB)	High	Limited
Other features	More complex backwash than UPFB	Less efficient mass transfer than FBBR	Poor removal of particulates	Efficient

Table 13.9 Design parameters for packed and fluidized bed reactors (Grady et al., 1999).

Process	Media	Size (mm)	Specific surface area (m^2/m^3)	Hydraulic loading rate Average (m/hr)	Hydraulic loading rate Peak (m/hr)	Porosity (%)
Packed bed downflow	Fired clay	2–6	1000–1500	2–3	5–6	40
Packed bed downflow	Rounded sand	2–3	1500	2–3	5–6	40
Packed bed upflow	Fired clay	2–6	1000–1500	2–3	5–6	40
Packed bed upflow	Polystyrene beads	2–3	1000–1100	2–3	5–6	40
Fluidized bed	Sand	0.3–0.7	2600–3900	0.4	0.6	60
Fluidized bed	Granular activated carbon	0.6–1.4	2300–3300	0.45	0.6	60

- Determine the reactor's height and cross-sectional area.
- Calculate the organic loading rate, oxygen requirement (if applicable), alkalinity and additional nutrient requirements, and sludge production rate.

The design of fluidized bed reactors may be summarized as follows (Grady et al., 1999; Rittmann and McCarty, 2001):

- Characterize the waste, develop treatment goals, and resolve regulatory and permitting issues. (After this stage, design engineers would consult fluidized-bed manufacturers to complete the reactor design using manufacturer-supplied data.)
- Select the degree and mode of fluidization.
- Select the bed's porosity (typically about 0.60) in consultation with the manufacturer or supplier. For example, the smallest porosity may be selected to prevent particles from agglomerating or having a collision frequency that causes excessive shear (Andrews, 1982).
- Select the media.
- Select the superficial velocity, calculate the biofilm thickness, and select the recirculation rate.
- Determine the reactor's height and cross-sectional area.
- Calculate the organic loading rate and hydraulic loading rate. Estimate requirements for oxygen (if applicable), as well as nutrient amendments and alkalinity.

Upflow Anaerobic Sludge Blanket Reactors. Upflow anaerobic sludge blanket (UASB) reactors have been used in a wide range of industrial waste treatment applications (Rittmann and McCarty, 2001). The UASB combines the features of the fluidized-bed reactor with a dispersed-growth reactor. Granulation of microorganisms in the reactor is a key feature of the UASB reactor. The wastewater is fed to the bottom of the reactor and flows upwards through the blanket of granules that are formed by microorganisms. The granules serve as a support media for additional biological growth. The rising gas bubbles, generated by rapid methanogenesis, fluidize the granules and result in efficient mass transfer (Rittmann and McCarty, 2001). Granules are a characteristic feature of UASBs. The granules are dense and settle quickly, eliminating the need for quiescent conditions (Speece, 1996). Upflow anaerobic sludge blanket reactors can operate under very high loading rates. Because UASB reactors with biomass retention and no biomass recycle are susceptible to biomass washout, an external solids capture system may be planned to avoid biomass washout if a process upset occurs.

Expanded granular sludge bed (EGSB) reactors consist of two or more UASB compartments set one on top of another. They have been reported to handle three to six times the organic loading of conventional UASB systems with comparable treatment efficiency (Vallinga et al., 1986).

The upflow anaerobic sludge blanket process and its uses in industrial waste treatment have become much better understood over the last decade. Table 13.10 and Table 13.11 present some typical loading rates and design parameters for UASBs operated under different conditions. A model exists to more completely characterize the granulation process (Sam-Soon et al., 1987). Speece (1996) provides a summary of some case studies on UASBs and other anaerobic systems, with data on loading rates and BOD removal efficiencies.

Anaerobic Treatment. Anaerobic treatment is particularly well-suited for high-strength industrial wastes. In this process, a consortium of microorganisms (Figure 13.6) breaks down complex wastes into volatile fatty acids, acetate, hydrogen, and methane. Other byproducts (e.g., hydrogen sulfide) may also be produced, depending on the wastewater's characteristics. Following are the major steps in anaerobic treatment:

- Particulate organics are solubilized into complex soluble organic molecules (often a rate-limiting step).
- Complex organics are converted into intermediate organic acids.

Table 13.10 Recommended COD loading for upflow anaerobic sludge blankets at 30° C to for 85 to 95% COD removal (Lettinga and Hulshoff Pol, 1991).

		Volumetric loading (kg COD/m^3·d*)		
Wastewater COD (mg/L)	**Fraction as particulate COD**	**Flocculent sludge**	**Granular sludge with TSS removal**	**Granular sludge with low TSS removal**
1000–2000	0.1–0.3	2–4	2–4	8–12
	0.3–0.6	2–4	2–4	8–14
	0.6–1.0	NA	NA	NA
2000–6000	0.1–0.3	3–5	3–5	1–28
	0.3–0.6	4–8	2–6	12–28
	0.6–1.0	4–8	2–6	NA
6000–9000	0.1–0.3	4–6	4–6	15–20
	0.3–0.6	5–7	3–7	15–24
	0.6–1.0	6–8	3–8	NA
9000–18 000	0.1–0.3	5–8	4–6	15–24
	0.3–0.6	NA	33–7	NA
	0.6–1.0	NA	3–7	NA

*kg COD/m^3·d × 62.480 = lb/d/1000 cu ft.

Table 13.11 Recommended volumetric organic loadings as a function of temperature for soluble COD substrates for 85 to 95% COD removal[1, 2] (adapted from Lettinga and Hulshoff Pol, 1991; Metcalf and Eddy, 2003).

	Volumetric loading			
	VFA wastewater		Non-VFA Wastewater	
Temperature (°C)	**Range (kg sCOD/m^3·d)**	**Typical (kg sCOD/m^3·d)**	**Range (kg sCOD/m^3·d)**	**Typical (kg sCOD/m^3·d)**
15	2–4	3	2–3	2
20	4–6	5	2–4	3
25	6–12	6	4–8	4
30	10–18	12	8–12	10
35	15–24	18	12–18	14
40	20–32	25	15–24	18

[1] kg/m^3·d × 62.480 = lb/d/1000 cu ft.

[2] Average sludge concentration is 25g/L.

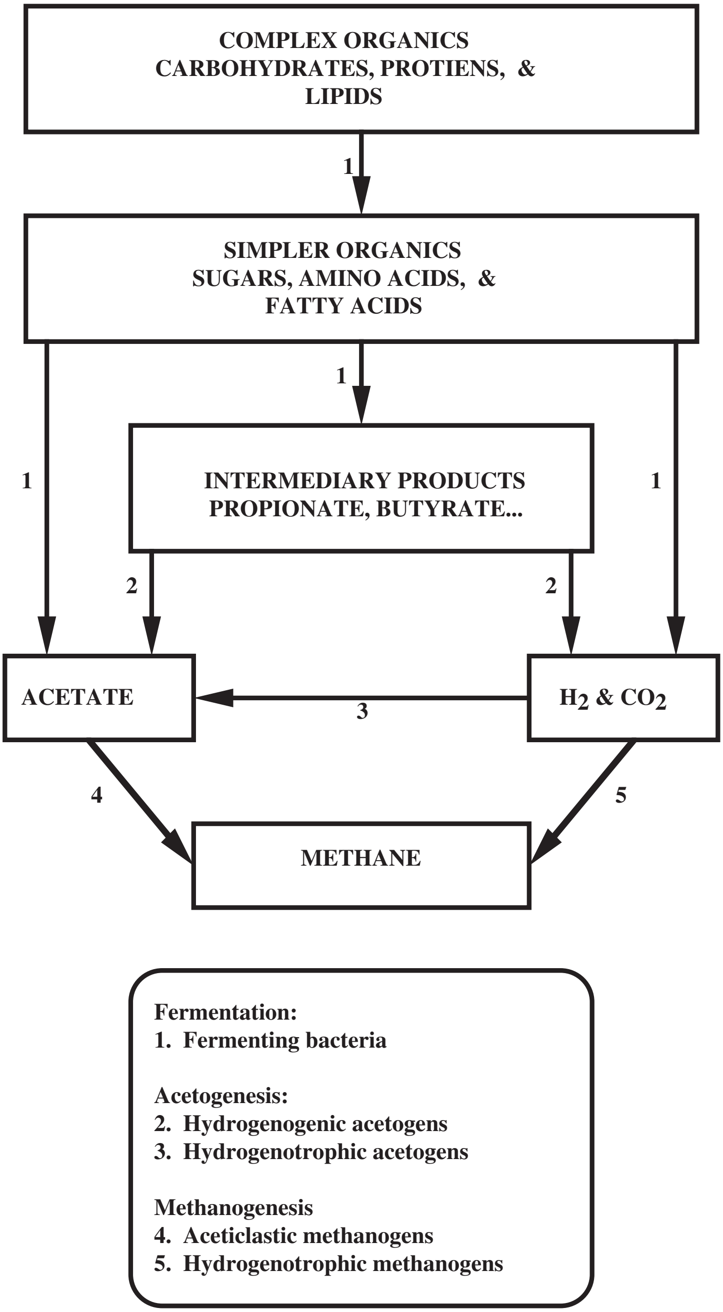


Figure 13.6 A flow diagram of methanogenesis in anaerobic processes (developed from Parkin and Owen, 1986).

- Intermediate organic acids are converted into acetate, hydrogen, and carbon dioxide. (The conversion of propionic acid to acetate and hydrogen is a significant step. If the microbial population is imbalanced, particularly for methanogens converting hydrogen to methane, this step may be inhibited. The result is an accumulation of propionic acid and eventually other volatile acids, leading to sour digesters or potential reactor failure.)
- Acetic acid (produced during steps 2 and 3) is converted to methane and carbon dioxide.
- Hydrogen is converted to methane (using carbon dioxide).
- Other gases (e.g., hydrogen sulfide) are produced from sulfate in the influent sludge (this happens throughout the treatment process).

Table 13.12 notes the parameters that should be monitored to ensure that an anaerobic reactor is functioning optimally. This list may be expanded to include any site- or process-specific parameters.

Anaerobic treatment systems have been used to treat sulfate-, sulfite- or sulfide-laden wastewaters (e.g., from the paper and pulp, fermentation, meat and poultry, edible oil, petrochemical, and mining industries). Generated or inherent sulfide can

TABLE 13.12 Selected process parameters to be monitored for anaerobic reactors.

Parameter	Preferred range or value
pH	6.5–8.5
Methane percent in the gas	>55%, preferably >65%
Alkalinity	2500 mg/L as $CaCO_3$
Mesophilic anaerobic treatment	30–40° C
Thermophilic anaerobic treatment	50–55° C
Extreme thermophilic anaerobic treatment	55–75° C
Volatile acids (particularly propionic acid)	Varies
Hydrogen in digester gas	<100 ppm (not critical but should be watched)
Micronutrients and trace nutrients	Iron, cobalt, and nickel should be added if not present in industrial wastestream.
Hydrogen sulfide and ammonia	Monitor if industrial waste contains significant sulfate or nitrogen.

be problematic. Hydrogen sulfide is odorous and toxic to humans. It can partition into the biogas and oxidize to sulfuric acid, which is corrosive. So, hydrogen sulfide must be monitored and removed. It also inhibits the activity of anaerobic bacteria, which can ultimately result in impaired performance and treatment system failure. In addition, sulfide production (the reduction of sulfate to sulfide) channels energy away from methane-producing bacteria to sulfate-reducing bacteria, thereby lowering methane yields. If the wastewater also is high in nitrogen (e.g., from feedlots and the meat and poultry industry), ammonia concentrations may need to be monitored (to protect both safety and treatment efficiency).

Table 13.13 provides the loadings and design rates for anaerobic processes to treat selected industrial wastewaters (Eckenfelder, 2000). (For a more complete listing, see Eckenfelder, 2000.) The design of anaerobic suspended-growth reactors may be summarized as follows:

- Characterize the waste and select treatment goal(s).
- Select an SRT to achieve the effluent-quality and COD-reduction goals

TABLE 13.13 Loading rates and design parameters for anaerobic reactors (Eckenfelder, 2000).

Wastewater	Loading ($kg/m^3 \cdot d$)	HRT (d)	Temperature (°C)	Removal (%)
Anaerobic contact process:				
Meat packing	3.2 (BOD)	12	30	95
Slaughterhouse	3.5 (BOD)	12.7	35	95.7
Upflow filter process:				
Pharmaceutical	0.56–3.5 (COD)	36–48	35	80–98
Rendering	2.0 (COD)	36	35	70
Landfill leachate	7.0 (COD)	—	25	89
Paper mill foul condensate	10–15 (COD)	24	35	77
Fluidized bed reactor process:				
Paper mill foul condensate	35–48 (COD)	8.4	35	88
UASB process:				
Sugar	22.5 (COD)	6	30	94
Brewery	95 (COD)	—	—	83
Paper mill foul condensate	4-5 (COD)	70	35	87
ADI–BFV process				
Cornstarch	0.45 (COD)	168	35	85
Dairy	0.32 (COD)	240	30	85

- Calculate the daily solids production and mass of solids in the system to maintain the desired SRT.
- Select the expected suspended solids concentration in the reactor, and determine the reactor volume.
- Determine nutrient needs—including trace nutrients needed to augment nutrient-deficient industrial wastewater—and calculate alkalinity requirements.
- Determine the gas-production rate, methane content, and wasted sludge.
- Check the volumetric organic loading rate.

The anaerobic digester's supernatant (effluent) can be a significant load if it is recycled to a primary or secondary treatment process.

NUTRIENT REMOVAL. The two major nutrients of concern are nitrogen and phosphorus. Nitrogen may be present as organic nitrogen (e.g., meat-packing wastes), ammonia (e.g., fertilizer wastes), or nitrate (e.g., surface runoff). Phosphorus may be present as organic phosphorus or orthophosphate.

Nitrogen Removal. Nitrogen can be removed via physical-chemical processes (e.g., breakpoint chlorination or air-stripping) or biological processes. Biological nitrogen removal is more commonly used in industrial waste treatment, particularly for high-strength wastes (e.g. meat-packing, poultry) because other methods may not be as cost-effective. If the wastewater contains organic nitrogen, deamination will be needed to convert it to ammonia. Then, ammonia is biologically nitrified in two steps:

Ammonium to nitrite (*Nitrosomonas*):

$$NH_4^+ + 1.5O_2 = NO_2^- + 2H^+ + H_2O \tag{13.5}$$

Nitrite to nitrate (*Nitrobacter*):

$$NO_2^- + 0.5O_2 = NO_3^- \tag{13.6}$$

The overall equation (ammonium to nitrate) is:

$$NH_4^+ + 2O_2 = NO_3^- + 2H^+ + H_2O \tag{13.7}$$

Nitrification is an autotrophic process in which energy for cell synthesis and metabolism is derived from an inorganic source (ammonium). Inorganic carbon is the carbon source. Nitrification also generates excess hydrogen ions, which destroy the wastewater's existing alkalinity. So, alkalinity must be added to keep the process operating and prevent the pH from declining. The exact alkalinity requirements may be calculated using stoichiometry and flowrates. About 7.14 mg/L of alkalinity (as $CaCO_3$) will be needed for each 1 mg/L of NH_3-N.

The conventional nitrification methods are single-stage nitrification (combined carbon-oxidation nitrification) and two-stage nitrification (in which BOD is removed in the first reactor and nitrifiers are active in the second). Some wastewater treatment plants use biofilm reactors or SBRs for nitrification.

In biological denitrification, nitrate is converted to nitrogen gas and then removed from the wastewater. Because denitrification follows nitrification, there may not be enough reducing equivalents (BOD) available, so an external source of energy is required. The denitrification rate depends mainly on the concentrations of biomass and electron donor in the system.

There are three commonly used denitrification methods: the single-sludge system (combined nitrification-denitrification); the multi-sludge system, and the four-stage Bardenpho process. Some use sludge as the source of both energy and carbon, while others use various combinations of aerobic and anoxic cells to nitrify and denitrify in one treatment process.

Phosphorus Removal. Phosphorus can be removed via precipitation with iron or aluminum salts or via biological processes. In aerobic-anaerobic activated sludge systems, inorganic phosphate is released under anaerobic conditions and taken up during aerobic conditions. Biological phosphorus removal systems (e.g., A/O process, the Phostrip process, and SBR) take advantage of this process.

Poly-P bacteria (e.g., *Acinetobacter, Pseudomonas, Aerobacter, Moraxella, Mycobacterium,* and *Beggiatoa*) can accumulate polyphosphate (volutin granules) in excess of normal requirements. Polyphosphate kinase catalyzes polyphosphate biosynthesis in the presence of magnesium ion by transferring a terminal phosphate group from ATP to the polyphosphate chain. Polyphosphate degradation is driven by several enzymes:

$$\text{polyphosphate}_n + \text{AMP} \xrightarrow[2\text{ADP} \rightarrow \text{ATP} + \text{AMP}]{\text{polyphosphate AMP phosphotranferase}} \text{polyphosphate}_{n-1} + \text{ADP} \qquad (13.8)$$

Several proprietary and nonproprietary processes [e.g., A^2/O, five-stage Bardenpho, University of Cape Town (UCT), Virginia Initiative Plant (VIP)] can remove both nitrogen and phosphorus. The design of nutrient removal systems typically begins with waste characterization and treatment goal selection. Then, engineers contact nutrient removal system manufacturers and use manufacturer-supplied design charts, procedures, and related equations to complete the design.

Phosphorus removal is not typically required in industrial wastewater treatment.

SECONDARY EMISSIONS. The Clean Air Act Amendments require industrial facilities to consider secondary emissions from both process and waste treatment operations. Such emissions may be determined via direct VOC measurement techniques, mathematical models, or emission factors.

Direct measurements can provide the most accurate data, but may be an expensive approach. To ensure that the samples help identify the worst-case scenario, the sampling protocol, frequency, and sample density per unit area of the property must be thoroughly accounted for.

Mathematical models, which are available from the U.S. EPA and software vendors, are less expensive then direct measurements. The Water 9, TOXCHEM+, and BASTE models are commonly used to estimate the emission rate of VOCs from POTWs. However, all of these models tend to overestimate emissions of certain compounds, particularly when the default, rather than site-specific, biodegradation constants are used for biological treatment units. A combination of sampling and mathematical modeling may be the most cost-effective approach.

The emission factor approach is another method to estimate VOC emissions from waste treatment facilities and may be traced back to the California Air Toxics 'Hot Spots' Information and Assessment Act of 1987 (AB 2588). The emission factor (EF) is the fraction of the total mass loading (ML) of the influent liquid stream, which is removed from the process through volatilization to the air (E) (i.e., EF = E/ML). The emission factors for different unit processes are developed based on actual field measurements. If the mass loading (ML) is known (based on flowrate Q and mass concentration C) and the emission factor (EF) is known and the area A of the emitting region is known, the emission rate (ER) in mass/time/area may be computed as ER = $(Q)(C)(\mathrm{EF})/A$.

CHEMICAL OXIDATION PROCESSES

Chemical oxidation processes remove organic contaminants by completely oxidizing them to carbon dioxide and water or transforming them into less objectionable intermediates or products (Table 13.14). These processes involve contacting wastewater with an oxidizing agent under predetermined conditions (e.g., pH and

TABLE 13.14 Oxidizing agents and their oxidation potentials.

Oxidation agent	Oxidation potential (V*)
Hydroxyl radical	2.80
Singlet oxygen	2.42
Ozone	2.07 (1.24)
Hydrogen peroxide	1.78
Permanganate	1.68 (0.60)
Chlorine dioxide	1.57 (1.15)
Hypochlorous acid	1.48 (0.41)
Chlorine	1.36

* Under acidic conditions; values in parentheses are the oxidation potential under alkaline conditions.

temperature) to effect a desired reaction. Sometimes catalysts are used to promote oxidation. The following is a typical oxidation reaction (in the presence of a ferrous iron catalyst and at pH 4):

$$C_6H_5OH + 14\ H_2O_2 \rightarrow 6\ CO_2 + 17\ H_2O \tag{13.9}$$

APPLICABILITY TO ORGANIC CONTAMINANTS. When selecting a chemical oxidation treatment process or oxidizing agent, design engineers should consider the following factors (Adams *et al.*, 1981):

- Economic feasibility (e.g., capital and operating costs);
- Reactions that will not produce an undesirable secondary pollutant (e.g., a compound that is more toxic than the one originally being treated);
- The oxidizing agent's treatment effectiveness;
- Integration of the oxidation process into an existing or proposed treatment system; and
- Site-specific constraints (e.g., space).

Chemical oxidation processes are used to control specific pollutants (e.g., phenolic compounds), but oxidation reactions are not specific; other wastewater constituents will be oxidized. For example, the stoichiometric requirement for hydrogen peroxide to oxidize monohydric phenol is 5.06 g of peroxide per gram of phenol (mole ratio of 14:1). When treating coke plant wastewater, however, 12 to 16 g of peroxide per gram of phenol was required for effective treatment (Wong-Chong and Dequittner, 1980).

Also, some organic compounds are more amenable to oxidation than others. Highly reactive compounds oxidize more readily than less reactive ones. Less reactive compounds may require larger doses of oxidant or longer reaction times. Highly reactive compounds include phenols, aldehydes, aromatic amines, and certain organic sulfur compounds (Weber, 1972). Moderately reactive compounds include alcohols, alkyl-substituted aromatics, nitro-substituted aromatics, and unsaturated alkyl groups, carbohydrates, aliphatic ketones, acids, esters, and amines. Less reactive compounds include halogenated hydrocarbons, saturated aliphatic compounds, and benzene.

Chemical oxidation is widely used as a pretreatment step before biological treatment or as a polishing step to ensure that the final effluent meets regulatory criteria. It is typically appropriate for concentrated wastestreams with relatively low flow; highly variable waste with moderate flow; wastewater that is corrosive or odorous; wastewater with highly reactive compounds; and wastewater with constituents that inhibit or upset biological treatment processes, making them more amenable to biological oxidation.

DESIGN CONSIDERATIONS. A chemical oxidation system typically consists of a contactor, which mixes the wastewater and oxidizing agent; storage and feed systems for the oxidant and catalyst (if required); pH-control facilities (if required); and other systems to control flow, chemical doses, and temperature.

Design engineers must understand the goal for chemical oxidation. If complete mineralization (oxidation to carbon dioxide, water, and a mineral salt) is the goal, the system must be designed to ensure that the contaminant is completely oxidized. If the goal is to reduce a contaminant's toxicity or break it down for further biological treatment, the oxidation byproducts must be understood because sometimes incomplete oxidation may produce a more toxic contaminant.

Engineers should also consider the hazardous nature of oxidants and the requirements for properly generating, storing, and handling the selected oxidant. Chemical oxidation is greatly affected by such conditions as wastewater pH, temperature, contaminant concentration, contact time, and the presence of other oxidant-consuming constituents such as other organics that increase the wastestream's total organic carbon (TOC) level and inorganic compounds in a reduced oxidation state. Oxidant-consuming constituents can impart a demand for the oxidant, thereby increasing the required oxidant dose (and related costs).

OXIDIZING AGENTS. Table 13.15 presents a list of oxidizing agents and their oxidation potentials measured in volts; the higher the oxidation potential, the greater the agent's reactivity and oxidation capacity. Commonly used oxidants include ozone, hydrogen peroxide, permanganate, chlorine dioxide, and chlorine. More recent developments in oxidation processes—called advanced oxidation processes (AOPs)—rely on ultraviolet (UV) light irradiation to generate the highly reactive hydroxyl radical from hydrogen peroxide and ozone. Interestingly, the chemical oxidation process involving Fenton's reagent is more than 100 years old, and it too relies on the formation of the hydroxyl radical for oxidation.

Hydrogen Peroxide/Fenton's Reagent. Because hydrogen peroxide (H_2O_2) is unstable and readily gives up its extra oxygen atom, it is an excellent oxidizing agent (Noyes, 1994). It has been used to oxidize amines, aldehydes, and cyanide without catalysts. When a catalyst is needed for more-difficult-to-oxidize compounds, ferrous iron (Fe^{+2}) is the one most commonly used.

The Fenton reaction is one of the oldest, most powerful oxidation treatments available (Fenton, 1894). Mixing hydrogen peroxide and ferrous sulfate ($FeSO_4$) or another ferrous salt at low pH results in the catalytic decomposition of hydrogen peroxide by ferrous ions to produce hydroxyl radicals:

$$H_2O_2 + Fe^{+2} \rightarrow Fe^{+3} + OH^- + OH^\bullet \qquad (13.10)$$

Because iron is an abundant, nontoxic element and hydrogen peroxide is easy to handle and has no detrimental effect on the environment, the process is cost-effective and environmentally friendly. Fenton's reagent has been used to oxidize many organic pollutants (e.g., dye-laden wastewaters and groundwater, pharmaceutical wastewater, trihalomethanes, aromatic amines, chlorinated aliphatic organics, chlorinated aromatics, landfill leachate, pesticides, phenolic wastes, and refractory organics). It has a relatively short reaction time and can degrade wastes with high COD concentrations (< 5000 mg/L). However, it requires a lot of hydrogen peroxide to achieve complete mineralization (Höfl et al., 1997).

Oxidation via hydrogen peroxide or Fenton's reagent can be an effective pretreatment step, producing byproducts that are more readily degradable or reducing the wastestream's toxicity to microorganisms in biological treatment processes (Miller et al., 1996).

Table 13.15 Summary of oxidization agents and processes and their typical applications.

Oxidation agent or process	Organic compounds	Advantages	Disadvantages
Hydrogen peroxide	Aldehydes, amines	Easy to transport, store, and apply. Proven effectiveness. Decomposes to oxygen.	Limited number of compounds without catalyst.
Fenton's reagent	Aldehydes, amines, dyes, hydroquinones, mercaptans, pesticides, phenols and phenolic compounds, polycyclic aromatic hydrocarbons (PAHs), surfactants	Forms hydroxyl radical and treats variety of organic compounds. Many commercial applications.	Reaction proceeds only at low pH. Heat generation can lead to volatilization of contaminants.
Chlorine	Not commonly used in industrial applications	None.	Forms chlorinated organic compounds.
Chlorine dioxide	Alcohols, aldehydes, amines, mercaptans, phenols and phenolic compounds	More effective oxidant than chlorine.	Must be made on site. Decomposes in sunlight.
Ozone	Color, dyes, phenols and phenolic compounds	Short contact time. Decomposes into oxygen. Proven ability to convert biorefractory organic materials to biodegradable materials.	Requires expensive equipment for onsite generation. High energy cost.
Permanganate	Alkenes, alcohols, aldehydes, chlorinated solvents, ketones, mercaptans	Easy to transport, store, and apply. Proven effectiveness.	Relatively long contact time required.

Oxidation agent or process	Organic compounds	Advantages	Disadvantages
UV oxidation	Chlorinated solvents, explosives (e.g., DNT and TNT), fuel hydrocarbons [benzene, toluene, ethylbenzene and xylene (BTEX)] and additives (MTBE), pesticides, phenols and phenolic compounds, polychlorinated biphenyls (PCBs), solvent stabilizers (1,1-dioxane)	Forms hydroxyl radical and treats variety of organic compounds.	Limited by UV transmittance of wastewater. Process equipment can be expensive and require large amount of space.
Sonication	Chlorinated solvents, pesticides, phenols and phenolic compounds	Forms hydroxyl radical and treats variety of organic compounds. Not limited by UV transmittance.	Limited commercial experience.
Wet air oxidation	Wastewaters with COD >10 000 mg/L. Chemical agents, munitions, pesticides, process liquor streams (petrochemical plants), spent caustic wastewater (ethylene plants and refineries), biological wastewater sludge	Broadly applicable to any oxidizable organic compound. Complete destruction of material. More commercial experience than SCWO.	High temperatures and pressures require special equipment, reactor materials, and safety precautions. High cost.
Supercritical water oxidation (SCWO)	Acrylonitrile, aromatic hydrocarbons, chemical agents, energetic materials (i.e., solid rocket propellants), explosives (e.g., DNT and TNT), halogenated aliphatics and aromatics, ketones, organic nitrogen compounds, pesticides, phenols and phenolic compounds, PCBs	Broadly applicable to any oxidizable organic compound. Complete destruction of material.	High temperatures and pressures require special equipment, reactor materials, and safety precautions. High cost.

Chlorine. Chlorine is typically used in industrial wastewater treatment to oxidize cyanide. This process, called *alkaline chlorination,* is common in the metal-plating and mining industries. (For more information on alkaline chlorination of cyanide, see Chapter 12.)

When chlorine reacts with organic compounds, however, many complex chlorinated compounds can be produced. So, chlorine oxidation of organic compounds is not common in wastewater treatment.

Chlorine is used in the form of free chlorine (chlorine gas) or hypochlorites (sodium and calcium hypochlorite). Whether chlorine or hypochlorite is used, there is an equilibrium between hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), and hydrogen ion (H+) ions. Hypochlorous acid is predominant at higher pH and a slightly stronger oxidizer than the hypochlorite ion. Chlorine tends to lower pH, while hypochlorites raise it.

Chlorine Dioxide. Unlike chlorine oxidation, the effectiveness of chlorine dioxide (ClO_2) oxidation does not depend on pH and the byproducts are typically of less concern to downstream processes or the environment. For example, when chlorine is used to oxidize phenols, the byproducts are highly odorous. However, when chlorine dioxide is used, the byproducts are odorless. Also, chlorine dioxide can oxidize alcohols, while chlorine cannot.

Chlorine dioxide is generated onsite by reacting sodium chlorite solution with chlorine gas or with sodium hypochlorite and hydrochloric acid (Noyes, 1994).

Ozone. Ozone (O_3) is a powerful oxidant that reacts rapidly with most organic compounds in wastewater. It is commonly used to oxidize phenols, cyanide, and organic compounds associated with color.

Ozone is produced by passing an oxygen gas stream through an ozone generator, which adds nearly 5000 V to a series of dielectrics to produce a corona discharge (Helmig et al., 2002). In this electric field, oxygen molecules are split into oxygen singlets that rapidly combine to produce ozone gas. The resulting gas stream contains between 3 and 10% ozone (by weight). The concentration depends on the power applied to the dielectrics and the gas flow into the generator. Varying the power and gas flow can control ozone-generation costs. At a given power setting, an increase in gas flow will decrease the ozone concentration but can increase the overall mass of ozone emitted (e.g., pounds per day). Because ozone is unstable, it must be generated onsite just before it is applied.

The solubility of 10% ozone (by weight) is only 31 mg/L at 1 atmosphere and 30° C, according to *Lange's Handbook of Chemistry* (McGraw-Hill, 1973). Ozone's water solubility is directly proportional to pressure; more ozone is present in a high-pressure stream. Therefore, ozone is typically injected into a pressurized wastestream or is introduced via diffusers at the bottom of a deep contact chamber (Weber, 1972).

Permanganate. Permanganate (MnO_4^-) compounds can be added to wastewater to oxidize both inorganic and organic pollutants. Commonly treated pollutants include cyanide, hydrogen sulfide, and phenols. Permanganate has also been used to oxidize iron, manganese, and compounds associated with taste and odor.

The most common form of permanganate is potassium permanganate. It is typically stored dry, in crystalline form. Potassium permanganate solutions range from pink to purple and are noncorrosive.

ADVANCED OXIDATION PROCESSES. Processes that generate highly reactive oxidants (e.g., the hydroxyl radical) are called *advanced oxidation processes* (AOPs). They emerged during the 1990s as viable alternatives for destroying or detoxifying aqueous and gaseous hazardous wastes, and for tertiary treatment of industrial effluents, sludge, and leachate (Bauman and Stenstrom, 1990; Ince et al., 1997; Ince, 1998; Kusakabe et al., 1991). Advanced oxidation processes are typically used to treat chlorinated solvents, pesticides, polychlorinated biphenyls (PCBs), phenolic compounds, fuel hydrocarbons [benzene, toluene, ethylbenzene, and xylene (BTEX)], and explosives (e.g., DNT and TNT).

Free radicals may be generated in various ways using processes catalyzed by strong oxidants, light, and photoreactive semiconductors, to more complex systems using sonochemical and electron-beam technologies. Some AOPs also support the degradation of organic contaminants to simpler oxidation byproducts by dissociating chemical bonds and rupturing aromatic rings. The major advantage of AOPs is that they do not form solids in any stage of the process. The major drawback is that many are expensive to operate because of energy and chemical requirements.

Advanced oxidation processes try to enhance oxidation kinetics by combining different oxidants, using ultraviolet radiation, or using a metal catalyst. Their enhanced reactivity results partly from the formation of the hydroxyl radical—a powerful, nonspecific oxidant. The rate constants for many organic compounds are high, implying half-lives on the order of minutes even when the $OH^\bullet$ concentration is small (Komisar et al., 1999).

Ultraviolet Light-Enhanced Oxidation. In ultraviolet light (UV)-enhanced oxidation, UV radiation—electromagnetic radiation with a wavelength between X-ray radiation and visible light—reacts with an oxidant (e.g., hydrogen peroxide or ozone) to create hydroxyl radicals, which oxidize organic contaminants. The two common UV enhanced oxidation processes—UV/peroxide and UV/ozone—are established treatment technologies that first found prominence in the groundwater treatment industry (DeMarco and Cordone, 2002). As with other oxidation processes, it can be designed to totally destroy the contaminants of concern. Under optimal conditions, the final products would be carbon dioxide, water, and mineral salts. Alternatively, the process can convert the contaminant into low-molecular-weight organic compounds that are biodegradable.

Ultraviolet radiation itself can break chemical bonds, thereby degrading organic contaminants (a separate process called *photolysis*). Photolysis products vary depending on the wastewater, but it typically cannot convert an organic contaminant to carbon dioxide and water. Photolysis is used for difficult-to-treat organic contaminants [e.g., N-nitrosodimethylamine (NDMA)]. Photolysis plays a part in UV-enhanced oxidation, but oxidation is the primary treatment mechanism.

The ultraviolet light dose is a control parameter in UV-enhanced oxidation. The maximum UV dose is based on the number of UV lamps in the reactor. Turning lamps off or on adjusts both the dose and power consumption. Water clarity affects the transmittance of UV energy, so the wastewater may need to be pretreated to remove particles or iron and manganese. Also, the lamps should be cleaned periodically (to remove metal precipitates, scaling, or biofouling) to ensure that the wastewater receives the full UV dose.

Sonication. In sonication, sound waves are imparted to a wastestream containing a dissolved gas. The sound waves cause acoustic cavitation—the formation of tiny gas bubbles. When they implode, the bubbles create localized high-temperature and -pressure regions, enabling radical species (e.g., the hydroxyl radical) and hydrogen peroxide to form (a process called *water sonolysis*). High ultrasound frequencies favor the production of hydroxyl radicals.

Sonication can treat reactive-dye bathwater to enhance the rate and extent of decolorization, so the water can be reused (Matthews and Pavlostathis, 2001). It also can be used to catalyze ozone oxidation (a process called *sonocatalytic ozonation*).

OTHER OXIDATION PROCESSES. Other oxidation processes that can pretreat organic constituents in industrial wastewater include wet air oxidation and supercritical water oxidation. These processes are called *thermal oxidation technologies.*

Wet Air Oxidation. Wet air oxidation is based on the principle that the oxidation rate increases at high temperatures and pressures because oxygen is more soluble under pressure. Wet air oxidation typically occurs at temperatures of 175 to 320° C and pressures of 2100 to 21 000 kPa (300 to 3000 psi). Air typically carries the oxygen into the reactor. The reaction temperature is moderated by the evaporation of water, which removes the heat generated during the oxidation process. If the waste's organic content is high enough (10 000 mg/L of COD), the process can sustain itself thermally (Lenntech, 1998 to 2004).

Wet air oxidation is used for wastes that are too toxic to treat biologically but too dilute to incinerate. It can treat pesticide wastes, petrochemical process wastes, wastewaters containing phenolic compounds, and organic chemical production wastewaters as well as chemical agents and munitions. This technology is typically limited to low-flow, high-strength hazardous wastewaters and solids because of its high costs.

Supercritical Water Oxidation. Supercritical water oxidation is basically a wet air oxidation process operated at higher temperatures (>374° C) and pressures [>22 000 kPa (218 atm)]. Under these high conditions, water is supercritical and organic compounds are almost completely soluble. Because both the organic contaminant and the oxidant (oxygen or air containing oxygen) are miscible, oxidation occurs under homogeneous conditions and higher destruction efficiencies are achieved.

Supercritical water oxidation is used for wastes that are too dilute to incinerate but contain enough organic content to sustain high temperatures. It can handle higher volumes of waste than wet air oxidation. The process completely and rapidly oxidizes organic constituents, but it is expensive because of the sophisticated equipment and corrosion-control materials required.

PHYSICAL TREATMENT PROCESSES

Air stripping, steam stripping, and adsorption are common methods for physically separating a solute from a solvent. Physical processes do not reduce the mass of a pollutant; they simply move it from one phase (gas, liquid, solid) to another. They should be followed by another process that actually captures or destroys the pollutant. An air stripper, for example, moves a pollutant from water to air, so the air should then be treated via pyrolysis, catalytic combustion, or activated carbon adsorption.

Physical processes distrubute a solute between two phases until an equilibrium is reached, at which point one phase will contain more of the solute than the other.

The processes are engineered to manipulate the phases so the solute will move to the desired phase at a reasonable rate. The solute's transfer rate is controlled by the resistance to mass transfer and the magnitude of the driving force.

AIR-WATER DISTRIBUTION. Henry's Law is a linear approximation of the equilibrium distribution of a solute between the vapor and solvent phases. Most volatile compounds at low concentrations in water (mole fractions >0.01) follow Henry's law.

Simplified discussions of Henry's constants are presented in many standard texts (e.g., Treybal, 1980; Corbitt, 1998). Thermodynamic derivations are presented in many other references (e.g., Mackay and Shiu, 1981; Yaws et al., 1991). The calculation of the air-water distribution coefficient depends on the solute's inherent tendancy to form a discrete solid, a discrete liquid, or to dissolve as a gas in the solvent, yielding at least four methods of calculating or measuring Henry's constants (Gossett, 1987). Each method has its own strengths and weaknesses, but the resulting constant for a given compound can vary by as much as 30%, so engineers should consult several references before beginning design.

There are several conventions for presenting volatility data on dilute solutions. These expressions are based on the vapor's partial pressure and the liquid concentration, which can be expressed in moles, moles per volume, or mass per volume:

$$p = H_{\mathrm{x}}x = H_{\mathrm{M}}C_{xM} = H_{\mathrm{m}}C_{xm} \tag{13.11}$$

Where

p = the vapor's partial pressure (atm),
$H_{\mathrm{X}}, H_{\mathrm{M}}, H_{\mathrm{m}}$ = Henry's constants,
x = mole fraction,
C_{xM} = moles per volume, and
C_{xm} = mass per volume.

Henry's constants are also presented in dimensionless formats (designated as $K_{\mathrm{subscript}}$). For example, K_{H}^* is the ratio of the mole fraction of solute in the vapor (y) to the mole fraction in the liquid (x). K_{H} is the ratio of the mass or moles of solute per unit volume of gas (C_{ym} or C_{yM}) to the mass or moles per unit volume of liquid (C_{xm} or C_{xM}). Many engineers favor the latter format for Henry's constant because it directly relates to volumes of liquid and gas. For a guide to unit conversions, see Sander (1999a, 1999b).

Yaws et al. (1991) compiled Henry's constants for 362 organic compounds in water at 25° C and 1 atmosphere total pressure (see Table 13.16 for a partial list). Meanwhile, Gossett (1987) compiled Henry's constants for chlorinated hydrocarbons, Burkhard et al. (1985) compiled them for polychlorinated byphenyls, and Corbitt (1998) and Mackay and Shiu (1981) compiled them for general thermodynamic reviews. A database of several thousand compounds from 950 references is available on the Internet (Sander, 1999b).

Henry's constants are temperature-dependent. Generally, a gas's partial pressure increases by a factor of 1.6 to 2 for every 10° C increase in water temperature. Many references (e.g., Corbitt, 1998; Gossett, 1987; Sander, 1999b) relate the temperature dependence using the van't Hoff analysis:

$$\frac{K_{H_1}}{K_{H_2}} = \exp\left(\frac{-\Delta H_{sol}}{R^*}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \tag{13.12}$$

Where

K_{H1} = Henry's constant at temperature T_1,
K_{H2} = Henry's constant at temperature T_2,
ΔH_{sol} = the heat of solution of the solute in the solvent (kcal/kmol),
R^* = the universal gas law constant (1.987 kcal/kmol − °K^{-1}), and
T_1, T_2 = temperature (°K).

For temperature dependency data for 900 compounds, see Sander (1999b).

Table 13.16 Henry's constants at 25° C and 1 atm (Yaws et al., 1991).

Compound	H_x (atm) or K_{H^*} (unitless) at 1 atm	HM (atm-m^3-mol^{-1})	K_H
Benzene	309	0.0056	0.228
Carbon tetrachloride	1634	0.0294	1.208
Chlorobenzene	252	0.00454	0.185
1,1-Dichloroethane	326	0.0059	0.241
1,1-Dichloroethene	1270	0.0229	0.937
Ethylene	35 390	0.638	26.1
Ethylbenzene	446	0.00804	0.34
Propane	38 030	0.685	28.0
Tetrachloroethene	1492	0.0269	1.10
Toluene	353	0.0064	0.260
Trichloroethene	648	0.0056	0.478

Table 13.17 Some liquid and gas diffusion coefficients (Makay et al., 1982; Munz and Roberts, 1983).

	Diffusion in water D_L (cm^2/s*)		Diffusion in air D_G (cm^2/s*)	
	20° C	25° C	20° C	25° C
Benzene	9.75×10^{-6}	10.90×10^{-6}	0.0797	0.0817
Toluene	8.45×10^{-6}	9.63×10^{-6}	0.0732	0.0751
Chlorobenzene	8.05×10^{-6}	9.69×10^{-6}	0.0705	0.0724
Carbon tetrachloride	8.22×10^{-6}	9.90×10^{-6}	0.0695	0.0713
1,2 Dichloropropane	8.09×10^{-6}	9.75×10^{-6}	0.0716	0.0734
Dichloromethane	10.8×10^{-6}		0.1011	
Trichloromethane	8.65×10^{-6}		0.0944	

* To convert to m^2/s, multiply values by 10^{-4}.

DIFFUSION COEFFICIENTS. Liquid- and gas-phase diffusion coefficients (D_L and D_G) are used in various estimates of mass-transfer resistance. Some estimates for some common organic chemicals at 20 and 25° C are reproduced in Table 13.17. (For more diffusion coefficients, see Mackay et al., 1982, and Munz and Roberts, 1983.)

LIQUID TO GAS SYSTEMS. Three common methods for removing a volatile solute from a wastestream are countercurrent packed towers, subsurface aeration, and mechanical agitation. Subsurface aeration and mechanical agitation are also used to aerate activated sludge tanks. Steam stripping is also popular, especially if low-quality steam is available.

Stripping Towers. Air stripping applications are typically designed using a countercurrent packed tower or tray tower. The liquid is added to the top of the tower, and the gas is added to the bottom. Air stripping has been used to remove a variety of gasoline components, chlorinated solvents (e.g., TCE and PCE), and ammonia from polluted groundwater (Byers and Morton, 1985; Gross and TerMaath, 1985). For environmental projects, the inlet gas is virtually pure air and the liquid is considered a dilute solution. This allows for several simplifying assumptions (Treybal, 1980). Engineers need the following information to begin the design:

- Henry's constant at the design temperature,
- The solute's diffusion constant in water at the design temperature,

- Influent and effluent solute criteria,
- The mass flow water (solvent) to be treated, and
- The packing parameters (e.g., surface area per volume, pressure drop coefficients, and flooding limits).

They then calculate the following information:

- The mass airflow rate required to meet the liquid effluent criteria,
- The number of theoretical transfer units required to achieve the liquid effluent criteria,
- The tower's height and diameter,
- The gas and liquid mass-transfer coefficients,
- The effective wetted surface area per unit volume of packing, and
- The height of a theoretical transfer unit.

Stripper towers are designed by estimating the number of theoretical stages (N_{OL}) and the height of a theoretical stage (H_{OL}). A *stage* is a contact between two phases that promotes mass transfer. A theoretical stage is one with enough contact time for equilibrium to be reached. The number of theoretical stages required is based on the desired treatment efficiency, the Henry's constant, the liquid flow rate, and the gas flow rate. The height of a theoretical stage is calculated from the gas and liquid mass transfer rates, the liquid flow, and the available area. The overall height of the tower is calculated as follows:

$$Z = N_{OL} H_{OL} \tag{13.13}$$

Where

Z = the overall height of the tower,
N_{OL} = the number of theoretical stages, and
H_{OL} = the height of a theoretical stage.

The number of theoretical stages is based on estimates of the liquid and gas flow rates. The molar balance around a countercurrent stripper tower is shown in Figure 13.7. The molar flowrate of the water phase is L (mol/s) and the molar airflow is G (mol/s). The mole fraction of solute in the water phase is x, and the mole fraction of the solute in

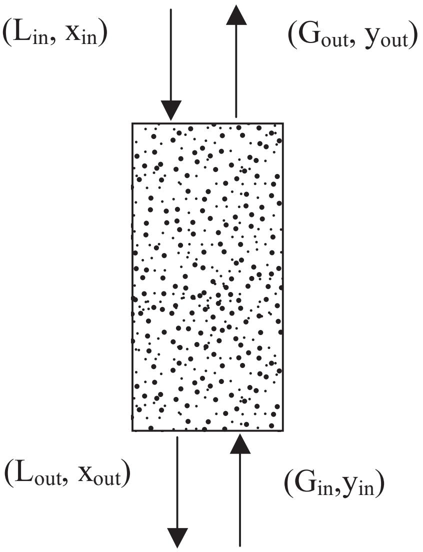


FIGURE 13.7 An illustration of the molar balance across a counter-current air stripper, without reaction.

the air phase is y. If the mole fractions of the solute are small compared to the total molar flows of water and air, then:

$$L_{\text{in}} \cong L_{\text{out}} \tag{13.14}$$

and

$$G_{\text{in}} \cong G_{\text{out}} \tag{13.15}$$

The molar mass balance is

$$\left(x_{in} - x_{out}\right)L = \left(y_{out} - y_{in}\right)G \tag{13.16}$$

The inlet air is assumed free of pollutant ($y_{\text{in}} = 0$).

The minimum theoretical gasflow per unit liquid flow is calculated as follows:

$$\left(\frac{G}{L}\right)_{minimum} = \frac{(x_{in} - x_{out})}{K_{H^*}X_{in}} \tag{13.17}$$

This represents the condition where there is no driving force between phases, so an infinitely tall column is required. As more gas is used per unit of liquid, fewer theoretical stages are required. The economic tradeoff is between the cost of providing (and treating) the stripping gas and the cost of a larger tower. Starting points for design assume gasflows 50 to 100% above the theoretical minimum.

The ratio of Henry's constant (K_{H^*}) to the operating conditions (L/G) is called the *stripping factor* (S):

$$S = K_{H^*}\frac{G}{L} = K_H\frac{G'}{L'} \tag{13.18}$$

Where

G' = gas flow (m^3/s), and
L' = liquid flow (m^3/s).

All calculations can be made in terms of mass per unit volume by replacing K_{H^*} with K_H. The volumetric ratio of gas flow to liquid flow (G'/L') is equal to 1245 × (G/L) at standard conditions.

The number of theoretical stages required is the ratio between the total desired transfer and the logarithmic mean of the driving force across the entire column. The driving force for mass transfer is the difference between the concentrations of solute in the two phases and the equilibrium concentrations in the phases at any point in the column. Treybal (1980) gives the number of plates of a stripping tower for dilute solutions:

$$N_{OL} = \frac{1\text{n}\left(\left(\frac{x_{in} - x^*}{x_{out} - x^*}\right)\left(1 - \frac{1}{S}\right) + \frac{1}{S}\right)}{1 - \frac{1}{S}} \tag{13.19}$$

Where

x has units of mole fraction, and
x^* = the theoretical mole fraction of the solute that is in equilibrium with the inlet air ($x^* = y_{in}/K_{H^*}$; in fresh air, $x^* = 0$).

Figure 13.8 is a graphical solution of eq 13.19. To use this graph, obtain an estimate of the Henry's constant for the solute and find the appropriate diagonal line. Use K_{H^*} if molar flows (G/L) are used, or K_H if volumetric flows (G'/L') are used. Select a value of

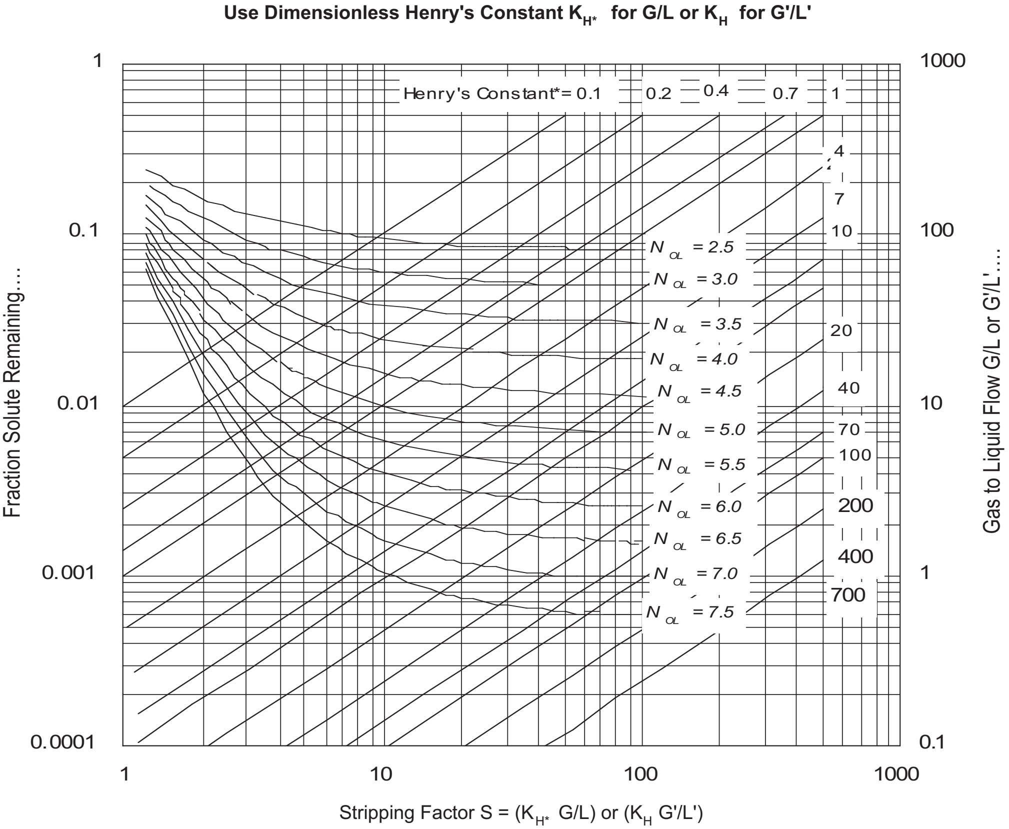


FIGURE 13.8 Graphic solution for stripper column: use dimensionless Henry's constant K_H* for G/L or K_H for G'/L'.

G/L that is between 50 and 100% above the minimum (eq 13.17). The intersection of the G/L operator (right vertical axis) and the Henry's constant diagonal gives the stripping factor (S) along the x axis. Moving vertically up and down along a constant stripping factor implies a constant value for G/L (or G'/L'). Determine the fraction of solute remaining after stripping, and find this on the left vertical axis. The point of intersection of the stripping factor vertical and the fraction remaining will fall on a curve representing the number of transfer units required (N_{OL}).

The height of a theoretical transfer unit is calculated as follows:

$$H_{\mathrm{OL}} \cong \frac{L/A}{K_{\mathrm{OL}} a_{\mathrm{W}} M_{\rho\mathrm{W}}} \cong \frac{L'/A}{K_{\mathrm{OL}} a_{\mathrm{W}}} \tag{13.20}$$

Where

H_{OL} = the height of a theoretical transfer unit (m);
L = the molar flow (mol/s);
A = the cross-sectional area of the tower (m^2);
K_{OL} = the overall liquid transfer (m/s);
a_{w} = the wetted area per unit volume of packing (m^2/m^3);
$M_{\rho\mathrm{w}}$ = the molar density of the solvent (mol/m^3); and
L' = the volumetric flowrate (m^3/s).

Experimental data for H_{OL} provide a direct means of estimating the tower's design height. Mcabe et al. (1985) correlated H_{OL} for water and oxygen at 25° C. Raschig rings (13 to 50 mm [0.5 to 2 in.]) were tested with gas flows of 0.11 to 0.26 m/s (100 to 230 lb/hr/sq ft) and water flows of 0.0065 to 0.026 m/s (500 to 20 000 lb/hr/sq ft). At 0.013 m/s (1000 lb/hr/sq ft), the values of H_{OL} for 25- to 50-mm (1- to 2-in.) rings ranged from 0.21 to 0.3 m (0.7 to 1.0 ft). At 0.13 m/s (10 000 lb/hr/sq ft), the values of H_{OL} ranged from 0.3 to 0.5 m (1.2 to 1.7 ft). H_{OL} for the 13-mm (0.5-in.) rings was 0.6 ft at 0.013 m/s (1000 lb/hr/sq ft) and 0.5 m (1.7 ft) at 0.13 m/s (10 000 lb/hr/sq ft).

Kittikul et al. (1990) investigated the effects of water temperature, air temperature, column depth, and gas-to-liquid flow ratios on the stripping efficiency of 15 organic compounds using a laboratory scale column. Water temperature was controlled at 15, 35, and 55° C. Gas flows were constant (960 $m^3/m^2 \cdot h$) at approximately 50% of the published flooding rate for the ceramic Intalox (3/8-in., 0.0095 m) saddles (similar to many generic saddles) used as the packing material. Gas to liquid flows (G'/L') were tested at ratios of 30, 90, and 150 (L' = 32, 10.7, and 6.4 $m^3/m^2 \cdot h$). These data were recalculated for Table 13.18 to present the results in terms of the overall height of a theoretical stage. The N_{OL} values were calculated from the solute removal data and the stripping factor (eq 13.19). Values for H_{OL} range from 0.29 to 1.46 m for the test conditions presented.

If literature values of H_{OL} are not found for the target solute, then correlations can be used to develop the value from transfer coefficients. The transfer coefficient

Table 13.18 Calculated N_{OL} and H_{OL} (data from Kittikul et al., 1990; reference K_H from Kittikul et al., 1990; H_{sol}/R^* from Sander, 1999).

	Temp. (°C)	k_H	G'/L'	S	Percent removal	N_{OL}	H_{OL} (m)
Ethylbenzene	15	0.21	30	6.2	96.6	3.8	0.31
K_H ref = 0.27 @ 20 °C	35	0.56	30	16.8	96.6	3.5	0.34
$\Delta H_{sol}/R^* = 4400$	15	0.21	90	18.7	94.0	2.9	0.41
	35	0.56	90	50.5	98.3	4.1	0.29
Chlorobenzene	15	0.11	30	3.2	93.5	3.5	0.34
K_H ref = 0.19 @ 30 °C	35	0.23	30	6.8	95.8	3.5	0.34
$2\Delta H_{sol}/R^* = 3400$	15	0.11	90	9.5	95.0	3.2	0.37
	35	0.23	90	20.5	99.2	5.0	0.24
Fluorine	15	0.047	30	1.42	56.8	1.1	1.08
K_H ref = 0.056 @ 20 °C	35	0.093	30	2.79	52.0	0.8	1.46
$\Delta H_{sol}/R^* = 3000$	15	0.047	90	4.25	56.4	0.9	1.33
	35	0.093	90	8.36	59.1	0.9	1.29
Tetrachloroethane	15	0.015	30	0.46	40.0	1.3	0.91
K_H ref = 0.02 @ 20 °C	35	0.043	30	1.29	74.8	2.3	0.53
$\Delta H_{sol}/R^* = 4600$	15	0.015	90	1.37	54.8	1.0	1.14
	35	0.043	90	3.87	94.0	3.4	0.35

[K_{OL} (s^{-1})] is the overall liquid side transfer coefficient representing the series resistance across the liquid and gas boundries (eq 13.21). If the Henry's constant (K_H) is more than approximately 0.25, then the resistance to mass transfer is dominated by k_{OL}, and k_G may be ignored (MacKay et al., 1979).

$$\frac{1}{K_{OL}} = \frac{1}{k_L} + \frac{1}{K_H k_G} \tag{13.21}$$

For water and oxygen studies, the ratio k_G/k_L has been found to be between 139 and 224 in wind tunnel tests (Liss, 1973), about 150 for the air-sea interface (Liss and Slater, 1974), or higher for some liquid contacting equipment (Munz and Roberts, 1983). Little error is generated by using an estimate of $k_G/k_L = 150$ for compounds with a Henry's constant (K_H) greater than approximately 0.1.

Experimentally determined values for k_L (or $k_L a_w$) for specific compounds on specific media are presented in various references [e.g., trichloroethylene on 16 mm Pall Rings (generically like perforated cylinders) (Gross and TerMaath, 1985) and chlorobenzene, napthalene, and 2,6-dinitrotoluene on 3/8-in. ceramic saddles (Kittikul et al., 1990)]. Tablulated values of $k_g a_w$ for several compounds with low volatility are presented in Eckert (1975). Graphic represetations for $k_g a_w$ and H_{OG} for the water system are developed in Yoshida (1955).

Estimates of the oxygen and water transfer coefficients (k_L and k_G, respectively) can be derived from the gas flow, liquid flow, and packing material data. The information should be available from the media manufacturer or through correlations in the literature. One of the best known correlations was developed by Onda for water vapor and oxygen (Onda et al., 1968; Perry, 1975). The Onda correlations are typically regarded as being valid within ± 20 to 30% of measured values. These correlations have been used to succesfully predict TCE removal from spiked groundwater (Gross and TerMaath, 1985). Some values of k_G (water vapor) and k_L (oxygen) were calculated for some common packing materials (Table 13.19). In these calculations, k_G is a function of gas loading (G'/A), while k_L is a function of liquid loading (L'/A). (Further discussion of the Onda correlations is beyond the scope of this chapter.)

The transfer coefficients for the solute must be estimated from the correlations for oxygen and water. If the value of k_G for water is available, a gas side transfer coefficient for the compound of interest can be estimated as follows:

$$\Psi_G = \frac{k_G}{k_{G-water}} \approx \left(\frac{D_G}{D_{water}} \right)^{1/2} \tag{13.22}$$

Liquid side transfer rates can be estimated from oxygen data. The reference oxygen diffusion coefficient (D_L) equals 2.4×10^{-5} cm^2/s at 20° C. To convert k_L from the oxygen reference to a value for the target solute, use the following ratio:

$$\Psi_L = \frac{k_L}{k_{L-oxygen}} = \left(\frac{D_L}{D_{L-oxygen}} \right)^{1/2} \tag{13.23}$$

Many of the compounds of interest (Table 13.20) in environmental work have liquid diffusion coefficients in water between 0.8 and 1.2×10^{-5} cm^2/s, so the correction factor (Ψ_L) typically will be between 0.6 and 0.7.

Onda also correlated the ratio of the wetted surface area [a_w (m^{-1})] to the specific surface area [a_v (m^{-1})] of the packing materials (Onda et al., 1968; Haas and Vamos, 1995; Roberts et al, 1984). Table 13.19 shows some examples of the wetted surface ratio (a_w/a_v) for selected packing materials. Data for the specific area (a_v) were reproduced from Treybal (1980).

Table 13.19 Physical constants for some example column packing materials.

Packing type and specific surface area[c]	Specific for liquid loading[a] (L'/A)			Specific for gas loading[a] (G'/A)		L'/A and G'/A that Yield P[b]			
						P = 0.1		P = 0.2	
	L'/A	k_L	a_w/a_v	G'/A	k_G	L'/A	G'/A	L'/A	G'/A
Berl saddle	0.004	0.00011	0.45	0.8	0.044	0.004	1.4	0.004	1.9
0.75 in.	0.008	0.00015	0.55	1.2	0.059	0.008	1.2	0.008	1.7
ceramic	0.012	0.00018	0.61	1.6	0.072	0.012	1.0	0.012	1.4
a_v = 269	0.016	0.00021	0.65	1.9	0.081	0.016	0.8	0.016	1.2
Berl saddle	0.004	0.00012	0.45	1.0	0.033	0.004	1.7	0.004	2.4
1 in.	0.008	0.00017	0.55	1.4	0.044	0.008	1.4	0.008	2.0
ceramic	0.012	0.00021	0.61	1.9	0.052	0.012	1.2	0.012	1.7
a_v = 249	0.016	0.00024	0.65	2.4	0.061	0.016	1.0	0.016	1.5
Berl saddle	0.004	0.00015	0.53	1.7	0.054	0.004	2.5	0.004	3.5
1.5 in.	0.008	0.00021	0.63	2.3	0.067	0.008	2.2	0.008	3.0
ceramic	0.012	0.00026	0.69	2.9	0.079	0.012	1.9	0.012	2.7
a_v = 144	0.016	0.00030	0.73	3.5	0.090	0.016	1.7	0.016	2.4
Intalox saddle	0.004	0.00014	0.38	1.2	0.052	0.004	1.9	0.004	2.7
1 in.	0.008	0.00020	0.47	1.7	0.066	0.008	1.7	0.008	2.3
plastic	0.012	0.00024	0.53	2.3	0.082	0.012	1.4	0.012	2.0
a_v = 207	0.016	0.00028	0.57	2.7	0.091	0.016	1.2	0.016	1.7
Raschig ring	0.004	0.00010	0.46	0.5	0.040	0.004	1.1	0.004	1.5
0.75 in.	0.008	0.00014	0.56	0.8	0.055	0.008	0.8	0.008	1.2
metal	0.012	0.00017	0.62	1.2	0.073	0.012	0.7	0.012	0.9
a_v = 236	0.016	0.00020	0.66	1.5	0.086	0.016	0.5	0.016	0.7
Raschig ring	0.004	0.00011	0.55	0.5	0.033	0.004	1.2	0.004	1.6
1 in.	0.008	0.00016	0.65	0.9	0.051	0.008	0.9	0.008	1.2
metal	0.012	0.00020	0.71	1.2	0.062	0.012	0.7	0.012	1.0
a_v = 187	0.016	0.00023	0.75	1.6	0.076	0.016	0.5	0.016	0.8
Raschig ring	0.004	0.00014	0.59	1.0	0.041	0.004	1.8	0.004	2.6
1.5 in.	0.008	0.00020	0.69	1.5	0.056	0.008	1.5	0.008	2.1
metal	0.012	0.00025	0.75	2.1	0.070	0.012	1.2	0.012	1.7
a_v = 135	0.016	0.00029	0.79	2.6	0.081	0.016	1.0	0.016	1.4
Raschig ring	0.004	0.00016	0.63	1.2	0.045	0.004	2.0	0.004	2.8
2 in.	0.008	0.00023	0.73	1.7	0.058	0.008	1.7	0.008	2.4
metal	0.012	0.00029	0.78	2.2	0.070	0.012	1.5	0.012	2.0
a_v = 103	0.016	0.00034	0.82	2.8	0.082	0.016	1.2	0.016	1.7

L'/A = water flow (m/s).
G'/A = airflow (m/s).
P = pressure drop ($\mathrm{m_{water}/m_{column\ height}}$).
k_L = liquid side transfer coefficient for oxygen (m/s).
k_G = gas side transfer coefficient for water (m/s).
a_w/a_v = ratio of wetted surface area to specific surface area (dimensionless).
a_v = specific surface area (m2/m3).

[a] Calculated using Onda correlations in Perry (1984).

[b] Calculated using the Leva pressure drop correlation (Leva, 1954).

[c] Specific surface areas are from Treybal (1980).

TABLE 13.20 Some experimentally derived values for Ψ.

Compound	$\Psi = k_La/k_La_{O2}$	Reference
Benzene	0.53	Matter-Müller, et al. (1981)
Bromodichloromethane	0.55	Kaczmer et al. (1984)
Carbon tetrachloride	0.63 ± 0.03	Roberts and Dändliker (1983)
Dibromochloromethane	0.41	Kaczmer et al. (1984)
1,4-Dichlorobenzene	0.31-0.47	Matter-Müller, et al. (1981)
Dichlorodifluoromethane	0.67 ± 0.08	Roberts and Dändliker (1983)
1,1-Dichloroethane	0.71	Smith and Bomberger (1980)
1,1-Dichloroethene	0.61–0.63	Matter-Müller, et al. (1981)
Ethylene	0.89	Rathbun et al (1975)
Propane	0.72	Rathbun et al (1975)
Tetrachloroethene	0.63 ± 0.03	
	0.56 ± 0.04	Roberts and Dändliker (1983)
Matter-Müller, et al. (1981)		
Toluene	0.51–0.54	Matter-Müller, et al. (1981)
Tribromomethane	0.30	Kaczmer, et al. (1984)
Trichloroethene	0.63 ± 0.03	Roberts and Dändliker (1983)
Trichloromethane	0.66	
	0.63 ± 0.01	Smith and Bomberger (1980)
Kaczmer, et al. (1984)		
1,2,4-Trimethylbenzene	0.34–0.44	Matter-Müller, et al. (1981)

The final calculation to be made for the packing material is the unit air pressure drop at design loading rates. Pressure-drop correlations are available from a number of sources (e.g., Perry, 1984; Eckert, 1975; McCabe et al., 1985; Treybal, 1980); they are typically presented as the Sherwood graphical correlations. Other discussions of pressure drop are based on the Leva correlations for flow conditions below flooding (e.g., Perry, 1984; Haas and Vamos, 1995). Leva (1954) correlated available headloss data for several common packing materials using a modified orifice equation. (The original Leva article contains the most consistent presentation of the material. Details of the Leva correlation are beyond the scope of this chapter, but the data used include nominal diameters, Leva coefficients, packed surface area, and material surface tensions collected from a number of sources.)

Flooding occurs when too much water is loaded on the column for the airflow used. One common design point is based on developing gas and liquid flows that represent the pressure drop at half the flooding point. Treybal (1980) and Eckert (1975) summarize flooding conditions for several common media. In general, most media are overloaded when the pressure drop exceeds 0.2 m of water pressure per meter of column depth. Table 13.19 shows the gas flow (G'/A) and liquid flow (L'/A) that produce one-half flooding (P = 0.1 m/m) and near flooding conditions (P = 0.2 m/m) based on the Leva correlation (Leva, 1954).

Stripping with Conventional Aeration Equipment. Volatile organic compounds can also be removed from water via subsurface aeration or surface agitation. The principles of these forms of air stripping have design components similar to the aeration of activated sludge, and a large body of literature is dedicated to understanding that process (e.g., Roberts et al., 1984; Truong and Blackburn, 1984; Thibodeaux et al., 1984; Matter-Müller et al., 1981; Lurker et al., 1982; Schröder, 1987; Blackburn, 1987; and Namkung and Rittmann, 1987). In the activated sludge process, the removal of volatile organic compounds is presumed to be influenced by stripping, solids adsorption, and metabolism. A common assumption is that an aerated tank behaves as if it is completely mixed and at steady state. The mass balance is:

$$V_L \frac{dC_{xm}}{dt} = L'\left(C_{xi} - C_{xe}\right) - V_L K_{OL} a\left(C_{xe} - C^*_{xm}\right) - V_L\left(R_{bio} + R_{sorp}\right) = 0 \tag{13.24}$$

Where

V_L = tank volume (m^3);
L' = water flow (m^3/s);
C_{xi} = the influent concentration of the target compound (kg/m^3);
C_{xe} = the effluent concentration of the target compound (kg/m^3);
$K_{OL}a$ = the overall liquid side mass transfer coefficient for the solute (s^{-1});
C^* = the hyopothetical concentration of the target organic compound in the water phase at equilibrium with the contacting air (for surface aerators, the contacting air is assumed to have no organic concentration, so $C^* = 0$);
R_{bio} = the biological removal rate (a function of C_e and the biomass concentration); and
R_{sorp} = the sorption removal rate (a function of C_e, mixed-liquor biomass concentration, and the biomass waste rate).

The general relationship for surface aeration of a completely mixed, flow-through tank at steady-state (e.g., an equalization basin), where bioreaction and sorption are neglected, is:

$$\frac{C_{xe}}{C_{xi}} = \left(1 + \frac{V_L K_{OL} a}{L'}\right)^{-1} \tag{13.25}$$

If subsurface aeration is used, volatile organic carbon can saturate the air bubbles, impeding mass transfer from the bulk liquid. For example, bubbles used to strip benzene can be up to 26% saturated by the time the gas exits the tank (Mackay et al., 1979). The derivation for the correction for bubble saturation is presented in Matter-Müller et al. (1981). The fraction of gas saturation as it exits from the tank is:

$$\Omega = \frac{C^*_{xm}}{C_{xe}} = 1 - \exp\left(-\frac{K_{OL} a V_L}{K_H G'} \frac{t}{\tau}\right) \tag{13.26}$$

The fraction of volatile organic carbon remaining in a completely mixed, subsurface aeration tank at steady-state (assuming that stripping is the only removal mechanism) is:

$$\left(\frac{C_{xe}}{C_{xi}}\right) = \left(1 + \frac{V_L K_{OL} a}{L'}(1 - \Omega)\right)^{-1} \tag{13.27}$$

To estimate the stripping that occurs because of subsurface aeration, the transfer coefficient must be converted to one appropriate for the solute. Two-film resistance theory states that the overall transfer coefficient (K_{OL}) is a function of the liquid side transfer coefficient (k_L) and the gas side transfer coefficient (k_g) (see eq 13.21). For compounds with high Henry's constants, the transfer resistance lies mainly on the liquid side, and the overall transfer coefficient can be estimated as a proportion of the overall oxygen transfer coefficient.

There are numerous correlations available for estimating the solute's and oxygen's transfer coefficients. Rough estimates for the proportionality coefficient (Ψ_L) cover a wide range. Diffusion theory gives that the exponent n is unity (Bennet and Meyers, 1974:, Matter-Müller et al., 1981). This condition is typically met for long bubble contact and slow surface renewal. Others propose that the power function should be $n = ½$, as in the Higbe penetration theory and discussions by Danckwerts (Bennet and Myers, 1974). This correlation is typically more suited for high surface turnover rates at the liquid film (as occur in surface aerators).

Roberts and Dändliker (1983) measured a power function of $n = 0.66$ for tests performed with a lab-scale surface aerator. A similar relation using a power function of $n = 2/3$ was used by Thibodeaux et al. (1984) to describe the relation of organic diffusion to water-vapor diffusion on surface impoundments. Several authors published values of Ψ_L from experimental results (Table 13.20).

Little work has been done on the correlation of gas side transfer (k_G) in surface and subsurface aeration systems, mainly because the volatile compounds of interest are overwhelmingly influenced by liquid-phase resistance. The work of Liss (Liss, 1973; Liss and Slatter, 1974) is often taken as a starting point for estimating the relative ratio of kL to k_G in waterbodies, where the ratio $k_{G\text{-}water}/k_{L\text{-}oxygen}$ is about 150. Presumably, some correlation similar to eq 13.22 could be used to estimate k_G for compounds other than water. Dilling (1977) published k_L data and estimates of the fraction resistance in the liquid phase for 25 chlorohydrocarbons from laboratory tests with stirred vessels. These data may be used to estimate k_g for these compounds under these test conditions.

Steam Stripping, Steam Distillation. Steam stripping and steam distillation rely on differences in two liquids' partial pressures to separate them. When a mixture of two components is partially vaporized, heat or vacuum can be used to enrich the gas phase of the more volatile component (A), while the liquid phase of the less volatile component (B) is enriched. The typical chemical engineering application is for the separation liquids where both components A and B are in high concentrations (mole fraction A > 0.1). The liquid is contacted in vertical tray towers or countercurrent packed bed towers. Environmental applications are a modification of this process in that solute A may be extremely dilute (mole fraction A $\ll 0.1$).

This process has been used to remove cyanide, hydrogen sulfide, carbon dioxide, and cyanide from coal gasification wastes (Skinner and Hayes, 1985); to remove ammonia and sulfites from petroleum refinery wastes (U.S. EPA, 1980); to remove volatile solvents and organo-sulfur compounds from paper plant wastewaters (McKance and Burke, 1980); and to recover alcohols, aliphatic hydrocarbons, aromatic hydrocarbons, chlorinated hydrocarbons, esters, and ketones (DuPont SET Program, 2004). [For performance summaries of five operating steam strippers (Table 13.21) and cost-effectiveness models for steam stripping, see U.S. EPA, 1988.]

TABLE 13.21 Summary of steam stripping at five industrial sites (U.S. EPA, 1988).

Pollutant	**Height (m)**	**Dia. (m)**	**Feed (kg/hr)**	**Steam (kg/kg)**	**Feed (mg/L)**	**Effluent (mg/L)**	**Removal (%)**
CHC, benzene, chlorobenzene	NA	NA	48 960	0.03	5900	9.8	>99.8
CHC	3	0.2	1260	0.1	3900	5.2	99.8
nitrobenzene, nitrotoluene	19.2	0.46	29 900	0.07	634	47.8	92
benzene, nitrobenzene, phenol, nitrophenol	9.8	0.61	5452	NA	1192	250	76
chlorinated ethers, phenol, chlorinated phenols, CHC	6.1	1.07	12 693	NA	453	3.4	99

NA = not available from reference material.
CHC = generic chlorinated hydrocarbons.

For ideal two-component solutions with one true liquid phase, phase behavior is defined by Raoult's Law:

$$p_A = x_A P_A^* \qquad (13.28)$$

Where

p_A = the partial pressure of component A in the vapor,
x_A = the mole fraction of component A in the liquid, and
P_A^* = the pure product vapor pressure.

For component B, the phase behavior is

$$p_B = (1 - x_A) P_B^* \qquad (13.29)$$

Where

p_B = the partial pressure of component B in the vapor,
x_A = the mole fraction of component A in the liquid, and
P_B^* = the pure product vapor pressure.

For steam stripping, the water-steam system is typically presented as component B. The total pressure (P) is the sum of the partial pressures:

$$P = p_A + p_B \qquad (13.30)$$

When the vapor is also ideal, the mole fraction of component A in the vapor (y_A) is in equilibrium with its mole fraction in the liquid (x_A):

$$x_A = \frac{P - p_B}{p_A - p_B} \tag{13.31}$$

$$y_A = \frac{p_A}{P} = \frac{x_A P_A{}^*}{P} \tag{13.32}$$

$$p_a + p_B = P_T \tag{13.33}$$

The phase compositions for ideal liquids and vapors can be constructed from vapor-pressure data for the pure compounds (see CRC, 1973). Some liquid mixtures may show nonideal behavior [e.g., high and low boiling azeotropes (see CRC, 1973), higher mixture vapor pressures, or lower mixture vapor pressures].

Vapor pressure data can be plotted a number of ways (Treybal, 1980). One useful plot is the constant pressure diagram (Figure 13.9). In this example, the low boiling component (B) is water, and no azeotropes are formed between A and B. Consider a liquid containing $x_A = 0.5$ mole fraction of Component A and $(1 - x_A) = 0.5$ mole fraction of Component B. Component A has a boiling point bp_A, and Component B has a boiling point bp_B. If the temperature is raised, the liquid will

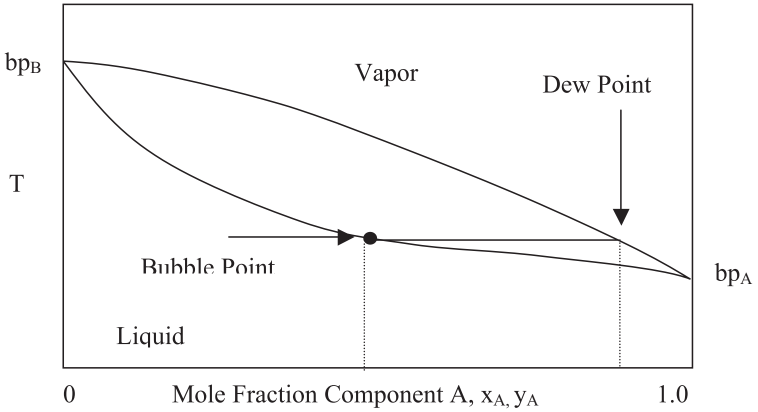


Figure 13.9 A constant-pressure liquid-vapor equilibrium plot for miscible fluids A and B.

begin to boil at temperature T. The temperature at which the solution just begins to boil is called the bubble point. The vapor has the same temperature, and the composition of the vapor is enriched in Component A with respect to Component B [the vapor contains $y_A = 0.8$ mole fraction of A and $(1 - y_A) = 0.2$ mole fraction of B]. The bubble point occurs at some intermediate temperature between bp_A and bp_B. The hypothetical separation between the bubble and dew points, and subsequent vapor condensation, represents one theoretical equilibrium contact. Tray towers and packed columns are designed to provide multiple equilibrium contacts in one unit process.

Steam distillation is a special case designated for immiscible fluids. For example, if the water has a high concentration of hydrocarbon, the partial pressures of Component A (water) and Component B (hydrocarbon) are independent of each other. Steam is added to raise the mixture's temperature until it boils. The boiling point is achieved when the sum of the partial pressures of each component equals the vessel's total operating pressure. (This temperature will be less than the normal boiling point of either component.)

[For more information on steam stripping and steam distillation for continuous processes (called the *McCabe-Theile method*) see Treybal (1980) and other texts on mass transfer.]

LIQUID TO SOLID SYSTEMS. Adsorption processes remove a solute from water via a selective solid resin. Physical adsorption involves weak van der Waal's forces. Chemical adsorption involves stronger interactions (e.g., ion exchange or hydrogen bonding between the solid and the solute). The solid may be activated carbon, activated alumina, organoclays, or another resin with a chemically active surface. Adsorption can occur in fluidized, moving, or fixed beds (Perrich, 1981), as well as in upflow pressure or gravity contact systems (in which the adsorbant is dropped through a column of water). The fixed resin bed is typically used in wastewater treatment; it involves passing wastewater down through a packed column of resin.

Activated Carbon. The most popular adsorbant is activated carbon because it is relatively inexpensive, adsorbs a wide range of organic and inorganic substances, and can be made from several materials (e.g., wood, sawdust, fruit pits, coconut shells, coal lignite, and petroleum residues). To make activated carbon, the chosen material is carbonized and then activated with hot air or steam (Reynolds, 1982). The starting materials and treatment intensity give each activated carbon a different capacity and selectivity. The extensive pore structure provides an extensive adsorption surface, which can range from 600 to 1100 m^2/g of active carbon (Perrich, 1981). (For more information about the properties of several commercial carbon products, see Perrich, 1981.)

The choice of sorbant depends on many variables, including selectivity and capacity, hydraulic throughput, strength of sorption, and ease of regeneration. Many sorbants' selectivity and capacity follow the Freundlich equation (Perrich, 1981):

$$q_m = K_F C^{\frac{1}{n_F}} \tag{13.34}$$

Where

q_m = the mass of solute per mass of sorbant,
C = the mass of solute per mass of solvent at equilibrium, and
K_F, n_F = empirical constants.

In general, high K_F and n_F values indicate good adsorption throughout the entire liquid concentration range, while low K_F and n_F values indicate poor adsorption at low liquid concentrations and better adsorption at high liquid concentrations (Table 13.22). [For a summary list of isotherm constants (K_F and n_F) for common wastewater components, see *Activated Carbon Adsorption for Wastewater Treatment* (Perrich, 1981).]

TABLE 13.22 Selected examples of sorption isotherm data (Perrich, 1981).

Compound	K_F (mg/g)	$1/n_F$	Compound	K_F (mg/g)	$1/n_F$
Phenol	21	0.51	Benzene	0.70	2.9
Styrene	120	0.56	Benzoic acid	0.8	1.8
Chlorobenzene	93	0.98	Carbon tetracholride	40	0.84
Nitrobenzene	68	0.43	Chloroform	11	0.84
Ethylbenzene	53	0.79	Ethyl chloride	36	1.5
Refinery wastewater	29	1.3	Refinery wastewater	6	1.67
oil separator effluent	36	1.25	activated sludge effluent	4	1.0
(three sites)	14	2.27	(five sites)	5	1.04
				4	0.93
				2	1.45

Activated carbon's adsorption capacity ranges from as low as 0.007 kg/kg carbon for methanol to as high as 0.18 kg/kg for propylene dichloride. In general, the sorption capacity increases as the solute's molecular weight increases (across a series of compounds with similar functionality). [For removal data on simple alcohols, acids, esters, ketones and aldehydes, amines and aromatic compounds, see *Activated Carbon Adsorption for Wastewater Treatment* (Perrich, 1981). For other sorption equilibrium models (e.g., Langmuir, Henry, and BET), see *Adsorption Technology for Air and Waste Pollution Control* (Noll et al., 1992).]

In wastewater treatment systems, multiple solutes often compete for adsorption sites on the activated carbon. Differences in carbon source, temperature swings, and other system-specific variances require that the project team conduct pilot tests (e.g., batch isotherm data and column studies) before designing an activated carbon process. Some wastestreams contain suspended solids, FOG, or other materials that must be removed before activated carbon treatment. A pilot study should identify these incompatable materials and suggest removal options.

Activated carbon is thought to remove a solute from solvent in three steps:

- Transfer across a liquid boundry,
- Sorption to the outer surface, and
- Migration into deep pores (Weber, 1972).

Scale-up models address these steps differently (if at all). In general, most highly sorbed solutes seem to be rate-limited by liquid boundry diffusion. A lesser number of solute systems seem to be rate-limited by pore diffusion. In the most common contact method—downflow fixed-bed—kinetic modeling is further complicated because sorption never reaches steady-state.

Figure 13.10 shows a typical breakthrough curve for a fixed-bed adsorption process. The process's influent is highly concentrated with solute. When the first batch of wastewater contacts the first layer of resin, equilibrium is reached rapidly, and the resin becomes saturated with solute. As the water moves downward, the remaining solute contacts fresh resin and a new equilibrium is formed until there is virtually no solute left in the water. The next batch of wastewater that enters the column immediately contacts saturated resin, so the solute is transported down to the next layer of resin until it reaches a layer that can adsorb it. Mathematically, a concentration wave front forms with a characteristic shape influenced by hydraulic conditions, temperature, initial solute concentration, column dimensions, and resin

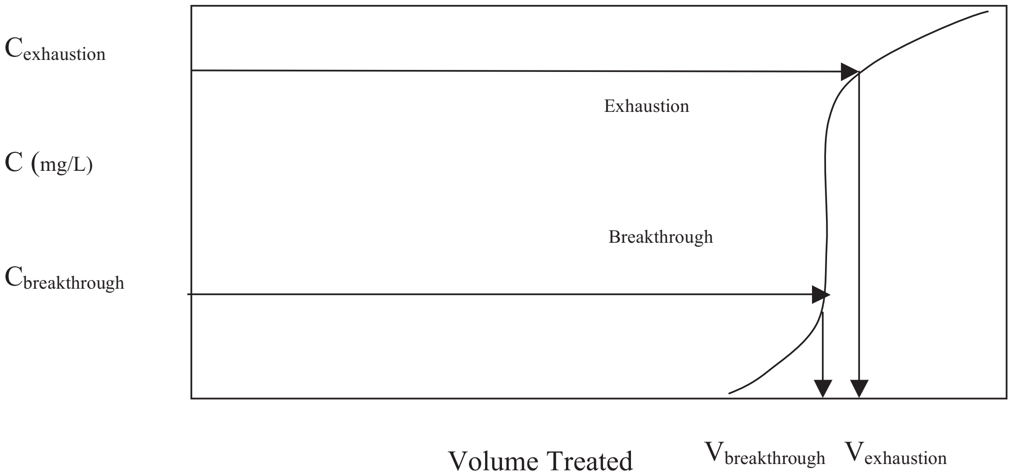


FIGURE 13.10 A graph of a typical activated carbon column run.

quality. At some point, the concentration exceeds the desired level, signaling breakthrough. An effective column run is defined by the run time until breakthrough. The resin's overall efficiency is roughly defined as the area of the curve to the left of the breakthrough point divided by the total area.

Because of the complexities of the sorption process and the inability to adequately predict the kinetics, researchers suggest that laboratory and pilot-scale design work are necessary whenever considering an adsorption process (Noll et al., 1992). The tests should address the following questions:

- How much pollutant can be loaded onto the sorbant?
- How long will this loading take?
- How will desorption be done?
- What is the recapture efficiency?

The simplest scale-up model is a direct method in which a test column is operated at the same contact rate to be used in the full-scale design (Reynolds, 1982; Fornwalt and Hutchins, 1966). The contact rate is typically two to three bed volumes per hour, and the superficial rate is typically between 0.0013 and 0.0034 m^3/s (2 and 5 gpm/sq ft). A breakthrough curve is constructed from the test data (Figure 13.10).

Using this information, designers then calculate the full-scale bed volume:

$$BV = \frac{L'}{Q_{Test}} \tag{13.35}$$

Where

BV = the full-scale bed volume (m^3),
L' = full-scale flow (m^3/s), and
Q_{Test} = the preselected flowrate (bed volume/sec).

They then calculate the mass of carbon required (M_{FS}):

$$M_{FS} = BVp_{carbon} \tag{13.36}$$

Where

BV = bed volume (m^3) and
p_{carbon} = the carbon density.

Next, they calculate the breakthrough volume for a predetermined effluent concentration:

$$V_B^* = \frac{M_{Test}}{V_B} \tag{13.37}$$

Where

$V_B{}^*$ = the volume of liquid treated (m^3),
M_{Test} = the mass of carbon in the test column, and
V_B = the breakthrough volume (m^3).

They use this value to estimate the run time until breakthrough in the full-scale column:

$$t_B = \frac{M_{FS} V_B^*}{L'} \tag{13.38}$$

Where

t_B = the run time until breakthrough (sec),
M_{FS} = the mass of carbon required,
$V_B{}^*$ = the volume of liquid treated (m^3), and
L' = full-scale flow (m^3/s).

Advanced models for fixed-bed adsorption may be found in many references (e.g., Noll et al., 1992). These models take many forms (e.g., analytical solutions for liquid-diffusion-dominated kinetics, pore-diffusion-donimated kinetics, or numerical analysis including pore and liquid diffusion).

After breakthrough, the column must be regenerated by removing the adsorbed solute from the activated carbon. The regenerated carbon is then reused. Depending on the solute and carbon involved, the column may be regenerated via steam stripping, vacuum stripping, or thermal regeneration.

Many full-scale designs incorporate two or three columns. In the two-column design, one column regenerates while the other is on-line. In the three-column design, two columns operate in series while the third regenerates. The first column in the series is allowed to reach breakthrough because the second one collects the pass-through solute. Once the third column is fully regenerated, it is valved to become the second in series. The second column is valved to become the first in series, and the first is taken off-line for regeneration. This design substantially reduces the regeneration cost per unit volume of carbon.

Activated Alumina, Organoclays, and Synthetic Resins. Activated alumina is produced by controlled (stepwise) drying of aluminum hydroxide to create a crystal structure that is relatively water-free. The final structure of the alumina is a function of the final temperature and the starting product. The resulting crystal phase is mostly boehmite (α-$Al_2O_3 \cdot H_2O$) or unhydrated (α-Al_2O_3) (Considine, 1974). The crystal may be produced to have the following properties: large specific surface area, high pore volume, defined pore size distribution, specific catalytic reactivity, specific adsorptive capacity, and high crushing strength with low dust formation. Specific values for density, porosity, pore diameter, surface area, and water sorption capacity may be found in the *Chemical and Process Technology Encyclopedia* (Considine, 1974) and *Adsorption Technology for Air and Waste Pollution Control* (Noll et al., 1992).

Activated alumina is used industrially as a catalyst to aminate alcohols and as a desiccant in air dryers (Considine, 1974). Activated alumina also has a high sorption capacity for arsenious acid [As(III)], arsenate [As(V)], and fluoride and is used in the water treatment industry and home water systems to control these inorganic contaminants. [For application data and design fundamentals, see *Water Quality and Treatment* (Letterman, 1999).]

Some natural clays have cation exchange capacity. Organoclays are formed by the exchange of inorganic cations (principally Ca^{++}) with organic cations (principally amines) containing long-chain organic tails. The organic fraction on the clay surface makes the clay hydrophobic so it better adsorbs organic compounds [e.g., benzene, toluene, and xylene (Jaynes and Vance, 1966)].

Synthetic resins can be constructed from polystyrene, phenolic esters, acrylic esters, and polyaminated cellulose. These materials have seen broad use as ion exchange resins because they attract specific solutes and can be easily reversed for recharge (Noll et al., 1992).

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Chapter 14

Process Instrumentation and Control

(continued)

PHILOSOPHY AND APPROACH

NEED FOR INSTRUMENTATION. Instrumentation is the science of using sensors, instruments, and computers for measurement and control. Instrumentation is important in industrial wastewater treatment both to control treatment processes and to provide data for regulatory compliance reporting (e.g., flow measurement and recording). Process control instruments range from a simple on-off control for a pump up to a programmable logic controller that provides completely automated control of a sequencing batch reactor.

The extent to which instrumentation and control systems are incorporated into the design of industrial wastewater treatment and disposal facilities depends on the size of the facility, the complexity of the unit operations and processes, the reliability requirements, the operational staffing, and the availability of maintenance personnel.

Appropriate instrumentation can improve a wastewater treatment facility's efficiency and reliability and reduce operating costs (e.g., chemicals, energy, and labor). Inappropriate instrumentation can result in process failures and higher maintenance costs due to excessive complexity.

REGULATORY REQUIREMENTS. The monitoring and reporting requirements typically will be detailed in a National Pollution Discharge Elimination System (NPDES) permit if the facility discharges to surface water or groundwater, or in a pretreatment permit if it discharges to a publicly owned treatment works. Typically, the permit will require flow monitors and specific sampling and analysis procedures. The permit may also require reporting of certain process control measurements (e.g., the return sludge flow rate in an activated sludge process). (For more details on regulatory requirements, see Chapter 2.)

MEASUREMENT

FLOW. Flow is the most common and probably most important measurement parameter in wastewater treatment. The *flow* is the cumulative amount of fluid measured. The *flow rate* is the amount of fluid (liquid or gas) passing through the measurement device in a unit of time.

Flow is measured by a sensor as the fluid passes through a primary flow element, creating a flow disturbance. Such elements may be open channel (e.g., weirs and flumes) or closed pipe (e.g., venturi tubes and vortex meters). Some sensors (e.g., magnetic and ultrasonic) directly measure flow velocity in a pipe section; they do not need a primary flow element to create a measurable disturbance.

Open Channel Flow. *Weirs.* A *weir* is essentially a bulkhead or wall across an open channel that flowing liquid must pass over. Weirs can be rectangular (e.g., sharp-crested or broad-crested), triangular (e.g., V-notch), trapezoidal (e.g., Cipolleti), or more complex shapes (e.g., proportional and Sutro weirs). Rectangular weirs (Figure 14.1) can have suppressed end contractions, meaning that the weir extends over the entire channel width or the ends can be contracted as they are in triangular or trapezoidal weirs.

The flow rate over the weir can be calculated based on the height of the liquid flowing over the weir crest. The height can be measured manually by a staff gauge or automatically by various types of transducers (e.g., floats, bubblers, submersible transmitters, and ultrasonic transmitters). The length of weir must be chosen so the full range of expected flows can be accommodated and changes in height can be accurately measured by the sensor.

A critical disadvantage of weirs in wastewater measurement is the tendency for settleable suspended solids to accumulate in the quiescent pool upstream of the bulkhead, creating nuisance conditions. So, weirs are preferred for treated effluent and typically avoided for raw wastewater.

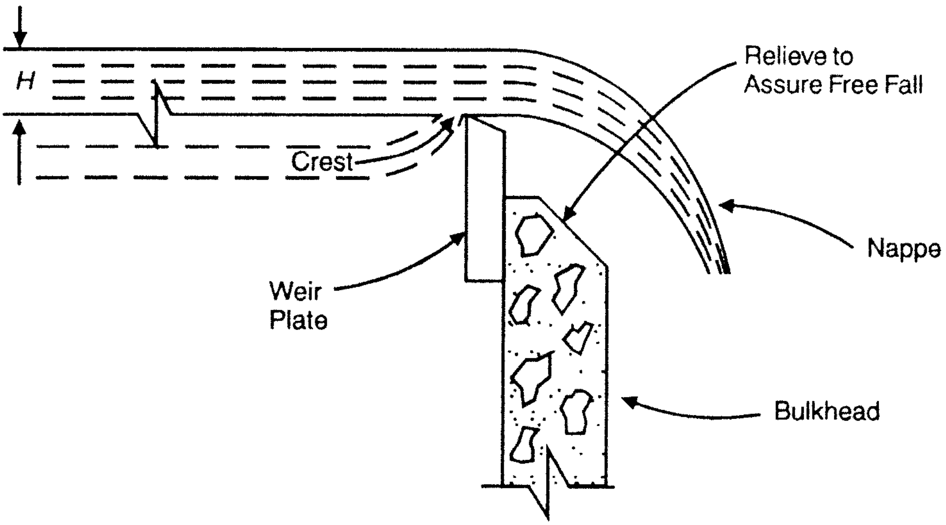


FIGURE 14.1 An example of a sharp crested rectangular weir.

Bazin's formula for sharp-edged rectangular weirs is:

$$Q = 0.66 \times cB \times (2g)^{0.66} \times H^{1.5} \tag{14.1}$$

Where

Q = water flow rate (m^3/s);
B = width of the weir (m) [If the weir is narrower than the channel feeding it, shorten B by $0.2 \times H$];
c = discharge coefficient (average 0.62);
g = gravitational constant (9.81); and
H = height of the water over the weir, measured behind the weir edge (m).

Weir flow tables are also available in several hydraulics handbooks, including the *Water Measurement Manual* (DOI, 2001). Most weir formulas and tables assume negligible approach velocity, as though the weir was measuring flow out of a large tank or reservoir. There are calculations to correct for approach velocity, but this is difficult to automate, so the designer should design the weir so the approach velocity is low and, therefore, the correction is not needed.

Flumes. A flume is the other principal open-channel primary flow element. It is a specially shaped section of an open channel used to measure the liquid's flow rate. The restricted throat portion of a flume produces a head differential that can be used to measure flow rate. The main advantages of a flume over a weir are the low headloss and the ability to pass suspended solids without impediment.

The most common flume is a special type of Venturi flume called a Parshall flume (Figure 14.2), which was invented by Ralph L. Parshall in 1922. The flow characteristics of various size Parshall flumes have been studied extensively, resulting in very accurate characteristic tables and curves. Flow tables for various Parshall flume throat widths are included in the Appendixes of the *Water Measurement Manual* (DOI, 2001). Table 14.1 gives the measurement range for Parshall flumes from 1 in. to 6 ft of throat width and can be used for preliminary sizing of the flow element.

Another type of open-channel flow element is the Palmer-Bowlus flume (Figure 14.3), which is sometimes inserted directly in pipelines flowing partially full. An H-flume (Figure 14.4) is well suited to measuring a very wide range of open-channel flow rates.

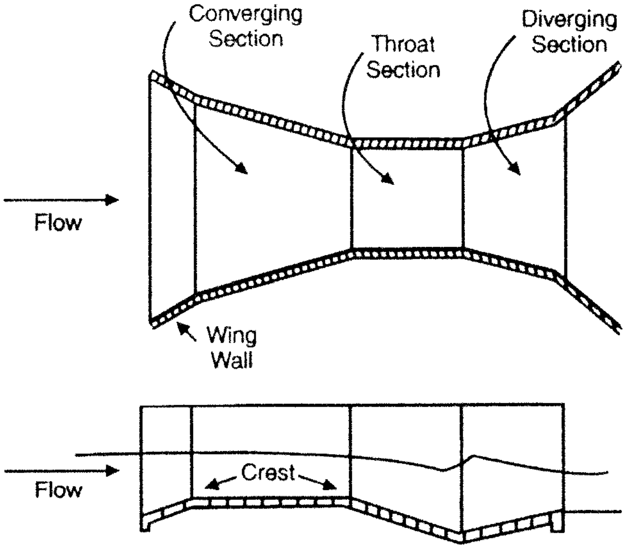


FIGURE 14.2 A schematic of a Parshall flume.

Table 14.1 Measurement range for Parshall flumes.

Throat width (in.[a])	Flow rate range (gpm[b])
1	2–90
2	5–175
3	20–800
6	30–1700
9	50–4000
12	60–7000
18	100–11 000
24	200–15 000
30	250–19 000
36	300–22 000
48	600–30 000
60	700–38 000
72	1200–45 000

[a] in. × 25.4 = mm.

[b] gpm × 5.451 = m^3/d.

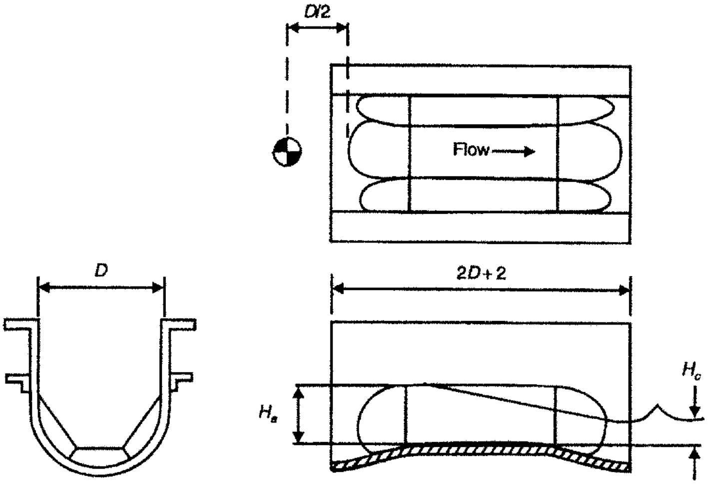


Figure 14.3 A schematic of a Palmer-Bowlus flume (courtesy of Free Flow, Inc., Omaha, Nebraska).

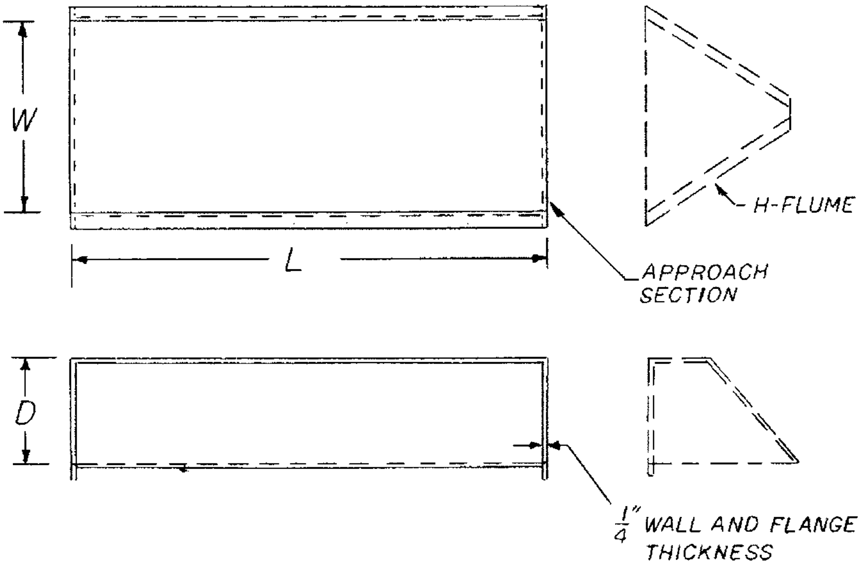


Figure 14.4 A diagram of an H-flume.

Velocity-Area Meters. Velocity area meters measure flowrate based on the Continuity Equation:

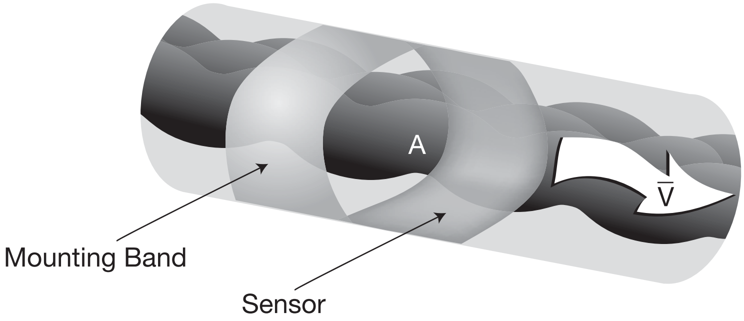
$$Q = VA \tag{14.2}$$

Where

Q = flow,
V = average velocity, and
A = area.

Velocity-area flow meters (Figure 14.5) typically use two sensors in tandem: one to measure flow depth and calculate the area from the channel cross-section dimensions, and another to measure average velocity. It is one of the most direct methods of flow measurement. (Indirect methods use level measurement to compute flow rate.) The sensors' relative accuracy and the directness of the measurement make this probably the most accurate open-channel flow meter currently available.

Submerged Orifices. An orifice primary flow element is a well-defined opening near the bottom of a bulkhead through which flow occurs. The dimensions orifice and height of the liquid above the opening are related to discharge flow rate.



$$Q = \overline{V} \times A$$

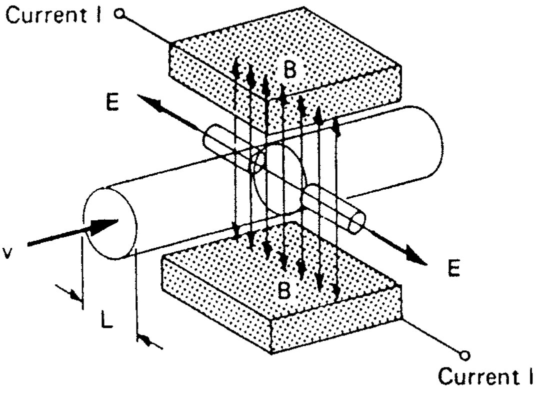
FIGURE 14.5 A schematic of a velocity-area meter (courtesy of Marsh-McBirney, Inc., A Hach Company Brand, Frederick, Maryland).

Submerged orifices are not used as often as weirs and flumes because of the excessive headloss associated with the amount of head required for an accurate orifice flow calculation. However, this type of primary element may be suitable for some industrial wastewater applications.

Closed Pipe Flow. *Magnetic Flow Meters.* Magnetic flow meters (“magmeters”) operate on Faraday’s principle, which states that when an electrical conductor moves in a magnetic field, a voltage is induced in the conductor that is proportional to the conductor’s velocity (Figure 14.6). The flowing liquid is the electrical conductor in magnetic flow measurement, and the velocity is the average liquid velocity across the flowtube’s cross-section. The magnetic field is produced by electromagnetic coils placed on either side of the flowtube, and the induced voltage is sensed by electrodes installed perpendicular to the magnetizing coils. Figure 14.7 shows a typical magmeter.

Considerations in the application of magnetic flow meters include:

- The process liquid must be an electrical conductor;
- The flow tube must be continuously completely submerged; and
- There is a length of straight pipe upstream (about ten pipe diameters long) and downstream (about five diameters long) to ensure that the velocity distribution between the electrodes is uniform.



$E = B \times L \times V$

E = Induced voltage
B = Magnetic field intensity (flux density)
L = Distance between the electrodes (pipe diameter)
V = Average flow velocity of liquid

FIGURE 14.6 An illustration of Faraday's Principle (courtesy of Sparling Instruments, Inc., El Monte, California).

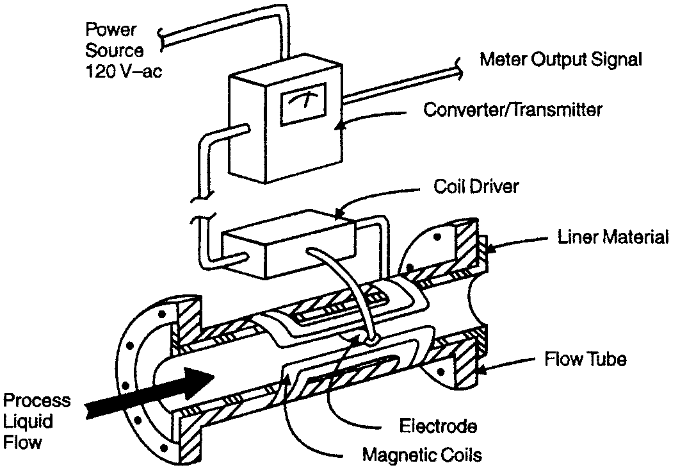


FIGURE 14.7 A schematic of a magnetic flow meter.

The electrodes may become fouled and should be cleaned periodically either by removal or by *in situ* cleaning systems (e.g., ultrasonic cleaning for scale type deposits or low-temperature boil-off for oil and grease fouling).

Ultrasonic Flow Meters. Ultrasonic flow meters are closed-pipe instruments that measure flow by sensing variations in sound waves. There are two distinct types of ultrasonic flow meters: Doppler effect and transit-time.

Christian Doppler identified the frequency shift of an acoustic signal emanating from a moving source in 1843. The Doppler-effect flow meter (Figure 14.8) transmits a known frequency ultrasonic signal into the flowing liquid and measures the frequency of the reflected signal. The frequency (Doppler) shift is related to the average velocity of the flowing liquid. As in most flow meters, the flow rate is computed by the continuity equation.

There must be enough suspended solids in the liquid to reflect the sonic signal. Otherwise, fine air bubbles must be introduced (provided that the treatment processes can accommodate entrained air).

The transit-time ultrasonic flow meter (Figure 14.9) uses opposing sonic generators and receivers set diagonally across the flow tube. Sonic pulses are transmitted alternately between the transducers and transit time is measured. The transit time is increased or decreased by the flowing liquid. The difference in sonic velocity between the alternating pulses is related to the average flow velocity.

In practice, ultrasonic flow meters must be carefully applied. They seem to be more susceptible to interference and signal-to-noise ratio issues than other electronic flow measurement systems. Ultrasonic metering applications should be pilot-tested and compared with an independent standard before permanent installation.

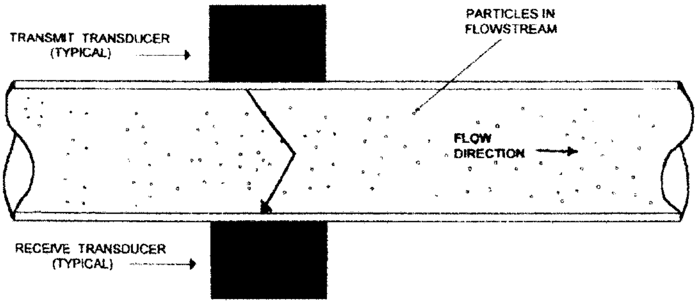


FIGURE 14.8 A schematic of a Doppler ultrasonic flow meter (courtesy of Siemens Energy & Automation, Inc., Alpharetta, Georgia).

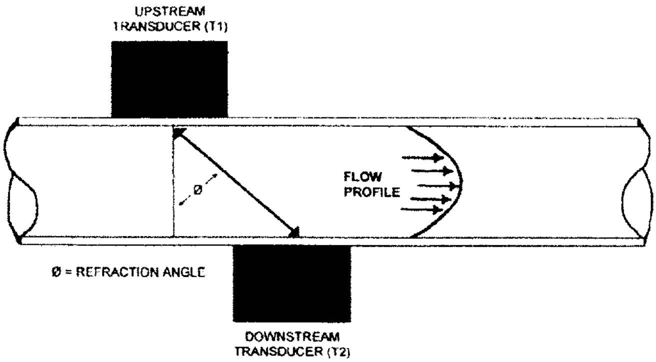


Figure 14.9 A schematic of a transit-time ultrasonic flow meter (courtesy of Siemens Energy & Automation, Inc., Alpharetta, Georgia).

Venturis. A venturi is a fluid flow measurement device that operates on the Bernoulli principle, which states that a fluid flowing through a pipe produces a pressure drop that is proportional to the square of the flow velocity. Venturi flow meters have a predetermined configuration and a pair of pressure taps (Figure 14.10).

The venturi flow tube can be direct-reading via a square-root extracting differential pressure gauge to the pressure taps, or it can produce an electronic signal via a differential-pressure transmitter. The transmitter output signal can be proportional to differential pressure (with the flow calculation performed in the receiving instrument), or the transmitter can include an integral electronic square-root calculator that produces an output signal proportional to flow rate.

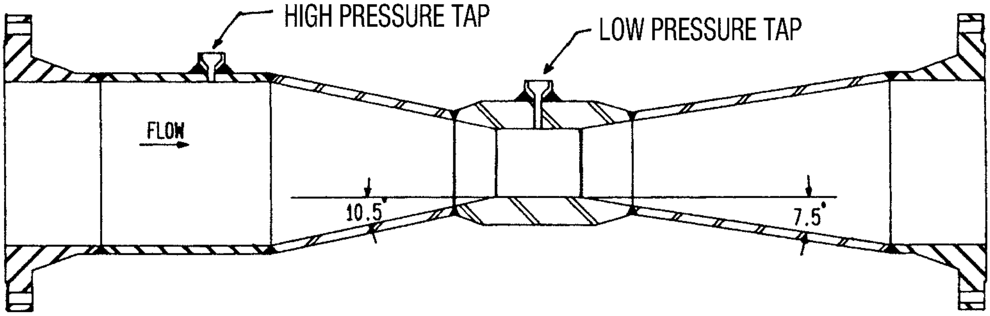


Figure 14.10 A schematic of a Venturi flow meter (courtesy of Vickery-Simms, a Division of FTI Industries, Inc., Mansfield, Texas).

Venturi flow meters are equally applicable to gaseous or liquid process fluids, but they do not work well on solids-bearing fluids because the pressure taps and capillary tubes tend to plug. Various measures (e.g., chemical seals and purges) were used to try to overcome this limitation, but recently less invasive measurement instruments have predominated when measuring wastewater and dirty gaseous flows.

Orifice Plates. An orifice plate is a pressure-differential-producing element; it is an obstruction plate with a round opening that is installed in a gaseous or liquid fluid pipeline. Pressure taps upstream and downstream of the plate are connected to a differential pressure square-root-indicating gauge or to an electronic differential pressure flow transmitter.

Orifice plates are relatively inexpensive but are limited to clean fluids and a maximum "turndown" of 3-to-1 (ratio of maximum-to-minimum measurable flow rate). The coordination of the orifice plate opening and sensor scales to the process fluid flow characteristics (i.e., pressure, temperature, and flow range) is critical. Even if the system works initially it may fail in time because of orifice erosion, changes in process flow rates, etc. In practice, the number of failed orifice plate installations probably exceeds the functional ones.

Mass Flow Meters. The previous flow meters measure volumetric flow rate, which is sufficiently accurate for water, typical wastewater suspensions, and other liquids with a nearly constant density. There are situations, however, where the density may vary and it is desirable to measure the mass flow rate (e.g., gaseous fluids whose density varies with pressure, as in activated sludge aeration systems). The mass flow rate of gaseous fluids can be calculated from simultaneous measurements of pressure and volumetric flow rate, or the flow rate can be measured more directly by a mass flow meter.

The mass flow rate of heavy slurries or reagent solutions can be measured accurately by a Coriolis effect mass flow meter. However, this type of instrument sees more use in industrial processes than in wastewater treatment because of its complexity and high cost.

A thermal mass air flow meter has a pair of closely spaced resistance temperature detectors in the process fluid flow path (Figure 14.11). One sensor is heated, and the other is unheated. The temperature differential between the two sensors increases because of the cooling effect of the flowing fluid—the greater the mass flow rate, the greater the temperature differential.

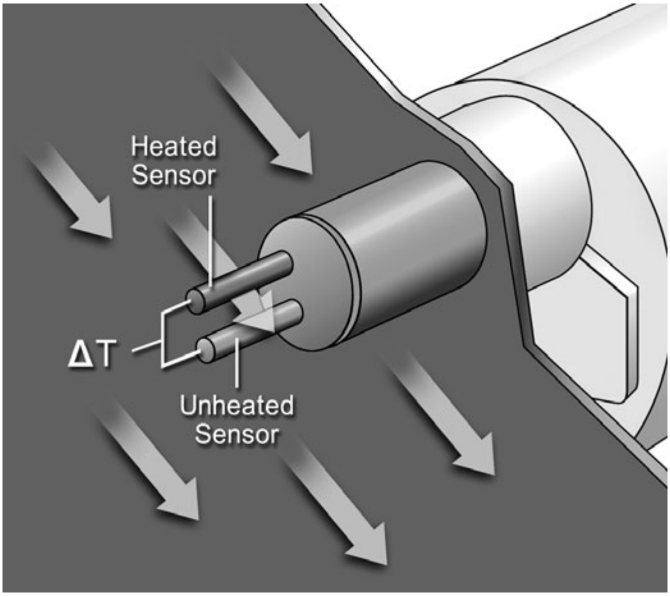


FIGURE 14.11 An illustration of a thermal mass flow meter (courtesy of Fluid Components International, San Marcos, California).

Thermal mass flow meters have proven superior to orifice plates and Venturis in such applications as aeration system airflow measurement. Water droplets and water vapor can interfere with temperature-differential measurement, so caution must be exercised when water-air mixtures are measured (e.g., the inlet to an aeration blower that can capture rainwater).

LEVEL. ***Bubbler Systems.*** Bubbler level measurement systems (Figure 14.12) operate on the principle that the pressure in a tube constantly discharging a small airflow in a liquid is proportional to the height of liquid above the end of the tube. This hydrostatic pressure can be sensed by pneumatic gauges or controllers, electric pressure switches, or electronic transducers.

Pressure Transducers. Pressure transducers (also called *transmitters*) are electronic devices that transmit an electronic signal that is proportional to the height of liquid above the instrument. Pressure transducers for liquid level measurement can be exterior mounted on a bulkhead fitting near the bottom of a process tank, or they can be submersible and suspended in the process media (Figure 14.13). The

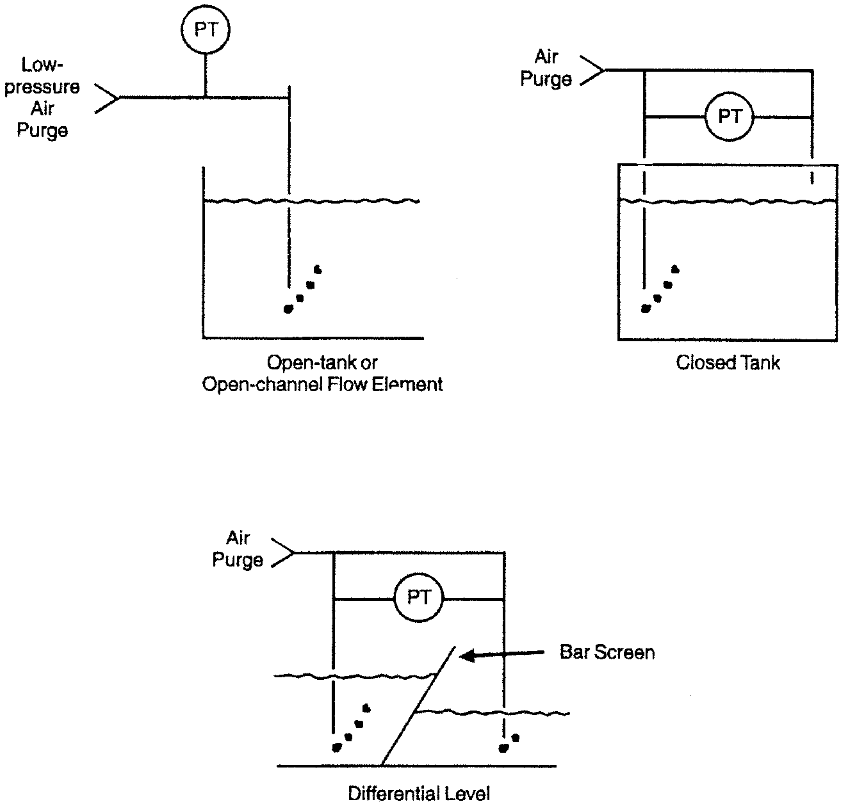


FIGURE 14.12 Examples of typical bubbler applications.

submersible transducer either has small orifices to the transducer mechanism, or the transducer mechanism is sealed in oil, with a flexible diaphragm that transmits the hydrostatic pressure.

Bulkhead and small orifice submersible transducers are well-suited to clean solutions, where plugging is unlikely to occur. Submersible diaphragm transmitters may be more appropriate for solids-bearing mixtures (e.g., wastewater) and liquid sludge. Diaphragm-type submersible transmitters are particularly well-suited for raw wastewater wetwell level measurement, where liquid vapor, scum, floating grease, and a turbulent surface will prevent reliable ultrasonic level measurement.

Impedance and Capacitance Probes. Impedance and capacitance probes operate on the principle that a probe's immersion depth in a conductive liquid changes some characteristic of an electrical circuit (e.g., resistance or capacitance), and that this change can be measured accurately.

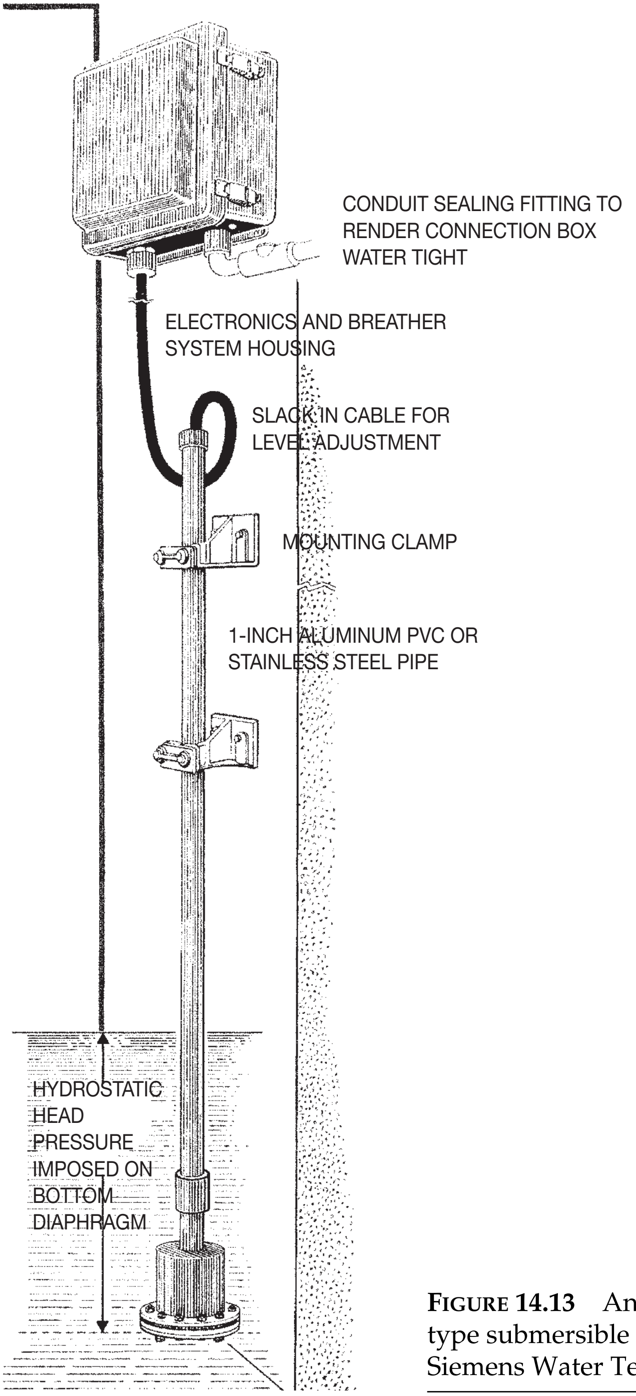


FIGURE 14.13 An illustration of a diaphragm-type submersible transmitter (courtesy of Siemens Water Technologies).

Capacitance probes must be insulated when measuring conductive liquids; resistive probes can only measure liquids that conduct electricity. Both types of probes are subject to failure because of fouling by the process liquid. Impedance and capacitance probes work reliably when measuring chemical reagents, but caution should be exercised when measuring less pure process liquids.

Ultrasonic. Ultrasonic level measurement systems transmit a sonic or ultrasonic pulse that is reflected from the liquid surface (Figure 14.14). The travel time from the transmitter to the liquid surface and back to the receiver is converted into a distance that is inversely proportional to the liquid level (i.e., the shorter the distance from the transducer head, the higher the liquid).

Ultrasonic level measurement is a non-invasive option that is well-suited for measuring quiescent liquids with a well-defined surface interface. It is not well suited for turbulent liquids where a stilling well would be required, or for applications in which dense vapor lies above the liquid, or where the surface interface is vague because of foam or a floating grease layer. So, ultrasonic level measurement should not be used in most raw wastewater wetwells.

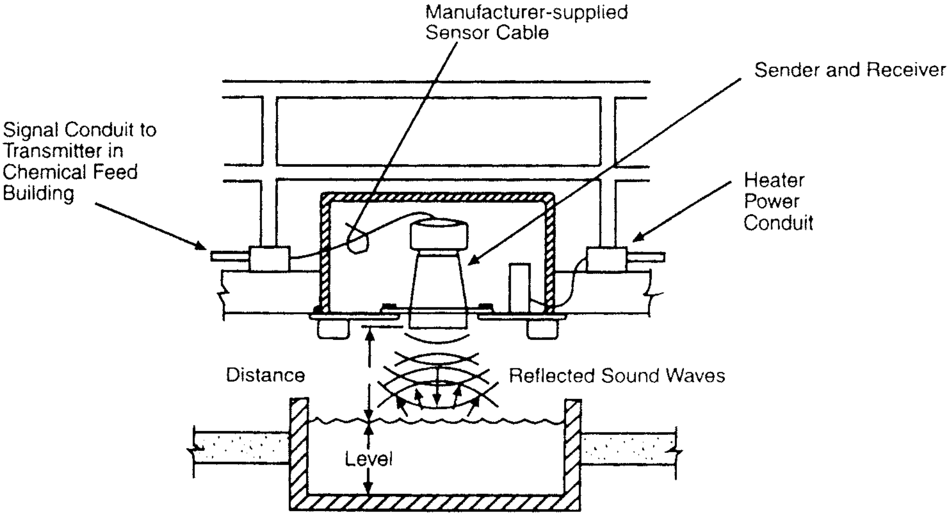


FIGURE 14.14 A diagram of ultrasonic level measurement.

Pressure. Pressure measurement is used on closed process lines conveying compressed gases and liquids. Pressure measurement devices can be local indicating (e.g., pressure gauges) or remote transmitting (e.g., electromechanical transducers). Diaphragm-type chemical seals are used to keep pressure-measurement instruments from being plugged in solids-bearing process fluids, and snubbers or liquid-filled gauges can be used to attenuate amplitude transients and fluctuations.

PROCESS ANALYZERS. Process analyzers have become much more reliable and have gained more widespread acceptance in recent years. They can be effectively integrated with supervisory control and data acquisition (SCADA) systems to provide real-time monitoring and efficient automation of wastewater treatment processes that previously required constant operator attention.

Following are just a few of the available process analyzers.

pH. A solution's pH is a measure of its concentration of hydrogen ions; it indicates acidity or alkalinity. For example, a low pH denotes a high concentration of hydrogen ions, indicating that the solution is acidic. A high pH denotes a small concentration of hydrogen ions, indicating that the solution is alkaline.

pH is measured electrochemically with an electrode pair. The measurement electrode is a glass membrane filled with a solution buffered to pH 7.0 (neutral), and the reference electrode is a porous membrane filled with a saturated potassium chloride solution. Electronic circuitry senses and amplifies the voltage potential that develops between the electrodes. A temperature sensor is included to compensate for the measurement differences associated with temperature.

The output of the pH-measurement system varies ("drifts") as the electrodes age, so frequent recalibration is required. pH electrodes are subject to fouling in wastewater applications, and frequent electrode cleaning or replacement is often required.

Dissolved Oxygen. The dissolved oxygen concentration is measured in a dissolved oxygen probe that consists of a pair of electrodes (a cathode and an anode) mounted in an electrolyte liquid that is separated from the process fluid by a gas-permeable membrane. The flow of electrons from the cathode to the anode (i.e., current) is proportional to the process liquid's dissolved oxygen concentration. This current flow is sensed, amplified, and displayed or transmitted. The current flow is highly sensitive to temperature, so dissolved oxygen measurement systems always contain a temperature sensor and compensatory circuitry.

Dissolved oxygen is a major concern in biological process control, so biological systems are the most common application of dissolved oxygen measurement.

Dissolved oxygen probes are subject to fouling by solids and fats, oils, and grease (FOG) in the process stream. They typically require frequent cleaning and recalibration. New devices are continually being brought to market because of the maintenance problems associated with dissolved oxygen probes.

Oxidation-Reduction Potential. A solution's *oxidation-reduction potential* (ORP; redox) is a measure of its electrochemical ability to make atoms or molecules lose electrons to other atoms or molecules. It is measured via an electrode system similar to that for pH, except that the glass membrane is not hydrogen ion-specific.

This analyzer is typically used in heavy metal reduction processes (e.g., chromium) and in alkaline chlorination of cyanides. A proprietary high-resolution ORP measurement system is sometimes used for precise control of chorine disinfection and bisulfite dechlorination systems.

Conductivity. Conductivity measures how well a solution of electrolytes conducts electricity. *Electrolytes* (e.g., acids, bases, and salts) are substances that ionize separately into charged particles called *ions,* which conduct an electrical current in solution.

A conductivity sensor uses two electrodes in contact with the solution (Figure 14.15). An alternating current (AC) voltage is applied to the electrodes, and the measured current is converted to standard units of conductivity [e.g., Siemens/cm (S/cm)].

Streaming Current Detector. A streaming current detector is a special type of conductivity instrument used to monitor and control coagulants in water wastewater treatment. Coagulants are organic electrolytes (e.g., polymers) and inorganic electrolytes (e.g., ferric and lime) that bind with colloidal particles to facilitate agglomeration and, ultimately, separation. The streaming current detector measures the electrokinetic charge of the process stream following coagulant addition and mixing. The resulting measurement is an indicator of residual coagulant that can be used to control the dose.

Turbidity and Particle Counters. Turbidimeters and particle counters are laboratory and on-line process instruments used to make fine measurements of suspended solids removal (e.g., sand and membrane filtration).

Turbidity is a measure of the concentration of suspended solids in a mixture. Suspended particles reflect light; dissolved solids do not. Light will pass straight through a solution that has no suspended solids, while some of the light passing

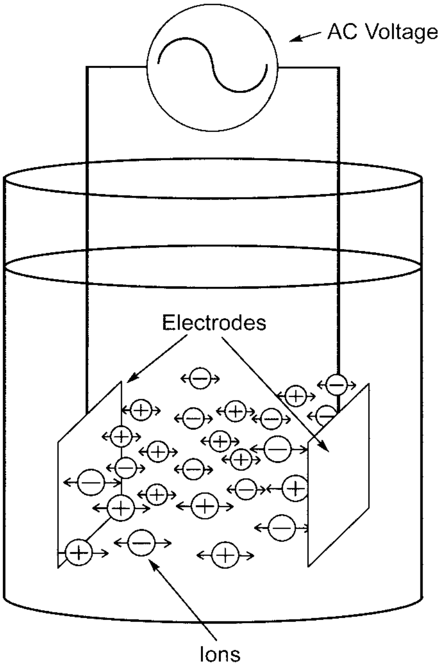


FIGURE 14.15 A schematic of conductivity measurement (Rosemont Analytical, Inc., 2004).

through a suspended-solids-laden solution will be reflected back and to the sides. A turbidimeter directs a light beam into a sample and uses a photocell to measure the portion reflected or scattered at a right angle to the beam. It used to be measured in Jackson turbidity units (JTU) when the light source was a candle. The current U.S. EPA method uses a nephelometric method of measurement calibrated relative to a formazin primary turbidity standard. The units are Nephelometric turbidity units (NTUs).

Particle counters are sometimes used for even finer measurement of suspended solids after highly efficient membrane treatment processes (e.g., ultrafiltration and reverse osmosis). Particle counters detect 2 to 750 μm and can display a count up to 1 billion particles in a 100 mL/minute sample flow.

Respirometry. A respirometer is an on-line process instrument that uses a small bioreactor to measure a wastewater stream's oxygen demand (Figure 14.16). On-line respirometry can be used to provide a real-time indication of changes in

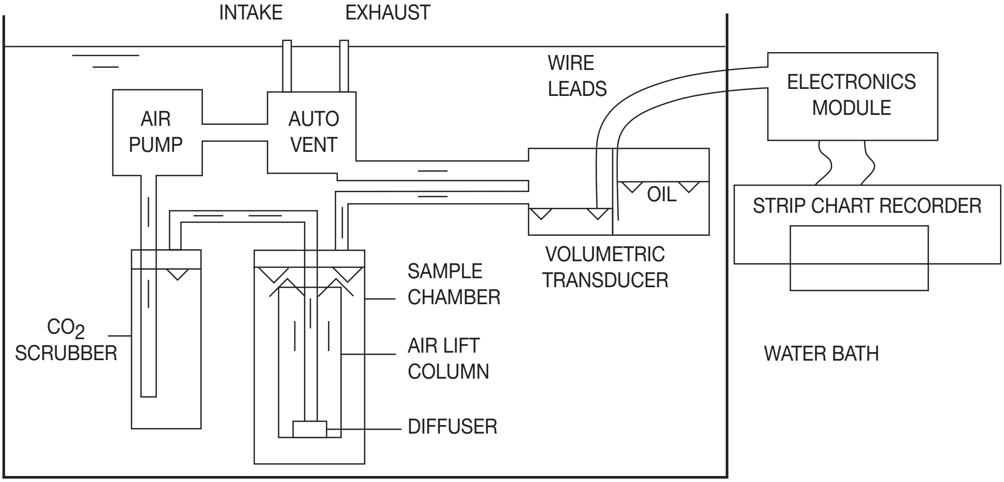


FIGURE 14.16 A schematic of a respirometer (courtesy of Respirometry Plus, LLC, Fond du Lac, Wisconsin).

organic loading or toxicity. An on-line respirometer's response time is typically less than 0.5 hour.

Total Organic Carbon. Total organic carbon is a measure of the organic material in the process wastewater. Total organic carbon process analyzers use one of the following technologies:

- The thermal oxidation method uses high-temperature combustion to covert organic material into carbon dioxide;
- In the ultraviolet (UV) light-persulfate oxidation method, the sample is mixed with a solution of persulfate and exposed to UV light; and
- Chemical oxidation-based analyzers use acids and bases to precondition a sample and various oxidizing agents (e.g., oxygen, ozone, or hydrogen peroxide) to react with the carbon present.

Chemical Oxygen Demand, Biochemical Oxygen Demand. Chemical oxygen demand (COD) analyzers use strong oxidants to measure the total quantity of oxidizable components in a sample (e.g., carbon, hydrogen from hydrocarbons, nitrogen sulfur, and phosphorus).

Biochemical oxygen demand (BOD) analyzers use a small continuous-flow bioreactor with a respirometer to measure the portion of COD that is oxidized by biological organisms and biochemical reactions.

Ammonia and Nitrates. Ammonium in receiving streams can be toxic to aquatic organisms and will reduce the dissolved oxygen concentration by oxidizing it into nitrite and nitrate. Nitrogen compounds, in virtually any usable form, can lead to eutrophication of surface waters. Nitrate contamination of underground drinking water supplies is a suspected cause of methemoglobinemia ("blue baby" syndrome).

Ammonium and nitrate are measured using various techniques (e.g., spectrophotometry and specific ion electrodes). Some of these analyzers are cabinet type, while some relatively new *in situ*-style immersion analyzers have emerged.

Chlorine/Sulfite Residual. Chlorine and its associated compounds are used to disinfect domestic sanitary wastewater before discharge to surface waters and some groundwaters. Sulfite compounds are used to remove residual chlorine after disinfection in cases where aquatic life would be adversely affected. Chlorine and sulfite feed systems are often controlled by compound loop systems that are flow paced and trimmed by a signal from a residual analyzer.

Residual analyzers are usually amperometric probes and, if combined chlorine residual must be measured, the analyzer includes a buffer reagent feed to lower the sample pH. An alternative system uses a proprietary high-resolution ORP probe to sense free or combined chlorine residual.

Disinfection can be eliminated in many industrial wastewater treatment facilities by segregating sanitary wastewater at the source. For example, metal-finishing wastewater that is not mixed with wastewater from bathrooms and kitchens would not require disinfection.

SAMPLERS. Automatic samplers are often used to monitor treatment process performance and collect data for permit-compliance reports. The samples collected in an automatic sampler are removed and analyzed in a wastewater laboratory. Automatic samplers include a sample line and pump that first purges the sample line then reverses and draws a sample aliquot that is collected in either discrete sample bottles or one composite-sample bottle. The cabinet housing the sample bottle(s) is typically environmentally controlled (i.e., heated and refrigerated) to preserve the sample integrity.

Automatic samplers contain electronics to initiate sample collection based on time or, more typically, flow rate (i.e., to gather “flow-proportional” composite samples).

CONTROL

CONTROL CONCEPTS. Process measurement devices allow operators to monitor and record wastewater characteristics and process performance. The devices may also be used in a system to control the process’s performance. This control can be either manual (e.g., physically opening a valve, starting a pump or dumping a bag of lime into a tank) or automated to various degrees, ranging from a simple on-off float control of a sump pump to a computerized SCADA system that controls an entire wastewater collection and treatment system.

The following sections describe some common control elements (e.g., valves and pumps). Automatic control devices (e.g., feed-forward and feedback controllers, and automated process control systems) are also discussed. Finally, pH control is common in industrial wastewater treatment systems, so the design of this type of control system is described in more detail.

FINAL CONTROL ELEMENTS. A device that modifies the process is called a *final control element.* The two most common final control elements are control valves and pumps.

There are two basic types of control valves: linear (e.g., gate, globe, pinch, and diaphragm) and rotary (e.g., ball, eccentric plug, and butterfly). Each type has different flow and pressure drop characteristics that must be considered when designing the control system (Table 14.2). The type of process media is also an important consideration in valve selection. Valves are sized based on such conditions as pressure drop, viscosity, cavitation, flashing condition, and noise generation.

Pumps can be either constant- or adjustable-speed and may control either the process media itself (e.g., influent and effluent pumps) or may control a treatment reagent (e.g., an acid or caustic feed).

Constant-speed pumps are turned on and off, either manually or automatically, as required by some process variable (e.g., tank level or pH) in a reactor. A constant-speed pump delivers flow at a relatively constant rate when it is operating. Sometimes a constant-speed centrifugal pump is used with an adjustable-discharge

Table 14.2 A comparison of linear and rotary valves.

Linear valves	Rotary valves
Tortuous flow path	Streamlined flow path
Low head or pressure recovery	Good head or pressure recovery
Throttle low flow rates	Higher capacity
High pressure suitability	Handles slurries and abrasives
Nonlinear modulation	High rangeability

control valve to deliver a varying rate of flow. This type of inefficient system has been largely abandoned in favor of adjustable-speed pumps.

Adjustable-speed pumps are also turned on and off as required. The pump's speed can also be controlled. The pump speed is typically controlled to vary the discharge flow rate, but occasionally the speed is controlled to keep the discharge flow rate constant under varying differential heads. For example, an adjustable-speed centrifugal pump would be used to provide a constant rate of flow to the treatment processes downstream of an influent flow-equalization tank.

Various methods can be used to vary the speed of pump (e.g., hydrostatic drives, electromagnetic slip couplings, permanent-magnet clutches, and wound-rotor electric motors with liquid or wire rheostats). Currently, the most common technique is an electronic adjustable-speed variable-frequency drive (VFD).

The variable-frequency drive (Figure 14.17) converts the single-phase or three-phase AC line voltage to direct-current (DC) via rectifier bridge circuits. Electronic inverter circuits then convert the DC back to AC with a varying voltage and frequency. The ratio of voltage to frequency is constant at every speed. For example, at 50% speed, the output of a VFD with 480-V, 60-Hz input would be 240 V at 30 Hz.

The adjustable voltage and frequency output effectively controls the speed of an induction motor with more efficiency and a higher power factor (ratio of apparent-to-real power) than other types of adjustable-speed pump control.

PROCESS CONTROLLERS. A process controller monitors the signal output from a process-measurement transmitter and, in response, changes the process via an actuator. The system of measurement sensor, controller, and actuator is called a *control loop* (Figure 14.18). Examples of control loops include pH, chemical feed paced

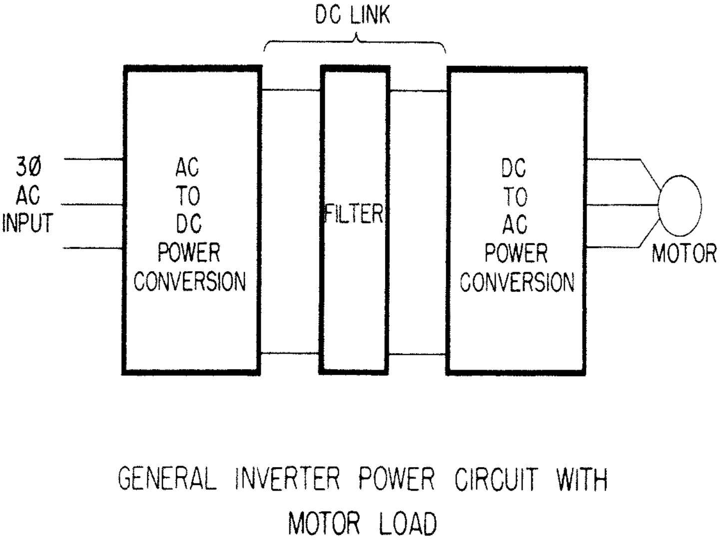


Figure 14.17 A schematic of a variable-frequency controller (courtesy of Siemens Energy & Automation, Inc., Alpharetta, Georgia).

off a variable (e.g., flow, pH, ORP), and automatic sampler control. If the sensor is measuring the process output, then the control system is called a *closed-loop system,* and the control strategy used is *feedback.* If the control signal is in the same direction as the process flow, then the control system is called an *open-loop system,* and the control strategy used is *feed-forward.*

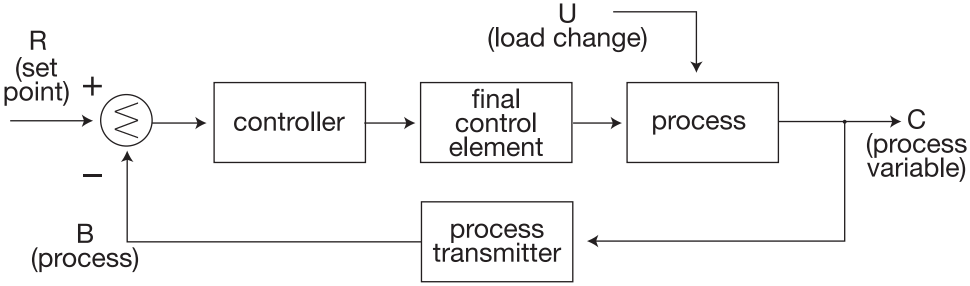


Figure 14.18 A block diagram illustrating the basic elements of a control loop (Keyser, 1992) (used with permission of Siemens Energy & Automation, Inc., Alpharetta, Georgia).

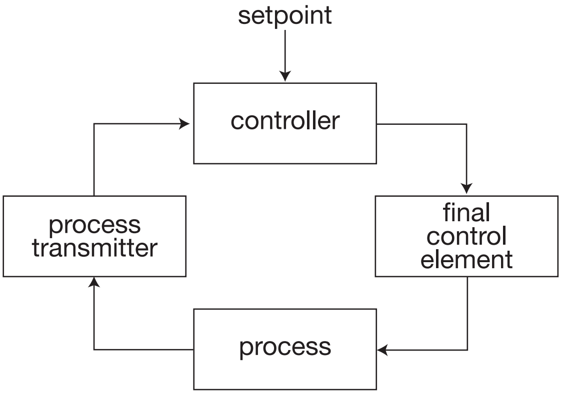


Figure 14.19 A block diagram of a single negative feedback control loop (Keyser, 1992) (used with permission of Siemens Energy & Automation, Inc., Alpharetta, Georgia).

There are basically three types of control strategies: feedback, feed-forward, and a combination of the two. Feedback control involves measuring a process *output* variable and manipulating the process to change that output (Figure 14.19). One of the simplest types of feedback control loops, the on-off controller, is a float switch controlling a sump pump. The measured variable is liquid level in the sump. When the level rises, the switch turns on the sump pump, which lowers the liquid level until the switch turns off the pump.

More complicated feedback control loops are based on analog process measurements and analog process-variable actuators. For example, if the sump's level is measured by a submersible pressure transmitter and the sump pump's speed is adjusted by a VFD to maintain a constant liquid level in the sump, then this system is called *analog-feedback closed-loop control.*

The control strategy can also be classified by the sophistication of the controller action: proportional band, proportional plus integral (PI), or proportional plus integral and derivative (PID). A proportional band controller has an output signal that is directly or inversely proportional to the process signal's deviation from the controller setpoint. A proportional plus integral controller is a proportional band controller with another feature that measures the offset in the proportional band and attempts to eliminate it to stabilize the process precisely at the setpoint. A proportional plus integral and derivative controller also modifies the controller output in response to the process variable's rate of change to decrease oscillations and upsets.

DESIGN OF pH-CONTROL SYSTEMS. A pH-control system measures the solution's pH via a sensor and controls the addition of a neutralizing agent to maintain the effluent within certain acceptable pH limits. In other words, it performs a continuous titration, except that the strength of the solution being neutralized is of no interest.

The control-system design is complicated because pH is a nonlinear function of concentration. For example, adding a certain amount of base to a strong acid solution with pH 2 will increase pH to 3. But to raise the solution's pH to 4, only about 10% of the original dose may be required. To raise it to pH 5, only about 1% of the original dose is added; and for pH 6, only about 0.1% of the original dose is required.

Raising a wastestream from pH 2 to pH 7 is a difficult control problem. A large amount of base is needed to produce any change in pH, but then adding small amounts will cause the pH to rise rapidly (depending on the wastewater's buffering capacity). So, to control pH precisely, an accurate and responsive control system is required.

Microprocessor-based technology enables many industrial controllers and analyzers to use configurable algorithms to characterize their function curves. A function curve is a plot of a controller's process control or output function versus the process variable or input signal. These algorithms are programmed to generate a segmented characterized curve that is inversely proportional to the titration curve for the wastewater and selected neutralizing agent. This results in a near-linear controller output with respect to reagent demand.

A single characterized curve will typically be sufficient for pH control, using a constant strength of neutralizing agent if the pH varies between 4 and 10. If the control system detects a pH outside of this operating band, an alternate characterized curve can be developed and electronically switched to replace the normal curve until the pH is returned to the routine control region.

For routine control of influent pH variations beyond 4 and 10, engineers should consider using a split-ranged controller to control two chemical-addition rates via different-sized control valves. A large valve is used for pH excursions outside of the 4 to 10 pH range, and a smaller valve is used for control within pH 4 to 10. Because of the nature of split-range control, the large valve can be throttling down the chemical feed rate while the smaller valve is fully open, allowing a smooth control of chemical addition at the pH 4 and 10 boundary points.

Another pH-control method is the use of an adjustable gain controller. As the measured pH deviates further from the desired pH setpoint, the controller gain increases, causing the controller output to add more chemical in proportion to the gain curve. As with the segmented characterized curve method, when the pH value deviates outside of the 4 to 10 range, split-range controller output should be used.

A pH-control system may be used in a batch or a continuous-flow system. The following paragraphs assume that the wastestream is acidic (which is typical in most industrial applications).

Batch-Control Systems. Plants with high wastewater volumes and flow rates typically use continuous-flow proportional or multimode control systems. Plants with intermittent or low volumes of spent acids or bases may use batch neutralization systems or continuous, two-position (on-off) control systems. The batch and on-off control systems have lower equipment costs than the multimode control systems.

Batch neutralizations are typically limited to situations in which wastestream flow is irregular, and the concentrations of spent acid or base liquors are high and variable (e.g., when strong sulfuric or hydrochloric acid pickling liquors are dumped infrequently). When the acid liquors are spent, they are pumped into a batch tank for neutralization before discharge to the collection system.

Figure 14.20 shows a typical batch neutralization system. For an acidic wastewater, the batch cycle is started by opening the waste valve. When the level in the

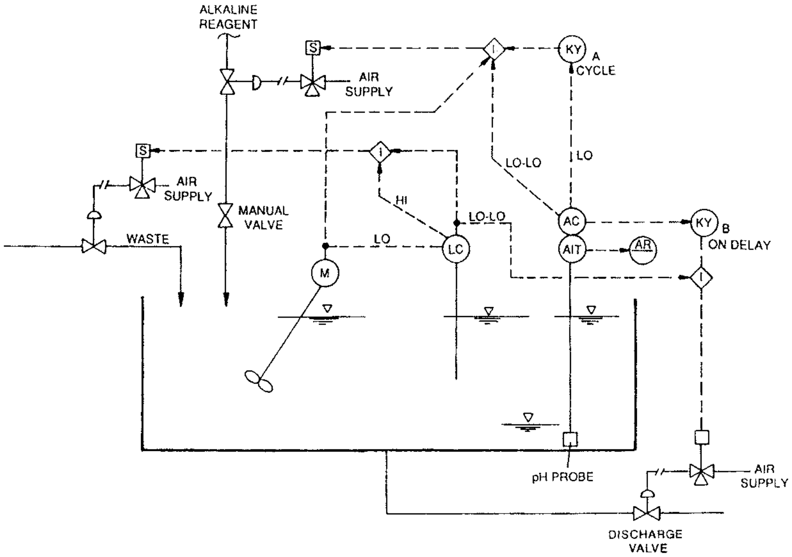


FIGURE 14.20 A schematic of a batch pH-control system for acidic wastewater.

neutralization basin reaches a low level, as measured by the level controller (LC), the mixer starts and the reagent-addition system receives a signal to begin operating. The pH is measured, and the analog value is recorded on a chart recorder (AR). Discrete switches (AC) associated with the pH analyzer (AIT) are used to control the reagent valve.

If the influent waste is below a low-low set value, the reagent valve will open to add chemicals to raise the pH. If the pH value of the waste exceeds the low value, the reagent valve will be controlled via a cycle timer (KY-"A"). This timer enables the valve to open for a specific period and then close to allow for reaction time. The system will continue using either feed-control method until the pH is within the desired range.

While the system is continuously controlling the waste pH, the waste valve is open, filling the basin. When the basin level reaches the high value, the waste valve will close. The pH will still need adjusting for a period after the waste valve is closed.

Once the pH has been adjusted to within the desired limits, an on-delay timer (KY-"B") is used to delay the opening of the discharge valve. This helps ensure that the pH does not fall outside the pH limits. If the on-delay timer times out and the equalization basin's pH is still within the limits, then the discharge valve will open, allowing the basin to empty.

When the basin level falls below the low value measured by the level controller (LC), the mixer will stop. The level will continue to decrease until the low-low level is reached. Then, the discharge valve closes and the waste valve opens, beginning a new batch cycle. (The low-low level in the basin should be above the pH probe element to ensure that the element remains submerged.)

In the system shown, the neutralizing agent typically is added via a solenoid or air-actuated valve. The tank typically is mixed via a propeller or the addition of air.

Segmented characterized curves can be used with batch control methods. With a known volume of wastewater in the equalization tank and measured pH, the curve can be used to set the time and, therefore, the amount of chemical addition. To enable the chemical reaction, this period may be lengthened to allow a lower chemical feed rate per unit of time. Neutralization of large batches still requires treatment in stages to prevent overcorrection of the pH.

Continuous-Flow Systems. *On-Off Control.* The two-position ("on-off") system (Figure 14.21) is so named because the element controlling the reagent addition is either fully open or fully closed. Wastewater continuously enters the retention basin and overflows the discharge weir.

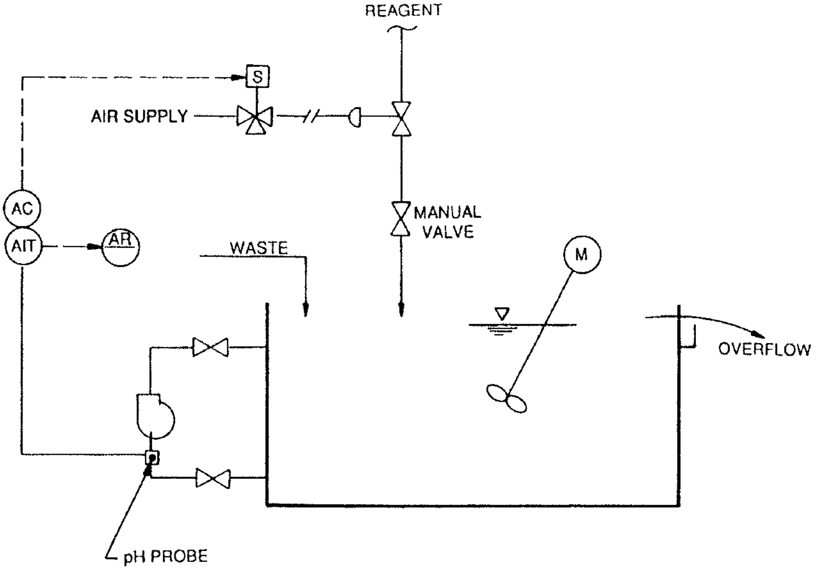


Figure 14.21 A process diagram of a simple on-off control switch.

The basin's pH is measured using a sidestream sampling system. Discrete switches (AC) associated with the pH analyzer (AIT) are used to control the reagent valve. As long as the sidestream's pH is low, the reagent valve will be open. The analog value is recorded on a chart recorder (AR).

This system is typically limited to processes in which the wastewater flow rate is relatively small and the hydraulic residence or liquid holdup time in the control system is relatively large. The detention time in the reaction vessel should be at least 10 minutes.

Adequate mixing and agitation prevent the pH electrodes from detecting an incorrect pH, which would result in the discharge of material outside the desired pH limits. Agitation turnover time of the tank contents should be less than 20% of the hydraulic residence time. For example, if the residence time is 10 minutes, the turnover time should be less than 2 minutes.

If the flow rate or the total acidity or basicity of the wastestream varies by a factor of 10 000 (e.g., a change of four pH units at a constant flow or a change of three pH units accompanied by a 10-fold change in flow rate), then two reagent valves are needed. A large valve may be required for the gross reagent addition and a small valve for the trim addition of the reagent.

Multimode Control. When the volume of spent acid or base is relatively high, it is impractical to provide the long hydraulic detention time required by on-off control systems. Systems for these conditions are designed with multimode control (Figure 14.22), which permits continuous flow-through of the neutralized material. Wastewater continuously enters the retention basin and overflows the discharge weir.

The pH value of the waste in the retention basin is measured external to the basin in a sidestream sampling system, and the analog value is recorded on a chart recorder (AR). An analog controller (AIC) is used to control the reagent valve. The input to the controller is the measured pH value of the waste in the retention basin. The amount of neutralizing agent added depends on the deviation of the liquid's pH from an internal reference pH, that is, the "setpoint" on the pH control system. The output will throttle the pneumatically controlled reagent valve via an electronic-to-pneumatic converter (FY-I/P).

Several considerations enter into the design of such a control system. A system's *buffering capacity* is its ability to absorb a neutralizing agent without a change in pH. Typically, a high buffering capacity is favorable for effective control because it levels out abrupt changes, allows adequate time for mixing, and, thus, reduces extreme changes in the position of the final control element.

Unfortunately, pH-neutralization systems seldom have high buffering capacity. Because pH is a logarithmic function of concentration, it is frequently desirable to use

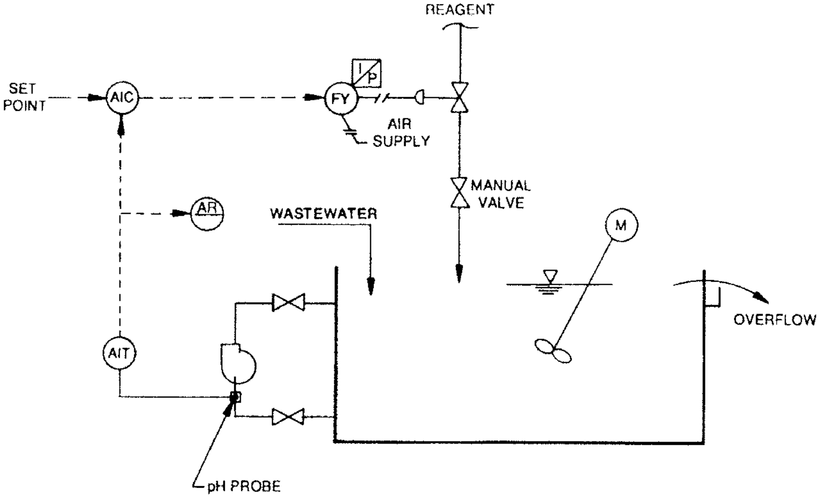


FIGURE 14.22 A process diagram of a simple multimode control system.

sodium carbonate or other weak bases to neutralize mineral acids. These agents offer some buffering capacity, which reduces sharp changes in pH.

The system must have enough hydraulic detention time to complete the neutralization reaction. This is extremely important when a slurry or dry chemical feed is used as the control agent. Proper mixing is also required to eliminate delays in the development of the desired pH level. Dead volume and short-circuiting in the reaction vessel create inefficient neutralization and pH control problems.

Cascade Control. Proper pH control can sometimes be obtained using a cascade control system with feed-forward and feedback controls (Figure 14.23). This system should only be considered, however, when the wastewater's pH does not vary widely. With the cascade system, wastewater continuously enters the first retention basin and overflows the discharge weir into the second retention basin.

The pH of the wastewater in the first retention basin is measured externally in a sidestream sampling system, and the analog value is recorded on a chart recorder (AR-"A"). An analog controller (AIC) is used to control the reagent valve. The input to the controller is the measured pH of the wastewater in the first retention basin.

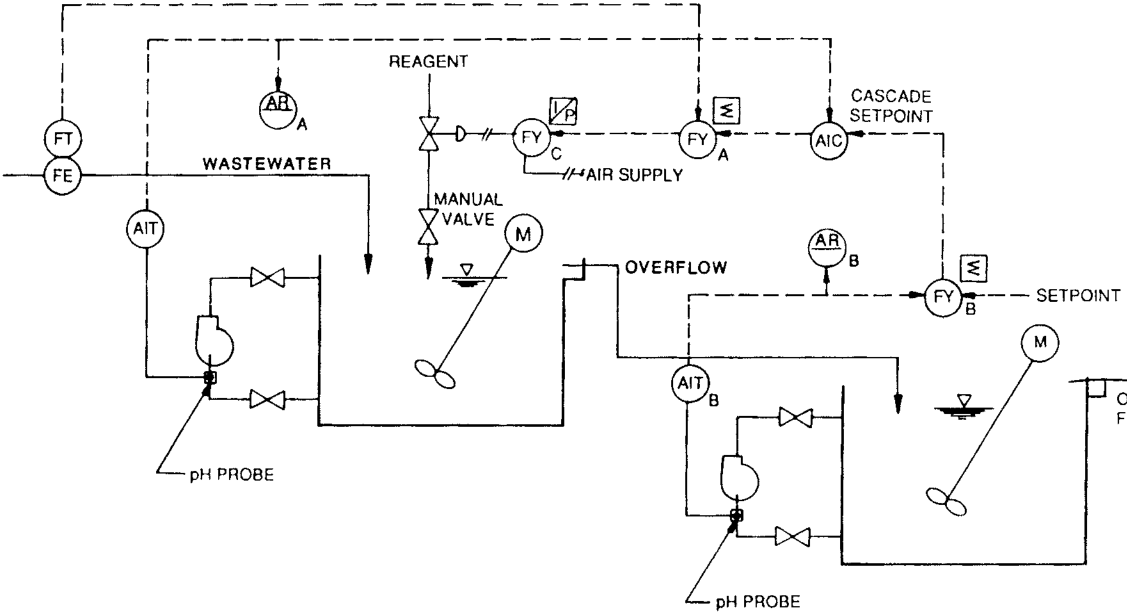


FIGURE 14.23 A process diagram of a cascade control system with feedback and feed-forward control loops.

The pH in the second retention basin is also measured using a sidestream sampling system, and the analog value is recorded (AR-"B"). The desired pH value of the waste in the first retention basin is entered as one input to a signal summer (FY-"B").

The second input to the summer is the actual pH value in the second retention basin. The output of this summer (FY-"B") is the cascade setpoint for the analog pH controller (AIC). The analog controller's output will be one input to another signal summer (FY-"A"). The second input to this integrator will be the feed-forward signal from the influent waste flow meter (FE/FT). The output of the other summer (FY-"A") will throttle the pneumatically controlled reagent valve via an electronic-to-pneumatic converter.

The first signal summer (FY-"B") adjusts the controller cascade setpoint up or down, depending on the actual pH in the second retention basin. If the desired pH is 7.0 and the actual value in the basin is 6.5, then FY-"B"'s output must increase, thereby increasing the analog controller's (AIC) output and causing the reagent valve to add more neutralizing chemical to raise the first retention basin's pH.

Likewise, if the actual pH was higher than 7.0, the signal summer (FY-"B") output would decrease the setpoint to the controller, thereby reducing the amount of reagent added to the first basin.

The function of the second signal summer (FY-"A") is to anticipate needed changes in reagent addition based on the actual volume of wastewater entering the first retention basin. If the inflow rate increases, more reagent would be required. This feed-forward signal allows the reagent valve to control changes in pH before the controller sees the addition error.

The reaction vessel should be cubic, with the volume dependent on the reaction and flow rates. The inlet and outlet on opposite sides of the reactor to reduce short-circuiting. The reagent may be added at the inlet, or it may be added to the influent before the stream enters the reactor. An agitator should be provided to ensure good mixing, and baffles should be installed in the tank to avoid a whirlpool effect.

A propeller or axial-flow impeller mixer or air injection may be used for mixing. The agitation should be vigorous enough that the system's dead time is no more than 5% of the vessel's hydraulic retention time. *Dead time* is the period between when the reagent is added when any change in pH is first detected. A short dead time is required so the control system is adjusting the reagent feed rate based on current information.

A hydraulic detention time of at least 5 minutes should be provided with liquid neutralizing reagents. Solid neutralizing reagents require a hydraulic detention time of at least 10 minutes. If dolomitic lime is used, as much as 30 minutes detention is required.

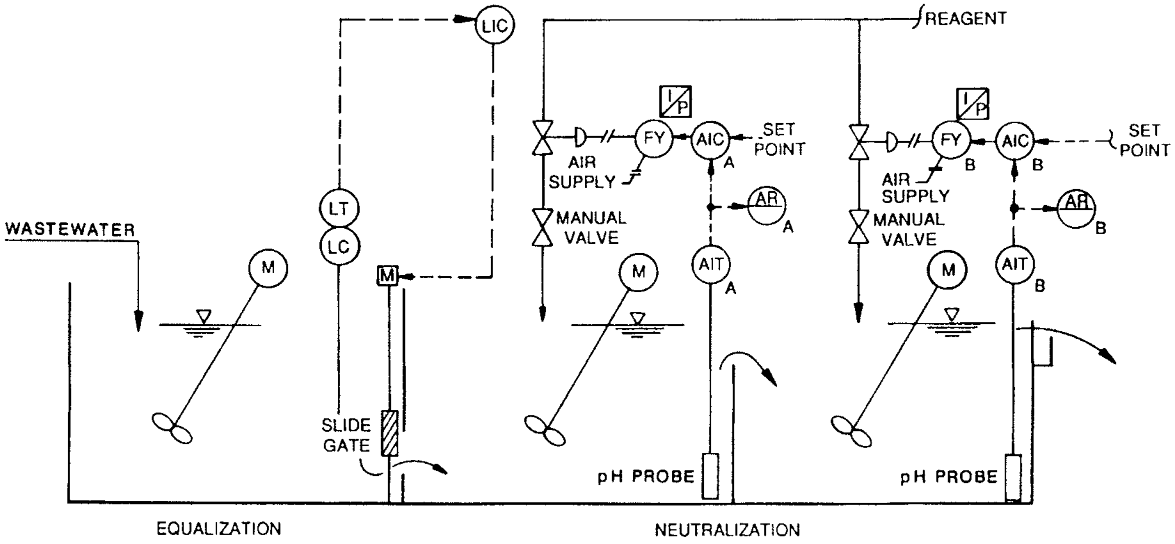


FIGURE 14.24 A process diagram of a two-stage neutralization system with equalization.

Two-Stage Neutralization. The accuracy of the final pH adjustment depends on the range of pH control required. If the influent pH is 1.0 and the effluent pH is supposed to be 7, then the control system must be accurate to 1 ppm. If the flow rate also fluctuates widely, the control system must be accurate from 1 ppm to perhaps 1 part per 100 million. No one control valve or element can be this accurate; an accuracy of 1-2% is more typical. The solution is to use upstream equalization and more than one control element (Figure 14.24).

For a wide pH adjustment range, three subsystems are sometimes used in series. For example, in the first stage, the pH is raised from pH 1 to about 3, a procedure that requires an accuracy of only about 1 part per 100. In the second stage, the pH would be raised to about 5, and in the third stage, the pH could be raised to about 7. Each stage is controlled in the same manner. The actual pH of each stage is measured and the analog value recorded on a chart recorder (AR). This measured value is the input to the analog pH controller (AIC) for each stage. The desired pH is selected at the second-stage pH controller, the output of which positions the reagent valve for continuous chemical addition.

An excellent reference for designing pH-control systems is *Advanced pH Measurement and Control* (ISA, 2005).

DESIGN OF ORP CONTROL SYSTEMS. The control systems for ORP and pH are virtually identical; the principal differences are that the pH probe is replaced with an ORP probe, and the acidic and caustic reagents are replaced with oxidizing and reducing reagents. The choice of construction materials depends on their chemical compatibility with the reagents and the process fluid.

A solution's ORP depends on its pH. Oxidation-reduction potential increases as the pH drops and decreases as the pH rises. So, for ORP control to be effective, the pH must be kept relatively constant or else the control loop must adjust as the pH changes.

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Chapter 15

Project Procurement

Early identification of environmental needs is critical to industry. Environmental projects must allow manufacturing operations to be uninterrupted, comply with regulatory and environmental requirements, and provide cost-effective, long-term environmental solutions.

Early project identification is especially important, because the project life-cycle for even a medium-size pretreatment project is often more than 2 years. Internal budgeting cycles and approvals could lengthen the project life even more.

This chapter introduces the steps required to procure an industrial pretreatment system. The discussions include both traditional and nontraditional procurement approaches.

REGULATORY REVIEW

Industrial pretreatment projects typically arise out of discussions with municipalities and state and federal regulators. Regulators may introduce new or stricter discharge limits for POTWs, for example, that trigger changes to industrial pretreatment standards and lead to the need for more industrial pretreatment. Municipalities can also change pretreatment requirements because of overall capacity limitations. Many states require municipalities to begin identifying projects (called *facilities planning*), when the POTW reaches a predetermined capacity, often 85% of design capacity.

To avoid this requirement, municipalities try to reduce industrial loads on their POTWs via more restrictive pretreatment standards or higher surcharges for organic loading, suspended solids, nutrients, etc.

Frequent interaction with regulators and municipal officials is advisable to identify upcoming changes as early as possible to allow for an orderly project-development process.

PROJECT LIFE CYCLE

A project's life-cycle typically consists of the following steps:

- Project identification,
- Feasibility study (facilities plan),
- Detailed design,
- Project construction, and
- Project startup and operation.

Some or all of these steps can be consolidated under more nontraditional procurement processes, but all must still be executed.

The life cycle of traditionally procured industrial pretreatment project is often 2-3 years, depending on the project's size and complexity and the company's capital budgeting cycle. As a result, early identification of projects is critical to obtaining the necessary funding and executing those projects to maintain environmental compliance.

PROJECT IDENTIFICATION

Project identification is the first step in the project life-cycle. It typically is initiated by in-house environmental staff, possibly with the assistance of a consultant.

Project identification begins with:

- A historical review of the pretreatment process's effectiveness in meeting pretreatment standards;
- A audit of existing pretreatment facilities (e.g., the age and condition of existing process tankage and equipment);
- An assessment of the existing processes' treatment capacity (e.g., wastewater treatment capacity, hydraulic capacity, and solids-processing capacity);
- A review of future production changes that could affect the quantity or nature of any wastes to be treated;
- Discussions with regulatory and municipal officials to determine upcoming changes to regulations or surcharges; and
- Development of preliminary needs and cost estimates.

FEASIBILITY STUDY

The *feasibility study* (facilities plan) is an evaluation to further define the project. The feasibility study typically is prepared by a consultant and includes the following:

- A summary of regulatory requirements and industrial surcharges, including any proposed changes;
- A summary of the existing facilities' past treatment performance;
- An assessment of new pretreatment needs (e.g., proposed production changes, municipal surcharge increases, or more restrictive discharge standards);

- The possible need for pilot-testing or treatability studies before final design (the cost and effort involved is often a small fraction of the cost of the full-scale facilities);
- Identification of alternatives to meet the anticipated changes;
- A preliminary (± 25%) estimate of the capital and operating costs of identified alternatives;
- Identification of the alternative's short- and long-term effects;
- A present value analysis of alternatives [the time period used should approximate the expected life of the facilities, but not be longer than 15 years; the discount rate used should be the company's weighted average cost of capital (WACC)—the weighted average of the company's after-tax cost of debt and its return on equity];
- Selection of a recommended approach; and
- Preparation of the preliminary process design, including materials balance, preliminary process design data, standards and codes to be used, and more refined estimates for capital and operating costs.

A feasibility study can be completed within 2 to 3 months. It forms the basis for procuring more services to complete the project.

DESIGN

Whether the design is created in-house, by a design consultant, or via a turnkey project, the detailed design phase builds on the feasibility study to produce detailed plans and specifications for construction, called *contract documents.*

IN-HOUSE ENGINEERS VS. OUTSIDE DESIGN FIRMS. One question that often arises is whether the facility should have its staff design the project or hire a design consultant. One major advantage of using a consultant is *professional liability insurance* (errors and omissions insurance), which covers design errors by a professional. Without such insurance, a facility may be exposed to more liability than it wishes to assume. For example, if a leak or an overflow from a poorly designed chemical feed system causes a health and safety problem in the community, the industry would almost certainly be liable for damages.

Also, municipalities and regulators frequently require that the design documents be prepared and stamped by professional engineers and architects who are registered in the state where the project is located. In practice, this requires that environmental process, structural, mechanical, electrical, and instrumentation engineers each stamp their drawings. This requirement typically makes a design engineer or design-build contractor a necessity for most substantial pretreatment projects.

DESIGN DRAWINGS. The number of design drawings needed for a pretreatment facility could range from a minimum of, say, 10 drawings for a simple project, to 50 or more for a large or complex project. The drawings provide the basis for taking bids and evaluating bids, as well as providing an overall plan for construction.

Design drawings include:

- General layout and civil site drawings;
- Architectural renderings (e.g., plans, elevations, and details) of any buildings, window and door schedules, and finish schedules;
- Structural drawings (e.g., foundation and wall details for buildings and process tankage);
- Mechanical drawings, schedules, and details of process equipment, plumbing, heating, and ventilation and air-conditioning (HVAC) systems;
- Electrical power plans and details, electrical single-line diagrams, motor control center elevations and wiring, and wiring schematics;
- Instrumentation piping and instrumentation (P&ID) diagrams and mounting details.

Table 15.1 is a typical drawing list for a medium-sized pretreatment facility with process tankage and equipment and a separate operations building. The construction contractors' bids will be based on these drawings, as will the evaluation of these bids. The overall plan construction plan will also be based on these drawings.

DESIGN SPECIFICATIONS. The contract specifications accompany and supplement the design drawings. The specifications include:

- Bid forms and the construction contract, including contractor payment terms;
- A written description of work to be performed;

Table 15.1 Typical drawing list for an industrial pretreatment facility.

Drawing	Discipline	Title
1	Process	Cover Sheet and Drawing Index
2	Process	Process Flow Diagram
3	Process	Materials Balance
4	Process	Hydraulic Profile
5	Instrumentation	Process and Instrumentation Diagram
6	Instrumentation	Process and Instrumentation Diagram
7	Civil	Site Plan
8	Civil	Civil Details
9	Structural	Structural Plans For Tanks and Building
10	Structural	Structural Sections
11	Structural	Structural Beam and Column Details
12	Architectural	Roof Plan, Elevations, and Schedules
13	Mechanical	Mechanical Plans
14	Mechanical	Mechanical Sections and Details
15	Mechanical	Mechanical Sections and Details
16	HVAC	Heating, Ventilating, & Air-Conditioning Plan
17	Mechanical	Plumbing Plan and Details
18	Electrical	Electrical Site Plan and Details
19	Electrical	Power and Lighting Plan
20	Electrical	Single-Line Diagram
21	Electrical	Motor-Control Centers
22	Miscellaneous	Miscellaneous Standard Details and Schedules

- A summary of appropriate codes and standards that the contractor must follow;
- General construction procedures and safety standards to be followed;
- Any special conditions or procedures (e.g., allowed contractor working hours, maintaining utilities to certain industrial processes);
- Testing procedures and services required;
- Standards and methods for supplying and placing concrete, reinforcing steel, steel tanks, piping, valves, and other appurtenances;

- Named suppliers of mechanical and electrical equipment, instruments and instrument panels, laboratory equipment, pre-fabricated buildings, doors and windows, and finishes. While suppliers and or model numbers are often named, the owner (or the owner's representative) may accept an alternate supplier or equipment that meets the intent of the specification.

The contract documents (both drawings and specifications) must often be submitted to regulators and municipal officials for review and comment. The design consultant may also evaluate them.

CONSTRUCTION

Under a conventional procurement, selected contractors submit bids based on the contract documents. Alternate bids may be allowed—at the discretion of the owner or owner's representative—so long as they are based on the contract documents. An *alternate bid* is a bidder's proposal to achieve the owner's goals using a different process or different materials than is specified. For example, an alternate bid might propose using plastic rather than ductile iron pipe, or using diffused rather than mechanical aeration. Alternate bids can complicate and lengthen the award process, so they should be limited in the contract documents.

Construction bids typically are lump sum: the contractor agrees to provide all services specified in the contract documents at a fixed price. The owner or owner's representative selects the contractor with the lowest, responsive bid or alternate bid (i.e., the lowest price that conforms to all of the contract's requirements). The bid price can be adjusted, however, via change orders if the contractor's scope of work changes (anticipated or not) or there are delays outside of the contractor's control.

The following are key areas of construction management outlined in the construction specifications.

BONDS. The contract documents typically provide for two types of bonds or sureties: a bid bond and a performance bond. A *bid bond* protects the owner from losses suffered if the low bidder refuses to enter into the contract at the bid price. If that happens, the bid bond is forfeited to the owner. The amount forfeited is the difference between the two lowest bids. This bond is often 5 to 10% of the estimated contract price.

A *performance bond* guarantees that the contractor will complete the project satisfactorily. If the contractor fails to complete the project or defaults, the bonding company or surety must then step in to complete the project. The performance bond is typically issued for the full contract price.

CONSTRUCTION INSPECTION. Typically, at least one construction inspector or resident engineer is onsite continuously during the construction. More inspectors may be required, depending on the project's size and complexity. The construction inspector is responsible for ensuring that the project is built according to contract requirements (e.g., process and material specifications). The inspector also typically receives the contractor's progress payment request and recommends approval or modifications. In addition, the inspector evaluates the need and justification for any change orders requested by the contractor.

Construction inspectors typically are provided by the design engineer rather than the owner to maintain a clear line of responsibility for the project's design and implementation.

SHOP DRAWINGS. Shop drawings are typically the construction contractor's responsibility. They typically include more detailed arrangement and installation drawings, catalog cuts of proposed equipment, detailed reinforcing steel drawings, wiring diagrams, and specific materials and manufacturers proposed for use.

These drawings are submitted for approval to the designer's site or office engineering staff. They also may be submitted to the owner for review or approval. The drawings are reviewed for both conformity to the contract documents and overall suitability for the project.

The contractor may not purchase any equipment or materials without approved shop drawings, so they must be processed expeditiously (typically within 2 weeks of receipt). Failure to review shop drawings promptly is a common source of change order or extension requests by the contractor.

PROGRESS PAYMENTS. Typically, the construction contractor prepares a monthly payment request and submits it to the construction inspector, who reviews it for completeness and accuracy. Unless otherwise specified in the construction contract, the contractor bills for materials delivered to the site, and partially for equipment to be installed. All monthly progress payments are reduced for retainage. Retainage is defined in the contract.

With regard to equipment, contractors typically bill a certain amount (30%) when the order is placed, a second (30%) when the equipment arrives onsite, a third (20%)

when the equipment is installed, and a final amount (15%) when a manufacturer's representative certifies that the equipment is ready for operation. These percentages are typical and assume 5% retainage.

RETAINAGE. Most construction contracts provide for *retainage*—a practice in which the owner keeps back a percentage of the contractor's progress payments (typically 5 to 10% of the total contract). The practice is intended to protect the owner against the contractor's failure to satisfactorily complete the project, particularly the "punch list" or "snag list" of incomplete items at the end of a project. The retainage is typically released to the contractor once the project has been completed and accepted.

CHANGE ORDERS. A *change order* (variation order) is an extra cost that results from a change in conditions or project scope that is beyond the contractor's control. A change order would be requested, for example, if:

- The contractor unexpectedly finds rock, groundwater, or soil conditions not disclosed in the design documents;
- The owner or engineer (with owner approval) requests more work or changes to the original contract;
- A delay occurs at no fault to the contractor (e.g., the owner or design engineer fails to provide site access or electricity, obtain contractual permits, or review shop drawings expeditiously); or
- A *force majeure (greater force)*—an extraordinary or unforeseen event beyond the control of the parties (e.g., floods, drought, strikes, terrorism, fire, etc.)—occurs. In the event of a force majeure, performance under the contract is suspended until the force majeure ends or the contract is terminated (if the project cannot continue).

In these cases, the contractor initiates a change order request and submits it to the construction inspector for review and comment. The request is then typically submitted to the designer and the owner. Change order requests are often negotiated based on the contract provisions and precedent.

LIQUIDATED DAMAGES. *Liquidated damages* are payments made by the contractor to the owner (or monies withheld by the owner) as a result of project-completion delays. Usually expressed in dollars per day of delay, liquidated damages are supposed to compensate the owner for the damage caused by the contractor's failure to complete the project within the contracted schedule.

These damages could include additional surcharges, fines from regulatory agencies, or other costs. The amount should reasonably represent actual damages; excessive damages will inflate all bids and may be ultimately uncollectible. Typical liquidated damages for environmental projects are $500 to $1000 per day.

STARTUP AND OPERATION

When the project is certified to be ready for startup, the design engineer will typically provide process assistance and training to the owner's operating staff for the startup period. Training would typically begin 1 to 2 weeks before plant startup.

The startup period depends on the processes used. If the processes used are physical and/or chemical processes (e.g., sedimentation, flotation, chemical addition, filtration, and carbon adsorption) the required startup period is 1 to 2 weeks. If the process is biological, the startup period is typically 2 to 3 weeks in summer and 4 to 6 weeks in winter to establish the microorganisms at the proper level for treatment.

OPERATIONS AND MAINTENANCE MANUAL. The operations and maintenance (O&M) manual is actually a combination of several manuals: a process manual typically prepared by the design engineer, and the collection of manuals provided with the new equipment. The process O&M manual typically consists of the following chapters or sections:

- Introduction,
- Permits and standards,
- Wastewater process operations and controls,
- Solids process operations and controls,
- Personnel,
- Laboratory testing,
- Recordkeeping,
- Maintenance,
- Safety, and
- Emergency response and troubleshooting.

The manual should be prepared about 1 month before startup so the owner's operating staff can become familiar with how to operate and maintain the new facilities. The manual and training materials are the primary training tools before startup.

WARRANTY PERIOD. Contracts typically include a 1-year warranty period, during which the contractor addresses any construction and equipment defects that arise. This period typically begins on the date of substantial completion.

In addition, most turnkey projects (e.g., DBO and BOT) also include process performance warranties, which require the contractor and the proprietary process or equipment subcontractors to demonstrate that the process or equipment meets the performance standards stipulated in the contract.

The presence of a warranty does not eliminate the owner's need to maintain the equipment properly. In fact, failure to maintain the equipment invalidates the warranty.

TRADITIONAL VERSUS ALTERNATIVE PROJECT PROCUREMENT METHODS

Industrial wastewater treatment facilities have become more complex as new processes and more treatment is used to meet stricter environmental regulatory requirements. Also, a decrease in the quality and quantity of water supply sources is increasing the use of reclamation/reuse strategies, and many industrial sites are finding zero-liquid-discharge options to be a cost-effective and timelier alternative to pretreatment for discharge. In addition, the number of treatment options is growing at the same time that the engineering and operating staffs of many industrial facilities are being reduced. So, facilities are looking for alternative to the traditional procurement and O&M methods; many industrial facilities are now outsourcing some or all of the environmental services required at their plants.

In this context, *outsourcing* is the process of relying on a vendor to provide treatment services at a predetermined and guaranteed cost, typically through a long-term partnership focusing on safety and compliance. The vendor may simply operate and maintain the facility's pretreatment system or may design, build, own, and operate the system, which is housed onsite, under a contract with facility.

The traditional project delivery approach involves discrete, sequential project components and contractual relationships between an owner and multiple vendors. Alternative project delivery models reduce the number of contractual relationships and increase the vendor's roles and responsibilities. Following is a review of the contractual framework of several of the most common project delivery methods (Table 15.2).

TABLE 15.2 Summary of project procurement methods.

Procurement method	Abbreviation	Summary/ Application	Advantages	Disadvantages
Design-bid-build	DBB	• Traditional method • Separate owner-designer and owner-contractor contracts • Owner finances • Designer monitors contractor	• Well understood method • Owner has high level of control	• Longest implementation period • Lack of emphasis on life-cycle costs and innovative processes and techniques
Design-build	DB	• Single owner-contractor contract • Owner finances • Single point of responsibility/ liability	• Single point of responsibility • Shorter schedule than DBB • Lower costs through innovation	• Less owner control of project • Possible need for technical oversight staff • Owner must operate
Construction manager at risk	CMR	• Variation of DB method • CM assumes more project risk including development and capital cost risk than DB	• Benefits of DB method • Owner has lower development and capital cost risk	• Disadvantages of DB • Financial stability of CM is critical
Engineer-procure-construct	EPC	• Single owner-engineer contract—large contracts • Owner finances • Project is performance-based rather than specification-based • Most of project subcontracted through competitive bids • Used on large projects	• Benefits of DB method • Owner has lower development and capital cost risks	• Less owner control of project • Possible need for technical oversight staff • Financial stability of engineer is critical

Procurement method	Abbreviation	Summary/ Application	Advantages	Disadvantages
Design-build-operate	DBO	• Single owner-contractor contract • Owner finances • Contractor also operates facilities at fixed price • Single point of responsibility/ liability	• Single point of responsibility • Shorter schedule than DBB • Lower costs through innovation	• Less owner control of project • Possible need for technical oversight staff
Design-build-own-operate-transfer	DBOOT	• Single owner-contractor contract • Contractor finances and owns through contract period • Contractor also operates facilities at fixed price • Single point of responsibility/ liability • Ownership transferred to industry at contract end	• Single point of responsibility • Shorter schedule than DBB • Lower costs through innovation	• Less owner control of project • Possible need for technical oversight staff • May restrict industrial operations • Contractor's cost of capital may not be comparable to industry
Operations and maintenance service contract	O&M	• Single owner-operator contract • No financing, operations only • Operator assumes performance liabilities	• Reduced risk of operations to owner • Generally lower cost to owner	• Less owner control • Potential for union protest if non-union operator used or if new procedures and work rules proposed

TRADITIONAL PROJECT PROCUREMENT (DESIGN-BID-BUILD). The traditional project-procurement model used by many industries and municipalities is called *design-bid-build* (DBB). Under this approach, the owner has separate contractual relationships with the design engineer and construction contractor (and later with an O&M firm, if the owner chooses not to run the system itself). First, the owner identifies the need for a new project. Then, the owner prepares a feasibility study or facilities plan that identifies and describes the proposed project, any alternatives, the project's capital, and operating costs. The owner also prepares a cost, benefit, and payback analysis to obtain internal financial support for the project. These evaluations may be prepared by in-house staff or by consultants.

Once the project has been funded internally, a design engineer is hired to design the facility and prepare the contract documents: detailed design drawings, technical specifications, and bid documents. Once bids are received, the design engineer evaluates the bids before the owner chooses one (typically, the contractor with the lowest responsive price). The design engineer then typically oversees the contractor during project construction, construction inspection, and shop drawing review.

The owner is typically responsible for obtaining all permits, arranging funding, and operating the plant it now owns when construction is complete. The owner also bears responsibility for most of the cost, performance, and scheduling risk.

The design-bid-build approach is well understood and allows the owner a lot of control and involvement. It also is more transparent and facilitates public review of the contract process. However, the sequential phasing of DBB projects makes them longer to complete than other procurement models. The projects are also vulnerable to delays if disputes arise among participants.

Also, because DBB contracts typically are focused on capital costs, innovative technologies may be ignored, even if their life-cycle costs are lower than those of the chosen technologies. Neither the engineer nor the contractor has an incentive to promote such technologies.

DESIGN-BUILD. In the design-build delivery model, there is only one contractual relationship: the one between the owner and a design-build contractor. (The owner may hire an O&M firm later or operate the system itself.) The design-build contractor may be one party or another entity (e.g., joint venture) comprised of a design consultant and a construction contractor.

The project criteria (e.g., performance specifications and partial design), which may be prepared by the owner or an independent consultant, are the basis of the request for proposals (RFP) solicitation used to select the design-build contractor and establish a fixed (lump-sum) or guaranteed maximum price for the project.

This approach has several benefits. The owner only has to hold one contractor accountable for project success. Project schedules should be streamlined because of the concurrent work and closer alliance between the design engineer and contractor. There also should be fewer conflicts or disputes between them.

The owner must concede some control over design details, but may benefit from newer, more innovative technology while transferring the resulting risk to the design-build contractor. The owner is responsible for obtaining all permits, although some of this responsibility may be shared with the contractor.

A design-build approach will provide the owner with a guaranteed cost, schedule, and performance for the project. Sometimes, a guarantor will be part of the project structure guaranteeing the contractor’s obligations to the owner. Design-build projects should result in an earlier identification of the total project cost and shorter project delivery schedules, which may result in lower overall project costs.

CONSTRUCTION MANAGER-AT-RISK. One variation of the design-build project is the construction manager-at-risk (CMR) model—sometimes called engineer-at-risk (EAR)—in which the construction manager accepts more project-development, permitting, design, and capital-cost risks. Owners typically define the project criteria and complete up to 35% of the design before selecting a CMR/EAR contractor. These projects tend to focus on an aggressive schedule and low delivered cost.

ENGINEER-PROCURE-CONSTRUCT. Engineer-procure-construct (EPC) contracts are frequently used to develop large industrial projects whose schedule and performance are particularly important. They are similar to design-build contracts, but are performance-driven, rather than specification-based, so most of the construction work is subcontracted to specialty contractors and technology providers. Also, EPC projects tend to be larger (e.g., more than $50 million). EPC contractors usually bid most elements of work competitively to specialty subcontractors and technology providers.

DESIGN-BUILD-OPERATE. A design-build-operate (DBO) project involves a single contractual relationship between an owner and a DBO service provider. It streamlines the project delivery schedule and reduces costs by eliminating separate selection processes for engineering, construction, procurement, and operating services. This approach is often used on projects where project performance and service are more important than procurement details.

DBOs are particularly popular for fast-track and complex projects involving new technology or special O&M expertise. The contracts are complex, addressing project development, engineering, construction, *and* operations. So, the owner's management-support team should include a procurement advisor, design engineer, attorney, and financial advisor.

Owners may grant DBO contractors wide latitude in both the choice of technologies and their application. The DBO project team often includes a technology provider specializing in process treatment. So, the team may be willing to accept the risk of using new and innovative solutions, to lower production costs and improve operability. Also, because DBO contractors have a vested interest in controlling operating expenses, they are more likely to "value engineer" plant designs and use more expensive, state-of-the-art technology with lower life-cycle costs.

One DBO participant will be the project guarantor, who provides the owner with cost, schedule, and performance guarantees (e.g., the project will perform as required and the equipment will be maintained, repaired, and replaced according to reasonable and measurable standards).

DESIGN-BUILD-OWN-OPERATE-TRANSFER. Design-build-own-operate-transfer (DBOOT) projects are an expansion of the DBO concept in which the DBOOT contractor also finances the project and owns the asset. The contract itself often serves as collateral to secure commercial financing.

The entity desiring treatment services—supported by financial, legal, technical, and environmental advisors—selects the successful DBOOT contractor from other pre-qualified consortiums based on a conceptual design, operating plan, and guaranteed treatment cost. The contractor's team may consist of two or more shareholders, who form a special-purpose (project) company to execute the project.

The contract defines all aspects of the service delivery agreement (e.g., contract term, production requirements, water tariff, financing arrangements, guarantees, warranties, and all remedies). It also contains provisions to transfer ownership of the asset from the project company to the industrial owner. It may occur at the end of the contract term or on a mutually agreeable date before the contract expires. The transfer payment is either the "fair market value" of the enterprise or the amount of remaining indebtedness.

The primary benefit of a DBOOT approach is that the contractor assumes both the technical and commercial risks (e.g., the risks of development, permitting, and financing). The owner is relieved of the project's financial burden and well-insulated from its liabilities and risks; the facility only pays for wastewater treatment.

OPERATIONS AND MAINTENANCE SERVICE CONTRACT. Under an O&M service contract, a facility hires another organization to operate and maintain its wastewater treatment system, typically at a fixed price. The term of the contract can vary, but is typically 5 years. The contractor typically indemnifies the owner against fines for discharge violations and industrial surcharges from municipalities.

Operations and maintenance contracts are increasingly used for complex projects, large projects requiring several new staff, and labor-intensive projects. The principal benefits of the O&M contract are:

- No need to hire more operating staff;
- A fixed price that often is less than in-house operation;
- Guaranteed performance; and
- Indemnification against additional costs and regulatory fines.

While providing significant benefits, O&M contracts can lead to labor difficulties with existing employees. To keep operations costs low, most O&M contractors use less labor, employ more automation, streamline personnel procedures and work rules, and offer performance incentives. However, the contractor may not wish to hire all existing workers, or may propose work rules that do not conform with the owner's work rules.

PREDICTIVE MAINTENANCE CONTRACTS. A new area of interest to both industries and municipalities with expensive equipment is preventive or predictive maintenance. *Predictive maintenance* is the practice of monitoring critical equipment to anticipate and prevent a major or catastrophic failure.

Under a predictive maintenance contract, the equipment-owning industry retains a firm specializing in predictive maintenance to survey its operating equipment (either once or periodically). In environmental applications, predictive maintenance is typically applied to blowers, compressors, pumps, and engine-generator sets. The parameters typically monitored include vibration, shaft alignment, oil temperature, oil analysis, and hot spots in motor control centers and other electrical equipment.

Vibration analysis of rotating machinery is a major component of predictive maintenance contracts. Vibration analysis can reveal early problems with machinery imbalance, shaft misalignment, or impending gear or bearing failure.

A second key area of predictive maintenance is lubrication analysis. This involves evaluating a lubricant's condition and noting whether foreign material (e.g., metal chips or water) is present. A lubricant breakdown may cause catastrophic machine failure. Foreign materials may be an early indication of machine wear or corrosion.

Another key predictive maintenance area is *thermography*—the thermal analysis of transformers, motor control centers, and major electrical connections. Hot spots may indicate loose connections and poor efficiency.

Significant anecdotal evidence in the environmental industry indicates that predictive maintenance yields significant benefits (e.g., less downtime, lower overtime costs, and avoidance of noncompliance problems).

SUGGESTED READINGS

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Appendix

Conversions from SI to U.S. Customary Units

SI unit	Conversion equation	U.S. customary unit
centimeter (cm)	(cm)(0.3937) = in.	inch (in.)
cubic centimeters per liter (cm^3/L)	(cm^3/L)(0.2309) = cu in./gal	cubic inches per gallon (cu in./gal)
cubic meter (m^3)	(m^3)(35.31) = cu ft	cubic foot (cu ft)
	(m^3)(1.308) = cu yd	cubic yard (cu yd)
cubic meters per day (m^3/d)	(m^3/d)(0.1835) = gpm	gallons per minute (gpm)
	(m^3/d)(2.642×10^{-4}) = mgd	million gallons per day (mgd)
cubic meters per hour (m^3/h)	(m^3/h)(264.2) = gph	gallons per hour (gph)
cubic meters per minute (m^3/min)	(m^3/min)(264.2) = gpm	gallons per minute (gpm)
cubic meters per second (m^3/s)	(m^3/s)(2.119×10^3) = cfm	cubic feet per minute (cfm)
	(m^3/s)(35.32) = cfs	cubic feet per second (cfs)
	(m^3/s)(1.585×10^4) = gpm	gallons per minute (gpm)
cubic meters per meter per second ($m^3/m\cdot s$)	($m^3/m\cdot s$)(6.959×10^6) = gpd/ft	gallons per day per foot (gpd/ft)
cubic meters per square meter per day ($m^3/m^2\cdot d$)	($m^3/m^2\cdot d$)(1.704×10^{-2}) = gpm/sq ft	gallons per minute per square foot (gpm/sq ft)
cubic meters per square meter per hour ($m^3/m^2\cdot h$)	($m^3/m^2\cdot h$)(3.281) = cfh/sq ft	cubic feet per hour per square foot (cfh/sq ft)

SI unit	Conversion equation	U.S. customary unit
cubic meters per square meter per second ($m^3/m^2 \cdot s$)	($m^3/m^2 \cdot s$)(2.21×10^6) = gpd/sq ft	gallons per day per square foot (gpd/sq ft)
degrees Celsius (°C)	1.8(°C) + 32 = °F	degrees Fahrenheit (°F)
degrees Kelvin (K)	(K)(1.800) = °R	degrees Rankine (°R)
gram (g)	(g)(3.527×10^{-2}) = oz	ounce (oz)
grams per centimeter (g/cm)	(g/cm)(11.16) = oz/in.	ounce per inch (oz/in.)
grams per centimeter per second (g/cm·s)	(g/cm·s)(11.16) = oz/in./sec	ounce per inch per second (oz/in./sec)
grams per kilogram (g/kg)	(g/kg)(1×10^{-3}) = lb/lb	pounds per pound (lb/lb)
grams per liter (g/L)	(g/L)(0.1335) = oz/gal	ounces per gallon (oz/gal)
grams per liter per day (g/L·d)	(g/L·d)(0.1335) = oz/gpd	ounces per gallon per day (oz/gpd)
grams per mole (g/mol)	(g/mol)(3.527×10^{-2}) = oz/mol	ounces per mole (oz/mol)
hertz (Hz)	(Hz)(1) = cycles per second	cycles per second
kilogram (kg)	(kg)(2.205) = lb	pound (lb)
kilograms per cubic meter (kg/m^3)	(kg/m^3)(6.243×10^{-2}) = lb/cu ft	pounds per cubic foot (lb/cu ft)
kilograms per cubic meter per day ($kg/m^3 \cdot d$)	($kg/m^3 \cdot d$)(6.242×10^{-2}) = lb/d/cu ft	pounds per day per cubic foot (lb/d/cu ft)
kilograms per cubic meter per annum ($kg/m^3 \cdot a$)	($kg/m^3 \cdot a$)(6.242×10^{-2}) = (lb/yr/cu ft)	pounds per cubic foot per year (lb/yr/cu ft)
kilograms per day (kg/d)	(kg/d)(2.205) = lb/d	pounds per day (lb/d)
kilograms per hectare per day (kg/ha·d)	(kg/ha·d)(0.8922) = lb/ac/d	pounds per acre per day (lb/ac/d)
kilograms per liter (kg/L)	(kg/L)(8.347) = lb/gal	pounds per gallon (lb/gal)
kilograms per meter per hour (kg/m·h)	(kg/m·h)(0.6720) = lb/hr/ft	pounds per foot per hour (lb/hr/ft)
kilograms per metric ton (kg/tonne)	(kg/tonne)(0.4998) = lb/ton	pounds per ton (lb/ton)

SI unit	Conversion equation	U.S. customary unit
kilograms per square meter per day ($kg/m^2 \cdot d$)	($kg/m^2 \cdot d$)(0.2048) = lb/d/sq ft	pounds per square foot per day (lb/d/sq ft)
kilograms per square meter per hour ($kg/m^2 \cdot h$)	($kg/m^2 \cdot h$)(0.2048) = lb/hr/sq ft	pounds per square foot per hour (lb/hr/sq ft)
kilograms per square meter per second ($kg/m^2 \cdot s$)	($kg/m^2 \cdot s$)(0.2048) = lb/s/sq ft	pounds per square foot per second (lb/s/sq ft)
kilojoules per kilogram (kJ/kg)	(kJ/kg)(0.4300) = Btu/lb	British thermal units per pound (Btu/lb)
kilopascal (kPa)	(kPa)(9.872×10^{-3}) = atm	atmosphere (atm)
kilowatt (kW)	(kW)(1.341) = hp	horsepower (hp)
kilowatt per cubic meter (kW/m^3)	(kW/m^3)(5.076) = hp/1000 gal	horsepower per 1000 gallons (hp/1000 gal)
liter (L)	(L)(0.2642) = gal	gallon (gal)
liters per cubic meter per second ($L/m^3 \cdot s$)	($L/m^3 \cdot s$)(0.4888) = cfm/cu ft	cubic feet per minute per cubic foot (cfm/cu ft)
liters per day (L/d)	(L/d)(0.2642) = gpd	gallons per day (gpd)
liters per minute (L/min)	(L/min)(0.2642) = gpm	gallons per minute (gpm)
liters per second (L/s)	(L/s)(15.85) = gpm	gallons per minute (gpm)
liters per square meter per minute ($L/m^2 \cdot min$)	($L/m^2 \cdot min$)(40.73) = gpm/sq ft	gallons per square foot per minute (gpm/sq ft)
liters per square meter per second ($L/m^2 \cdot s$)	($L/m^2 \cdot s$)(2.121×10^3) = gpd/sq ft	gallons per day per square foot (gpd/sq ft)
meter (m)	(m)(3.281) = ft	foot (ft)
meters per minute (m/min)	(m/min)(3.281) = ft/min	feet per minute (ft/min)
meters per second (m/s)	(m/s)(3.281) = ft/sec	feet per second (ft/sec)
micrograms per liter ($\mu g/L$)	($\mu g/L$)(1) = ppb	parts per billion (ppb)
milligram (mg)	(mg)(1.543×10^{-2}) = gr	grain (gr)
milliliter (mL)	(mL)(3.382×10^{-2}) = oz	ounce (oz)

SI unit	Conversion equation	U.S. customary unit
milliliters per gram (mL/g)	(mL/g)(1.0429) = oz/oz	ounce per ounce (oz/oz)
milliliters per minute (mL/min)	(mL/min)(6.102×10^{-2}) = cu in./min	cubic inches per minute (cu in./min)
milligrams per liter (mg/L)	(mg/L)(1) = ppm	parts per million (ppm)
millimeter (mm)	(mm)(3.937×10^{-2}) = in.	inch (in.)
millimeters per second (mm/s)	(mm/s)(0.1969) = ft/min	feet per minute (ft/min)
newton (N)	(N)(1×10^{5}) = dyn	dyne (dyn)
newtons per square meter (N/m^2)	(N/m^2)(1×10^{-5}) = bar	bar (bar)
pascal (Pa)	(Pa)(1.450×10^{-4}) = psi	pounds per square inch (psi)
square centimeters per second (cm^2/s)	(cm^2/s)(0.3937) = sq in./sec	square inches per second (sq in./sec)
square meter (m^2)	(m^2)(10.76) = sq ft	square foot (sq ft)
square meter per cubic meter (m^2/m^3)	(m^2/m^3)(3.048) = sq ft/cu ft	square feet per cubic foot (sq ft/cu ft)
metric ton (tonne)	(tonne)(1.102) = ton	ton (short)
watt (W)	(W)(0.7380) = ft-lb/sec	foot-pounds per second (ft-lb/sec)
watts per cubic meter (W/m^3)	(W/m^3)(3.797×10^{-2}) = hp/1000 cu ft	horsepower per 1000 cubic feet (hp/1000 cu ft)

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