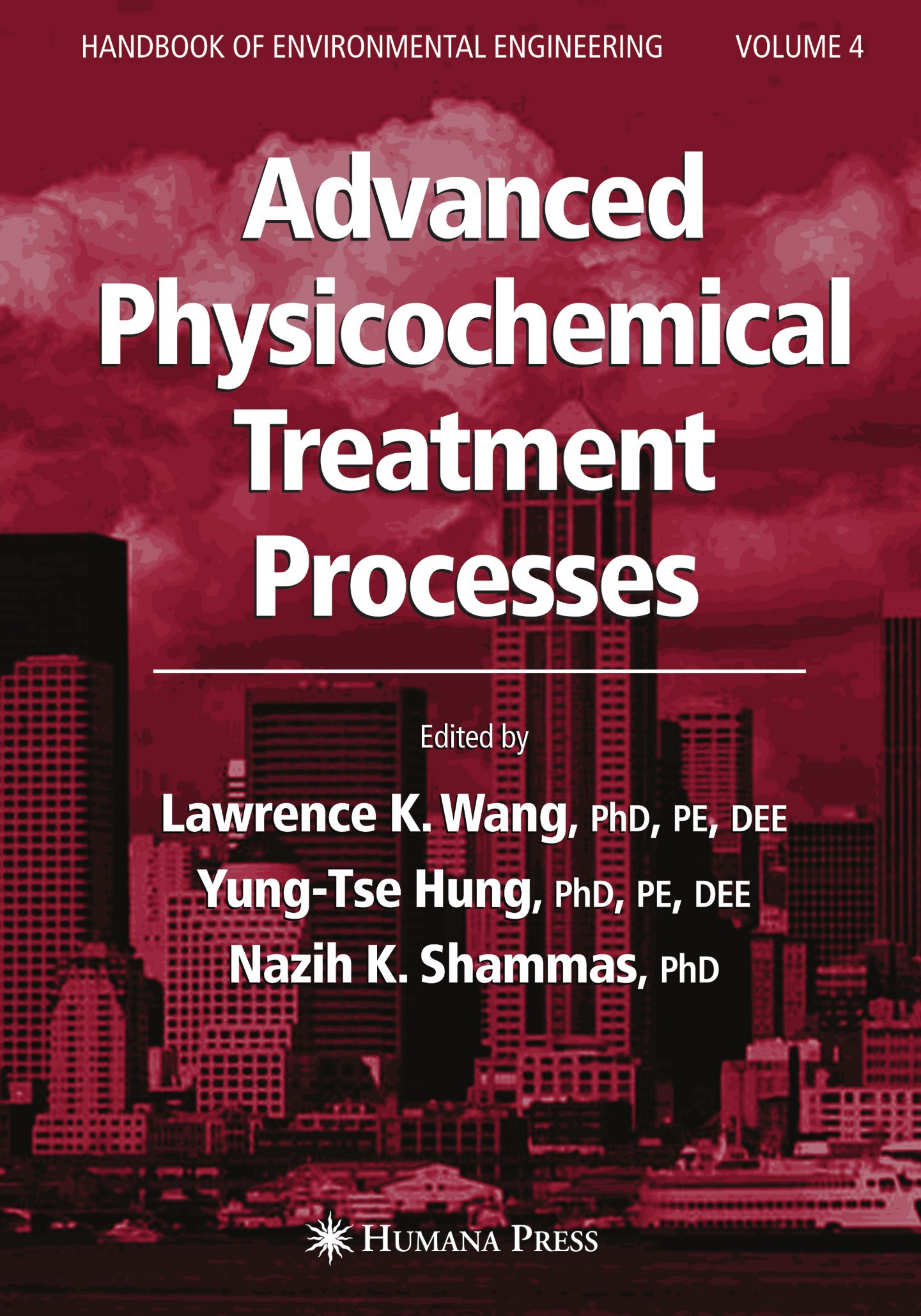
HANDBOOK OF ENVIRONMENTAL ENGINEERING VOLUME 4



Advanced Physicochemical Treatment Processes

Edited by

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Volume 4
Handbook of Environmental Engineering

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Preface

The past thirty years have witnessed a growing worldwide desire that positive actions be taken to restore and protect the environment from the degrading effects of all forms of pollution—air, water, soil, and noise. Because pollution is a direct or indirect consequence of waste, the seemingly idealistic demand for "zero discharge" can be construed as an unrealistic demand for zero waste. However, as long as waste continues to exist, we can only attempt to abate the subsequent pollution by converting it to a less noxious form. Three major questions usually arise when a particular type of pollution has been identified: (1) How serious is the pollution? (2) Is the technology to abate it available? and (3) Do the costs of abatement justify the degree of abatement achieved? This book is one of the volumes of the *Handbook of Environmental Engineering* series. The principal intention of this series is to help readers formulate answers to the last two questions above.

The traditional approach of applying tried-and-true solutions to specific pollution problems has been a major contributing factor to the success of environmental engineering, and has accounted in large measure for the establishment of a "methodology of pollution control." However, the realization of the ever-increasing complexity and interrelated nature of current environmental problems renders it imperative that intelligent planning of pollution abatement systems be undertaken. Prerequisite to such planning is an understanding of the performance, potential, and limitations of the various methods of pollution abatement available for environmental scientists and engineers. In this series of handbooks, we will review at a tutorial level a broad spectrum of engineering systems (processes, operations, and methods) currently being utilized, or of potential utility, for pollution abatement. We believe that the unified interdisciplinary approach presented in these handbooks is a logical step in the evolution of environmental engineering.

Treatment of the various engineering systems presented will show how an engineering formulation of the subject flows naturally from the fundamental principles and theories of chemistry, microbiology, physics, and mathematics. This emphasis on fundamental science recognizes that engineering practice has in recent years become more firmly based on scientific principles rather than on its earlier dependency on empirical accumulation of facts. It is not intended, though, to neglect empiricism where such data lead quickly to the most economic design; certain engineering systems are not readily amenable to fundamental scientific analysis, and in these instances we have resorted to less science in favor of more art and empiricism.

Because an environmental engineer must understand science within the context of application, we first present the development of the scientific basis of a particular subject, followed by exposition of the pertinent design concepts and operations, and detailed explanations of their applications to environmental quality control or remediation. Throughout the series, methods of practical design and calculation are illustrated by numerical examples. These examples clearly demonstrate how organized, analytical reasoning leads to the most direct and clear solutions. Wherever possible, pertinent cost data have been provided.

Our treatment of pollution-abatement engineering is offered in the belief that the trained engineer should more firmly understand fundamental principles, be more aware of the similarities and/or differences among many of the engineering systems, and exhibit greater flexibility and originality in the definition and innovative solution of environmental pollution problems. In short, the environmental engineer should by conviction and practice be more readily adaptable to change and progress.

Coverage of the unusually broad field of environmental engineering has demanded an expertise that could only be provided through multiple authorships. Each author (or group of authors) was permitted to employ, within reasonable limits, the customary personal style in organizing and presenting a particular subject area; consequently, it has been difficult to treat all subject material in a homogeneous manner. Moreover, owing to limitations of space, some of the authors' favored topics could not be treated in great detail, and many less important topics had to be merely mentioned or commented on briefly. All authors have provided an excellent list of references at the end of each chapter for the benefit of interested readers. As each chapter is meant to be self-contained, some mild repetition among the various texts was unavoidable. In each case, all omissions or repetitions are the responsibility of the editors and not the individual authors. With the current trend toward metrication, the question of using a consistent system of units has been a problem. Wherever possible, the authors have used the British system (fps) along with the metric equivalent (mks, cgs, or SIU) or vice versa. The editors sincerely hope that this duplicity of units' usage will prove to be useful rather than being disruptive to the readers.

The goals of the *Handbook of Environmental Engineering* series are: (1) to cover entire environmental fields, including air and noise pollution control, solid waste processing and resource recovery, physicochemical treatment processes, biological treatment processes, biosolids management, water resources, natural control processes, radioactive waste disposal, and thermal pollution control; and (2) to employ a multithematic approach to environmental pollution control because air, water, soil and energy are all interrelated.

As can be seen from the above handbook coverage, no consideration is given to pollution by type of industry or to the abatement of specific pollutants. Rather, the organization of the handbook series has been based on the three basic forms in which pollutants and waste are manifested: gas, solid, and liquid. In addition, noise pollution control is included in the handbook series.

This particular book Volume 4, *Advanced Physicochemical Treatment Processes*, is a sister book to Volume 3 *Physicochemical Treatment Processes*, which has already included the subjects of screening, comminution, equalization, neutralization, mixing, coagulation, flocculation, chemical precipitation, recarbonation, softening, oxidation, halogenation, chlorination, disinfection, ozonation, electrolysis, sedimentation, dissolved air flotation, filtration, polymeric adsorption, granular activated carbon adsorption, membrane processes, and sludge treatment processes. Both books have been designed to serve as comprehensive physicochemical treatment textbooks as well as wide-ranging reference books. We hope and expect it will prove of equal high value to advanced undergraduate and graduate students, to designers of water and wastewater treatment systems, and to scientists and researchers. The editors welcome comments from readers in all of these categories.

The editors are pleased to acknowledge the encouragement and support received from their colleagues and the publisher during the conceptual stages of this endeavor. We wish to thank the contributing authors for their time and effort, and for having patiently borne our reviews and numerous queries and comments. We are very grateful to our respective families for their patience and understanding during some rather trying times.

Lawrence K. Wang
Yung-Tse Hung
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Potable Water Aeration

Jerry R. Taricska, Lawrence K. Wang, Yung-Tse Hung, and Kathleen Hung Li

CONTENTS

1. INTRODUCTION

Water aeration has been long used in water treatment for the removal of odor and taste-causing compounds, the oxidation of iron and manganese, as well as corrosion control and aesthetics. Since the mid-1970s, however, the process has been used to remove carcinogenic and hazardous chemicals from water. These chemicals include volatile organics such as trihalomethanes, radon, trichloroethylene, tetrachloroethylene, 1,1,1-trichloroethane, chloroform, and toluene. As a result, water aeration may be the single most important water treatment process used in the 21st century.

1.1. Types of Aeration Process

Aeration may be accomplished in a variety of ways using different types of equipment including surface aeration, submerged aeration, and falling water unit (1–6). The equipment types are listed below:

- Falling Water Units (commonly used in water treatment)
  1. Spray aerators—water sprayed into the air. Problems include evaporation and freezing.
  2. Cascade aerators and hydraulic jumps—these operate using waterfalls over a structure.
  3. Fountain aerators or spray—water cascaded or sprayed over rocks or other types of material.

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4. Multiple tray aerators with and without coke (often used for iron and manganese removal)—water cascaded over manufactured tray constructed from slats and coke.
5. Packed column aeration—air flows up, water is sprayed down (these are efficient and the most common type).

- Surface Aerators (commonly used in the wastewater industry)
  1. Mechanical surface aerators—water surface is mechanically mixed to increase water to air interface.
     a. Brush: a series of circular brushes partially submerged are rotated through the water surface to cause turbulence. A support structure is required to suspend the brushes over the water.
     b. Floating: Floating aerator pumps the water from beneath it up through a draft tube to the surface,which disperses water into the air.

- Submerged Aerators (commonly used in the wastewater and water industries)
  1. Injection of air with blowers by static tube or diffuser (fine bubble and coarse bubble).
  2. Jet aeration (the injection of air into pumped water).

This discussion will be limited to equipment used for water treatment, specifically the falling-water-type equipment and submerged-aeration equipment. The critical factors that determine aeration efficiency include (a) time of aeration, (b) ratio of surface area of air to volume of water, and (c) ventilation. Normally, two approaches are used: (a) exposure of water films to air and (b) introduction of small bubbles. The rate of gas transfer with aeration depends on the concentration of contaminants in the water or air as well as temperature, pH, and the degree of agitation. Production of a large water–air surface is desired. Technically, aeration refers to the addition of air while air stripping refers to the use of air to remove dissolved gases. As a practical matter, the terms are interchangeable.

2. APPLICATIONS

2.1. *Taste and Odor Removal*

It is sometimes difficult to identify the actual cause of odor and taste problems in water. Some of common odor- and taste-causing compounds include hydrogen sulfide (H_2S), methane, algae, oils, phenols, cresols, and volatile compounds. Removal of taste and odor problems is a common application for the water aeration process. The process is suitable for H_2S, methane, and volatiles, but not for algae and oils, phenols, and cresols. The compounds must be volatile for aeration to be effective. Aeration is appropriate for many industrial compounds. A classic installation is at Nitro, WV, which utilizes aeration and granular activated carbon (GAC). The raw water had threshold odor numbers (T.O.N.) of 5000–6000 from industrial contamination. The process was effective for reducing the taste and odor down to levels of 10–12 T.O.N. Although taste and odor applications are most common, there are many other tastes and odors that simply cannot be removed by aeration alone, which may explain why so many early plants were abandoned (1–10).

2.2. *Iron and Manganese Oxidation*

When the total concentration of iron in water is 0.3 mg/L or greater, the iron will cause the water to have an unpleasant taste and redden in color—this may result in the staining of plumbing fixtures and clothes, and accumulations of iron deposits in the water mains. The aeration process is an excellent and common pretreatment application for the removal of iron. First, the process oxides iron by changing the iron from the ferrous state (Fe^{2+}) to the ferric state (Fe^{3+}), which converts the iron from a soluble form (Fe^{2+}) to a non-soluble form (Fe^{3+}) that precipitates from the water. This precipitation process occurs rapidly when the pH is around 7+. The removal of iron is accomplished through sedimentation and filtration of the precipitated iron. Theoretically, 1 mg/L of O_2 will oxidize about 7 mg/L of Fe^{2+}.

Manganese concentrations greater than 0.3 mg/L in water will result in dark brown staining. Oxidation will convert the manganese from Mn^{2+} to Mn^{4+} when the pH is above 9. Below a pH of 9, the process is negligibly slow. When tray aerators are utilized for aeration and trays become coated with manganese oxides, the removal is accomplished first by adsorption on accumulated oxidation products (Fe_2O_3 or MnO_2) followed by slow oxidation (2).

2.2.1. Air Injection into Groundwater for Iron Control

In order to lower the iron concentration in groundwater prior to pumping raw water to the municipal water treatment plant, air is injected into the groundwater source. The injected air oxides the iron in the groundwater. This process involves the periodical injection of air into groundwater via a series of wells that surrounds a production well. This application was implemented in a groundwater supply system in Pembroke, MA.

2.3. Hydrogen Sulfide and Carbon Dioxide Removal

Hydrogen sulfide and carbon dioxide (as carbonic acid and free carbon dioxide) are commonly found in well water. Even a low concentration of hydrogen sulfide can cause odor and taste problems. Hydrogen sulfide is a colorless gas which has a foul odor similar to rotten eggs and is slightly heavier than air (SG = 1.192). In water, molecular hydrogen sulfide is formed from the reduction, dissolves and disassociates in accordance with the reversible ionization reactions:

$$H_2S \leftrightarrow HS^- + H^+$$

$$HS^- \leftrightarrow S^{2-} + H^+$$

The equilibrium of sulfide in water, the percentages of H_2S, HS^-, and S^{2-} species, is dependent on the pH. Figure 1 shows the distribution of each species at various pH. At a pH of approx 5.7, the sulfide species in water would be near 100% H_2S and at approx pH 7, 50% of the sulfide species in water would be H_2S and the other 50% would be HS^- species. The H_2S species are volatile; as a result, the aeration process effectively removes it from the water. Therefore, the removal efficiency of sulfide depends on pH. As the pH increases, aeration becomes less effective because there are fewer sulfides in the form of H_2S, which is readily removed by aeration. This process is utilized by both municipalities and chemical industries. In water treatment, the process is called degasification, and is effectively used to remove both H_2S and carbon dioxide from well water and product water from the reverse osmosis process.

Dissolved carbon dioxide (CO_2) is commonly found in well water. CO_2 gas is soluble in water (1700 mg/L @20°C) and is volatile. When CO_2 gas is dissolved in water, it forms carbonic acid (H_2CO_3) and aqueous carbon dioxide ($CO_{2(aq)}$). Aqueous carbon

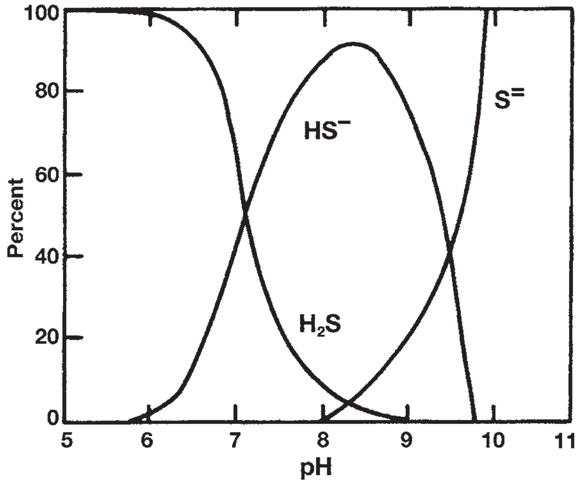


Fig. 1. Effect of pH on hydrogen sulfide equilibrium (US EPA) (10).

dioxide is sometimes identified as free CO_2. Using analytical procedures (titration), it is difficult to distinguish between H_2CO_3 and $CO_{2(aq)}$; therefore, a hypothetical species (H_2CO_3*) is used to identify combination of both H_2CO_3 and $CO_{2(aq)}$ in water.

H_2CO_3 is a weak acid. As the water CO_2 concentration is increased, then both the H_2CO_3 concentration and corrosion potential increase. Aeration drives off CO_2 and lowers the H_2CO_3 levels, which reduces the corrosion potential of the water. When both H_2S and CO_2 are present in water, aeration will remove both. As water is aerated, both CO_2 and H_2S are removed, but as the pH of the water increases due to the removal of CO_2, the removal efficiency of H_2S decreases (10).

2.4. *Ammonia Removal*

This is a limited application in the water industry, but is more commonly used in wastewater treatment. One of the processes utilized in the wastewater industry is the aerated suspended growth process, which utilizes nitrifying bacteria and aeration to convert ammonia to nitrites and nitrates.

2.5. *Aesthetic or Decorative Aeration*

Fountains are an attractive way to display product water. They can also be functional particularly for taste and odor improvement. Also, they conjure positive associations for many onlookers.

2.6. *Reservoir De-stratification and Oxygenation of Water*

In small reservoirs and ponds that have trouble maintaining dissolved oxygen levels in water near the bottom of the reservoir (stratification of dissolved oxygen level—high level near the surface and low level near the bottom), aeration can accomplish the following: it mixes the water, reduces stratification, and increases the dissolved oxygen level in the water. This is accomplished by placing diffusers on the reservoir floor and bubbling air into the water or by using floating aerators. In some cases, this has proved very beneficial, but in other cases it has not been effective; results cannot be determined until the process is implemented. Aeration restores oxygen to water, making the water taste better but it also increases corrosiveness, by increasing the CO_2 in the water (resulting from the oxidation of organic matter to CO_2). Therefore, there is often a trade off between benefit and detriment (11–20).

2.7. Dissolved Air Flotation for Flocculation/Flotation

Aeration has been used rarely for air flotation for flocculation. The purpose of this application is to increase flocculation size by inducing particle-to-particle contact. However, air bubbles attached to the flocculation particles often cause them to float rather than to settle. A newer, promising approach is flotation, which injects oxygen-saturated water at the bottom of shallow basins, resulting in flocculation forming a scum layer at the water surface, which is then removed (21).

2.8. Trihalomethanes Removal

The aeration process is rated as good to excellent for the removal of trihalomethanes (THM) because they are fairly volatile. This is an increasing application because THMs are not effectively removed by other processes such as granular activated carbon (GAC), although GAC is suitable for organic precursors that react with chlorine to form trihalomethanes. Aeration is a poor choice for THM precursors removal but suitable for removing trihalomethanes.

2.9. Volatile Organics Removal

The US EPA has identified many types of organic compounds in our water supplies. Some of the organic compounds are volatile, and, as a result, aeration would be a good process selection for removing them from water. For compounds that are non-volatile, adsorption would be a better process selection than aeration for their removal from the water. Some common volatiles include trihalomethanes, which have already been discussed: chlorobenzene, 1,1,1-trichloroethane, tetrachloroethylene, and trichloroethylene. Aeration can achieve up to 95% removal of these compounds.

Non-volatile organic compounds also create problems in water supplies. Adsorption is an excellent removal method for non-volatiles such as styrenes, benzene, phthalates, and fluorine. Therefore, it is often logical to couple air stripping with carbon adsorption, particularly when both volatile and non-volatile compounds are present. Air stripping is particularly suitable for volatile organics because (a) all volatile organics have an affinity for the vapor phase, (b) most organics are hydrophobic—they don't like water—and (c) air is readily available and inexpensive. Nearly 1000 types of organics have been identified in drinking water and we shall see more applications of air stripping. This will be true particularly in areas of gross contamination.

2.10. Hazardous Waste Cleanup

An increasing amount of contamination results from landfills, leaking containers, and accidental spills. Many of the contaminants are volatile and amenable to aeration. A twofold approach can be used: either clean the water supply or clean the contamination source. When a highly concentrated contaminant is aerated through a packed tower, then air pollution from the aeration process becomes a concern. Air discharge from the packed tower must be collected and treated.

2.11. Radionuclides Removal

Radionuclides are radioactive atoms. The number of protons and neutrons in their nucleus and their energy content are used to characterize the radioactivity of the atoms. The number following the chemical abbreviation describes the radionuclide composition. In drinking water, the most commonly found radionuclides are radium, uranium, and radon. Radioactive atoms emit three types of nuclear radiation: alpha, beta, and gamma radiation. Various methods are used to measure the level of radionuclides in drinking water, including counters (internal proportional, end-window, thin window, low-background beta counter, gamma spectrometer, alpha spectrometer, alpha scintillation counter, and liquid beta scintillation counter). The average estimated costs for analyzing these radiation types ranges from $25 to $100 per sample.

In the early 1970s, the inhalation of a radioactive gas such as radon gas (Rn-222) and its daughter progenies (Po-213 and Po-214) were linked to lung carcinogenesis and also associated with development of acute myeloid, acute lymphoblastic leukemia, and other cancers. Regions with granite areas that have relatively high uranium content and are fractured have been found to have a high radon emanation rate. The unit Becquerel (Bq) is used to express radioactivity as disintegrations per second. A more commonly used unit the Curie (Ci) is equal to 3.7×10^{10} Bq.

US EPA surveys of well drinking water sources showed that 74% of the sources had radon concentrations below 100 Bq/L and only 5% had concentrations above 400 Bq/L. The high levels were linked to deep wells. A concentration of 400 Bq/L will increase the indoor air radon concentration by about 0.04 Bq/L. Other sources of radon are:

1. Soil around buildings.
2. Cracks in floors and walls.
3. Construction joints.
4. Gaps in suspended floors and around pipes.
5. Cavities inside walls.

When the above sources are available, then the radon level in air could reach the US EPA action level of 150 Bq/m^3 (0.15 Bq/L). Because radon is highly volatile, the radon levels in groundwater may be lowered by using an aeration process, such as a packed tower. This aeration process increases the rate of desorption of radon by increasing the surface area for mass transport across the water–air interface. In Table 1, aeration is compared to other treatment technologies for effectiveness in removing radionuclides from water. Depending on the aeration process, aeration can achieve a removal efficiency ranging from 20% to 96% for radon (Rn), but is not used for radium (Ra) or uranium (U) removal. Aeration processes such as PTA [packed tower (column) aeration], which provides a large water–air interface, can achieve high removal efficiency.

3. UNIT PROCESSES FOR ORGANIC CONTAMINANT REMOVAL

The Safe Drinking Water Act (SDWA) through the 1986 Amendments requires the establishment of new maximum contaminant levels (MCLs) for many organic contaminants, including disinfection by-products (such as THMs). As a result, regulations passed in 1987 designated best available technologies (BATs) as well as MCLs for organic contaminants. Table 2 lists final regulations for eight volatile organic compounds (VOCs) that include the maximum contaminant level goal (MCLG) and the MCL (4,6).

Table 1
Treatment Technologies for Removing Radionuclides (US EPA) (4)

Treatment Technology	Radionuclide	Reported approximate process efficiency (percent)	Comments
Conventional treatment with coagulation-filtration	Ra	<25	High pH and Mg required
	U	18–98	High pH (10+) and high dosages of ferric chloride or alum only accomplished in laboratory studies with diatomaceous earth filtration
Lime softening	Ra	75–96	Best choice for large plants
		43–92	Plant-scale results
	U	80	Plant-scale results
		85–90	pH 10.6–11.5
		99	High pH, high Mg
Ion exchange	Ra	95+	Best choice for small plants; cation exchangers
		99	Brine disposal problem
	U	99	Anion exchangers; largely experimental but some full-scale plants on line
Adsorption	Ra	90+	Adsorption on any solids; experimental
		85–90	Sand adsorption; experimental
	Rn	62–99	GAC adsorption
Aeration	Rn	20–96	Depends on process
		93+	Depends on process
Reverse osmosis	Ra	87–96	Plant-scale data
		87–98	Based on eight plants
		95+	High-volume brine solution for disposal
	U	95+	High-volume brine solution for disposal

Table 2
Final MCLGs and MCLs for VOCs (US EPA) (4)

	Final MCLG[a] (mg/L)	Final MCL (mg/L)
Trichloroethylene	zero	0.005
Carbon tetrachloride	zero	0.005
Vinyl chloride	zero	0.002
1,2-Dichloroethane	zero	0.005
Benzene	zero	0.005
para-Dichlorobenzene	0.075	0.075
1,1-Dichloroethylene	0.007	0.007
1,1,1-Trichloroethane	0.2	0.2

[a] Final MCLGs were published Nov. 13, 1985. The MCLG and MCL for *p*-dichlorobenzene were reproposed at zero and 0.005 mg/L on April 17, 1987; comment was requested on levels of 0.075 mg/L and 0.075 mg/L, respectively.

Table 3
Treatment Technology Removal Effectiveness Reported for Organic Contaminants in Percent (US EPA) (4)

Contaminant	Coagulation/ filtration	GAC	PCA	PAC	Diffused aeration	Oxidation	Reverse osmosis
Acrylamide	5	NA	0–29	13	NA	NA	0–97
Alachlor	0–49	70–100	70–100	36–100	NA	70–100	70–100
Aldicarb	NA	NA	0–29	NA	NA	NA	94–99
Benzene	0–29	70–100	70–100	NA	NA	70–100	0–29
Carbofuran	54–79	70–100	0–29	45–75	11–20	70–100	70–100
Carbon tetrachloride	0–29	70–100	70–100	0–25	NA	0–29	70–100
Chlordane	NA	70–100	0–29	NA	NA	NA	NA
Chlorobenzene	0–29	70–100	70–100	NA	NA	30–69	70–100
2,4-D	0–29	70–100	70–100	69–100	NA	W	0–65
1,2-Dichloroethane	0–29	70–100	70–100	NA	42–77	0–29	15–70
1,2-Dichloropropane	0–29	70–100	70–100	NA	12–79	0–29	10–100
Dibromochloropropane	0–29	70–100	30–69	NA	NA	0–29	NA
Dichlorobenzene	NA	70–100	NA	NA	NA	NA	NA
o-Dichlorobenzene	0–29	70–100	70–100	38–95	14–72	30–88	30–69
p-Dichlorobenzene	0–29	70–100	70–100	NA	NA	30–69	0–10
1,1-Dichloroethylene	0–29	70–100	70–100	NA	97	70–100	NA
cis-1,2-Dichloroethylene	0–29	70–100	70–100	NA	32–85	70–100	0–30
Trans-1,2-Dichloroethylene	0–29	70–100	70–100	NA	37–96	70–100	0–30
Epichlorohydrin	NA	NA	0–29	NA	NA	0–29	NA
Ethylbenzene	0–29	70–100	70–100	33–99	24–89	70–100	0–30
Ethylene dibromide	0–29	70–100	70–100	NA	NA	0–29	37–100
Heptachlor	64	70–100	70–100	53–97	NA	70–100	NA
Heptachlor epoxide	NA	NA	NA	NA	NA	26	NA
High-molecular-weight Hydrocarbons (gasoline, dyes, amines, humics)	NA	W	NA	NA	NA	NA	NA

Lindane	0–29	70–100	0–29	82–97	NA	0–100	50–75
Methoxychlor	NA	70–100	NA	NA	NA	NA	>90
Monochlorobenzene	NA	NA	NA	14–99	14–85	86–98	50–100
Natural organic material	P	P	NA	P	NA	W	P
PCBs	NA	70–100	70–100	NA	NA	NA	95
Phenol and chlorophenols	NA	W	NA	NA	NA	W	NA
Pentachlorophenol	NA	70–100	0	NA	NA	70–100	NA
Styrene	0–29	NA	NA	NA	NA	70–100	NA
Tetrachloroethylene	NA	70–100	NA	NA	73–95	W	70–90
Trichloroethylene	0–29	70–100	70–100	NA	53–95	30–69	0–100
Trichloroethane	NA	70–100	NA	NA	NA	NA	NA
1,1,1-Trichloroethane	0–29	70–100	70–100	40–65	58–90	0–29	15–100
Toluene	0–29	70–100	70–100	0–67	22–89	70–100	NA
2,4,5-TP	63	70–100	NA	82–99	NA	30–69	NA
Toxaphene	0–29	70–100	70–100	40–99	NA	NA	NA
Vinyl chloride	0–29	70–100	70–100	NA	NA	70–100	NA
Xylenes	0–29	70–100	70–100	60–99	18–89	70–100	10–85

W = well removed.
P = poorly removed.
NA = not available.

Note: Little or no specific performance data were available for:
1. Multiple-tray aeration
2. Catenary aeration
3. Higee aeration
4. Resins
5. Ultrafiltration
6. Mechanical aeration

US regulations require water utilities with these contaminants to provide removals at least equivalent to those achieved by the designated BATs. Table 3 lists the typical technologies used in the water treatment industry with their removal capabilities for organic contaminants, including both VOCs and synthetic organic compounds (SOCs). As shown in this table, the packed column aeration (PCA) and granular activated carbon (GAC) provide 70–100% removal for many of the listed organic contaminants, which includes the eight VOCs for which the US EPA has established the MCL. Other technologies [coagulation/filtration, powdered activated carbon (PAC), diffused aeration, oxidation, and reverse osmosis (RO)] can be effective in removing selective organics. GAC and PCA, also referred to as packed tower aeration (PTA), are classified as BAT technologies for the removal of VOCs under the US EPA regulations promulgated in July 1987.

The removal efficiencies of GAC and PTA are different for each organic compound. GAC can also be effective for the removal of inorganics, whereas PTA is only effective for VOC removal. Sometimes selection of treatment technology is based on potential removal efficiencies for a specific organic contaminant. However, the best decision considers both removal efficiency and cost. As a result, PTA is often chosen for VOCs because it has a lower cost and high removal efficiency. Occasionally, both technologies are necessary to remove a particular combination of organic compounds or organic and inorganic compounds. In these instances, the resulting total costs are not always the sum of costs for each system, because the installation of both systems may result in some cost savings. The upstream system may reduce loading on the downstream system. Other types of aeration technologies are emerging from the laboratory and pilot-level stages, and provide promising alternatives for the near future. These technologies include catenary grid aeration, Higee aeration, and diffused/mechanical aeration.

3.1. Packed Column Aeration

Packed column aeration (2,4,6–9,11–13,22), also called PTA or air-stripping, mixes water with air to volatilize contaminants. The volatilized contaminants are either released directly to the atmosphere or are treated and then released. PCA is used primarily to remove VOCs, but is commonly used to remove hydrogen sulfide and CO_2. In this application, the aeration unit is described as degasifier.

The Henry's law constant indicates a contaminant's volatility and its affinity for the aeration process. Substances with high Henry's law constants are easily aerated, while those with low constants are difficult to remove with aeration. Table 4 presents Henry's law constants for several compounds. As the table indicates, vinyl chloride has an extremely large Henry's law constant relative to any other VOC.

If the solubility, vapor pressure, and molecular weight of a compound are known, Henry's law constant can be calculated using the Eq. (1). Table 5 presents the vapor pressures and solubilities and Henry's law constants for priority pollutants:

$$H_{\text{unitless}} = \frac{16.04\,VP\,M}{T\,S} \tag{1}$$

where H_{unitless} = Henry's law constant, dimensionless; VP = the vapor pressure expressed, mm; M = the molecular weight of the solute; T = the temperature, K; and S = the solubility, mg/L.

Table 4
Henry's Law Constants for Nine Organic Chemicals (US EPA) (4)

Type of organic chemical	Henry's law constant[a] (dimensionless units)
VOCs	
Vinyl chloride	265.00[a]
Trichloroethylene	0.41[a]
Tetrachloroethylene	0.82[a]
cis-1,2-Dichloroethylene	0.32[b]
Pesticides	
Aldicarb	0.00000017[b]
Chlordane	0.004[b]
Dibromochloropropane	0.01[b]
Chlorinated Aromatics	
Polychlorinated biphenols	0.059[b]
Dichlorobenzene	0.081[b]

Note: Constants estimated at about 20°C.
[a] AWWA Research Foundation and KIWA (1983).
[b] US EPA (1998).

Example

Determine the unitless form of Henry's law constant for benzene at 20°C using Eq. (1).

Solution

Benzene has chemical formula of C_6H_6; therefore, the molecular weight is determined as follows:

$$C_6\text{: } 12 \times 6 = 72$$
$$H_6\text{: } 1 \times 6 = 6$$
$$MW = M = 78$$

$$VP = 95.2 \text{ mm Hg (from Table 5)}$$

$$S = 1780 \text{ mg/L (from Table 5)}$$

$$T = (273.15 \text{ K} + 20°\text{C}) = 293.15 \text{ K}$$

Substituting into Eq. (1) yields the following:

$$H_{\text{unitless}} = \frac{16.04\, VP\, M}{T\, S}$$

$$H_{\text{unitless}} = \frac{(16.04)(95.2)(78)}{(293.15)(1780)} = 0.228$$

Henry's law constant is commonly expressed in units of atm m^3/mole for atmospheric conditions. Table 6 lists some of US EPA's priority pollutants with their Henry's law constants expressed as atm m^3/mole. To convert this form of the constant to the unitless form, use the following equation:

$$H_{\text{unitless}} = \frac{H}{RT} \tag{2}$$

where H = Henry's law constant, atm m^3/mole; R = universal gas constant, 0.000082057 atm m^3/mole-K; and T = temperature, K (K = 273.15 + °C).

Table 5
Chemical Characteristics of the Priority Pollutants with Henry's Law Constant (Unitless) Listed (US EPA) (6)

		$H^{(1)}$	$VP^{(2)}$ (mmHg)	$Solubility^{(3)}$ (mg/L)
1.	*Acenaphthene	0.009 (*c*)	3.0×10^{-2}	3.88
2.	*Acrolein	0.0046 (*b*)	300	200,000
3.	*Acrylonitrile	0.0030 (*b*)	100	93,000
4.	*Benzene	0.22 (*b*)	95.2	1780
5.	*Benzidine			
6.	*Carbon tetrachloride (tetrachloromethane)	1.2 (*c*)	91.3	800
	*Chlorinated benzenes (other than dichlorobenzenes)			
7.	Chlorobenzene	0.19 (*d*)	15	448
8.	1,2,4-Trichlorobenzene			
9.	Hexachlorobenzene			
	*Chlorinated ethanes (including 1,2-dichloroethane, 1,1,1-trichloroethane and hexachloroethane)			
10.	1,2-Dichloroethane	0.050 (*c*)	82	8700
11.	1,1,1-Trichloroethane	0.17 (*b*)	100	4400
12.	Hexachloroethane	0.05 (*c*)	0.33	8
13.	1,1-Dichloroethane	0.24 (*c*)	226	5100
14.	1,1,2-Trichloroethane	0.037 (*c*)	25	4420
15.	1,1,2,2-Tetrachloroethane	0.020 (*c*)	6.5	3000
16.	Chloroethane	0.73 (*c*)	1200	5700
	*Chloroalkyl ethers (chloromethyl, chloroethyl and mixed ethers)			
17.	*bis* (Chloromethyl) ether			
18.	*bis* (2-Chloroethyl) ether			
19.	2-Chloroethyl vinyl ether (mixed)			
	*Chlorinated naphthalene			
20.	2-Chloronaphthalene			
	*Chlorinated phenols (other than those listed elsewhere; includes trichlorophenols and chlorinated cresols)			
21.	2,4,6-Trichlorophenol			
22.	Parachlorometa cresol			
23.	*Chloroform (trichloromethane)	0.16 (*c*)	192	7840
24.	*2-Chlorophenol	0.001 (*b*)	5.0	28,000
	*Dichlorobenzenes			
25.	1,2-Dichlorobenzene	0.081 (*b*)	1.0	100
26.	1,3-Dichlorobenzene	0.13 (*c*)	2.0	123
27.	1,4-Dichlorobenzene	0.10 (*c*)	1.0	79
	*Dichlorobenzidine			
28.	3,3′-Dichlorobenzidine			
	*Dichloroethylenes (1,1-dichloroethylene and 1,2-dichloroethylene)			
29.	1,1-Dichloroethylene	7.80	598	400

(Continued)

Table 5 *(Continued)*

		H$^{(1)}$	VP$^{(2)}$ (mmHg)	Solubility$^{(3)}$ (mg/L)
30.	1,2-*trans*-Dichloroethylene	0.27	326	6300
31.	*2,4-Dichlorophenol	0.002	1.0	4500
	*Dichloropropane and dichloropropene			
32.	1,2-Dichloropropane	0.095 (*b*)	42	2700
33.	1,2-Dichloropropylene (1,3-dichloropropene)	0.095 (*b*)	43	2700
34.	*2,4-Dimethylphenol			
	*Dinitrotoluene			
35.	2,4-Dinitrotoluene			
36.	2,6-Dinitrotoluene			
37.	*1,2-Diphenylhydrazine			
38.	*ethylbenzene	0.27 (*b*)	7	152
39.	*fluoranthene			
	*haloethers (other than those listed elsewhere)			
40.	4-Chlorophenyl phenyl ether			
41.	4-Bromophenyl phenyl ether			
42.	*bis* (2-Chloroisopropyl) ether	0.005	0.85	1700
43.	*bis* (2-Chloroethoxy) methane			
	*Halomethanes (other than those listed elsewhere)			
44.	Methylene chloride (dichloromethane)	0.12 (*c*)	438	16,700
45.	Methyl chloride (chloromethane)	0.38 (*c*)	760	5380
46.	Methyl bromide (bromomethane)	4.39 (*b*)	760	900
47.	Bromoform (tribromomethane)	0.030 (*d*)	5.6	3190
48.	Dichlorobromomethane			
49.	Trichlorofluoromethane	5.11 (*c*)	760	1100
50.	Dichlorodifluoromethane	98.8 (*c*)	4250	280
51.	Chlorodibromomethane			
52.	*Hexachlorobutadiene			
53.	*Hexachlorocyclopentadiene			
54.	*Isophorone	0.0002 (*b*)	0.38	12,000
55.	*Naphthalene	0.017 (*c*)	0.87	30
56.	*Nitrobenzene	0.0005 (*b*)	0.15	1900
	*Nitrophenols (including 2,4-dinitrophenol and dinitrocresol)			
57.	2-Nitrophenol	0.0036 (*b*)	1.0	2100
58.	4-Nitrophenol			
59.	*2,4-Dinitrophenol			
60.	4,6-Dinitro-*o*-cresol	8×10^{-6} (*a*)	1×10^{-4}	130
	*Nitrosamines			
61.	*N*-nitrosodimethylamine			
62.	*N*-nitrosodiphenylamine			
63.	*N*-nitrosodi-n-propylamine			
64.	*Pentachlorophenol	0.0001 (*b*)	1.1×10^{-4}	14
65.	*Phenol	1.3×10^{-5} (*c*)	0.20	82,000
	*Phthalate esters			

(Continued)

Table 5 ***(Continued)***

	H(1)	VP(2) (mmHg)	Solubility(3) (mg/L)
66. *bis* (2-ethylhexyl) phthalate			
67. Butyl benzyl phthalate			
68. Di-*n*-butyl phthalate	0.0030 (*c*)	0.1	500
69. Di-*n*-octyl phthalate			
70. Diethyl phthalate			
71. Dimethyl phthalate	0.00002 (*b*)	0.01	5000
*Polynuclear aromatic hydrocarbons			
72. Benzo (*a*) anthracene (1,2-benzanthracene)			
73. Benzo (*a*) pyrene (3,4-benzopyrene)			
74. 3,4-Benzofluoranthene			
75. Benzo (k) fluoranthane (11,12-benzofluoranthene)			
76. Chrysene			
77. Acenaphthylene			
78. Anthracene	0.067 (*c*)	0.04	0.075
79. Benzo(ghi)perylene (1,12-benzoperylene)			
80. Fluorene	0.010 (*c*)	0.012	1.90
81. Phenanthrene	0.006 (*c*)	3.4×10^{-3}	1.18
82. Dibenzo(a,h)anthracene (1,2,5,6-dibenzanthracene)			
83. Indeno (1,2,3-cd)pyrene (2,3-*o*-phenylenepyrene)			
84. Pyrene			
85. *Tetrachloroethylene	1.1 (*c*)	18.6	150
86. *Toluene	0.27 (*c*)	28.0	515
87. *Trichloroethylene	0.48 (*c*)	74	1000
88. *Vinyl chloride (chloroethylene)	301.0 (*c*)	2660	60
Pesticides and metabolites			
89. *Aldrin	0.10 (*c*)	1.4×10^{-4}	0.027
90. *Dieldrin	8.2×10^{-6}	5.4×10^{-6}	0.19
91. Chlordane (technical mixture and metabolites)			
*DDT and metabolites			
92. 4,4′-DDT	0.0016 (*c*)	1.9×10^{-7}	3.1×10^{-3}
93. 4,4′-DDE (*p*,*p*′-DDX)			
94. 4,4′-DDD (*p*,*p*′-TDE)			
*Endosulfan and metabolites			
95. α-Endosulfan-Alpha			
96. β-Endosulfan-Beta			
97. Endosulfan sulfate			
*Endrin and metabolites			
98. Endrin			
99. Endrin aldehyde			
*Heptachlor and metabolites			
100. Heptachlor	0.11 (*c*)	3×10^{-4}	0.056
101. Heptachlor epoxide			
*Hexachlorocyclohexane (all isomers)			
102. α-BHC-Alpha	0.094 (*c*)	0.06	10

(Continued)

Table 5 *(Continued)*

	$H^{(1)}$	$VP^{(2)}$ (mmHg)	Solubility$^{(3)}$ (mg/L)
103. β-BHC-Beta	0.53 (*c*)	0.17	5
104. γ-BHC (lindane)-Gamma	1.5×10^{-5} (*c*)	9.4×10^{-6}	10
105. δ-BHC-Delta			
*polychlorinated biphenyls (PCB's)			
106. PCB-1242 (Arochlor 1242)	0.023 (*c*)	4.1×10^{-4}	0.24
107. PCB-1254 (Arochlor 1254)	0.11 (*c*)	7.7×10^{-5}	0.012
108. PCB-1221 (Arochlor 1221)			
109. PCB-1232 (Arochlor 1232)			
110. PCB-1248 (Arochlor 1248)	0.14 (*c*)	4.9×10^{-4}	5.4×10^{-2}
111. PCB-1260 (Arochlor 1260)	0.29 (*c*)	4.1×10^{-5}	2.7×10^{-3}
112. PCB-1016 (Arochlor 1016)			
113. *Toxaphene	2.97 (*c*)	0.40	3.0
114. *Antimony (total)			
115. *Arsenic (total)			
116. *Asbestos (fibrous)			
117. *Beryllium (total)			
118. *Cadmium (total)			
119. *Chromium (total)			
120. *Copper (total)			
121. *Cyanide (total)			
122. *Lead (total)			
123. *Mercury (total)			
124. *Nickel (total)			
125. *Selenium (total)			
126. *Silver (total)			
127. *Thallium (total)			
128. *Zinc (total)			
129. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD)			

$^{(1)}H$ is calculated Henry's law constant.
$^{(2)}VP$ is vapor pressure of compound.
$^{(3)}$Solubility is compound solubility in water.
*Specific compounds and chemical classes as listed in the consent degree.
(*a*) = 288 K (15°C).
(*b*) = 293 K (20°C).
(*c*) = 298 K (25°C).
(*d*) = 303 K (30°C).

Example

Utilizing Eq. (2) calculate the unitless form on the Henry's law constant for methylene chloride at 20°C.

Solution

From Table 6 the Henry's law constant is

$$H = 2.5 \times 10^{-3}\,\text{atm m}^3/\text{mole}$$

$$H_{\text{unitless}} = \frac{2.5 \times 10^{-3}}{(0.000082057)(293.15)} = 0.104$$

Table 6
Calculated Henry's Law Constants at 20°C for Organic Compounds on US EPA's Priority Pollutants (US EPA) (7)

Compound	atm H (m^3/mol)	Compound	atm H (m^3/mol)
Vinyl chloride	6.4	1,2-Dichloropropylene	2.0×10^{-3}
1,1-Dichloroethylene	1.7×10^{-1}	1,2-Dichlorobenzene*	1.7×10^{-3}
1,2-Dichloroethylene	1.7×10^{-1}	Anthracene	1.4×10^{-3}
Carbon tetrachloride	2.5×10^{-2}	Bromoform	6.3×10^{-4}
Tetrachloroethylene*	2.3×10^{-2}	PCB (Aroclor 1242)	4.9×10^{-4}
Trichloroethylene	1.0×10^{-2}	Naphthalene	3.6×10^{-4}
Methyl chloride	8.0×10^{-3}	Acenaphthene	1.9×10^{-4}
PCB (Aroclor 1260)	6.1×10^{-3}	Phenenthrene	1.3×10^{-4}
Toluene	5.7×10^{-3}	2-Nitrophenol	7.6×10^{-5}
1,1-Dichloroethane	5.1×10^{-3}	Acrylonitrile	6.3×10^{-5}
1,1,1-Trichloroethane*	3.6×10^{-3}	4,4' - DDT	3.4×10^{-5}
Chloroform*	3.4×10^{-3}	2-Chlorophenol	2.1×10^{-5}
PCB (Aroclor 1248)	3.0×10^{-3}	Nitrobenzene	1.1×10^{-5}
Methylene chloride	2.5×10^{-3}	Pentachlorophenol	2.1×10^{-6}
Heptachlor	2.3×10^{-3}	Lindane	3.2×10^{-7}
PCB (Aroclor 1254)	2.3×10^{-3}	Phenol	2.7×10^{-7}
Aldrin	2.1×10^{-3}	Dieldrin	1.7×10^{-7}

*Significant removal by air stripping.

For given compounds, van't Hoff-type relationships have been developed so that the Henry's law constant at different temperatures can be calculated from Eq. (3):

$$\log H_{\text{ATM}} = \frac{-A'}{T} + B' \tag{3}$$

In Eq. (3), A and B are empirical constants that are listed for commonly treated gases in Table 7, while T is temperature in kelvin (K).

Example

Using Eq. (3), calculate the Henry's law constant for carbon dioxide at 70°F.

Solution

Convert 70°F to °C then to K

$$\text{Temperature} = \frac{5}{9}(70 - 32) = 21°\text{C}$$

$$\text{T} = (273.15 + 21.11) = 294.26 \text{ K}$$

From Table 7

$$A' = 1012.46$$

$$B' = 66.06$$

Substituting these values into Eq. (3) and solving for H_{ATM}:

$$\log H_{\text{ATM}} = \frac{-A'}{T} + B'$$

Table 7
van't Hoff-type Empirical Constants for Various Gases in Water to Adjust Henry's Law Constant from Standard Temperature (8,9)

Gas	A'	B'	Henry's law constant at 20°C (atm)
Air	557.6	6.724	66,400
Ammonia	1887.12	6.315	0.75
Benzene	3680	8.68	240
Carbon dioxide	1012.4	6.606	1420
Carbon tetrachloride	2038.25	10.06	1290
Chlorine	875.7	5.75	579
Chlorine dioxide	1041.77	6.73	1500
Chloroform	4000	9.10	170
Hydrogen	187.04	5.473	68,300
Hydrogen sulfide	884.94	5.703	483
Methane	675.74	6.880	37,600
Nitrogen	537.62	6.739	80,400
Oxygen	595.27	6.644	41,100
Ozone	1268.24	8.05	5300
Sulfur dioxide	1207.85	5.68	36
Tetrachloroethylene	2159.03	10.38	1100
Trichloroethylene	1716.16	8.59	550

Note: The value A' represents (ΔH kcal/kmole/1.987 kcal/kmole K).

$$\begin{aligned}\log_{10} H_{ATM} &= \frac{-1012.46}{294.26} + 6.606\\ \log_{10} H_{\mathrm{ATM}} &= 3.166\\ H_{\mathrm{ATM}} &= 10^{3.166}\\ H_{\mathrm{ATM}} &= 1465.5 \text{ atm@ } 70°\mathrm{F} \text{ or } 21°\mathrm{C}\end{aligned}$$

Henry's law constant, H_{ATM}, in atm can be converted to unitless Henry's law constant, H_{unitless}, by using Eq. (4):

$$H_{\mathrm{unitless}} = \frac{H_{\mathrm{ATM}}}{4.559\, T} \tag{4}$$

Example

Applying Eq. (4), calculate the H_{unitless} for tetrachloroethylene at 20°C.

Solution

From Table 7, H_{ATM} for tetrachlorethylene is found to be 1100 atm@ 20°C.

$$H_{\mathrm{unitless}} = \frac{1100}{4.559(273.15 + 20)} = 0.823 @ 20°\mathrm{C}$$

Stripping systems are based on mass transfer from water to air stripping system. The following equations are used to design a PTA system:

$$Z = (\mathrm{HTU})(\mathrm{NTU}) \tag{5}$$

where HTU = height of transfer unit, ft or m; NTU = number of transfer units; and Z = packing height, ft or m.

$$\mathrm{HTU} = \frac{L}{aK_{La}} \tag{6}$$

where L = liquid loading, mole of water; K_{La} = volumetric mass transfer, s^{-1}; and a = area, ft^2 or m^2.

Valves for K_{La} are best determined from pilot studies for the specific compound to be stripped. The packing manufacturers must provide the HTU for particular compound to be stripped with a particular packing and guarantee the performance. When the stripping factor is the below 12 and greater, then NTU is calculated as follows:

$$\mathrm{NTU} = \left(\frac{\mathrm{MSF}}{\mathrm{MSF}-1}\right)\ln\frac{\left[\left(\frac{C_{\mathrm{in}}}{C_{\mathrm{out}}}\right)(\mathrm{MSF}-1)+1\right]}{\mathrm{MSF}} \tag{7}$$

$$\mathrm{MSF} = 0.00075\, H_{\mathrm{ATM}}\frac{A}{W} \tag{8}$$

where H_{ATM} = Henry's law constant, atm; A = air loading rate, cfm; W = water loading rate, cfm; C_{in} = concentration of contaminant in the inlet water, mass/volume; C_{out} = concentration of contaminant in the discharge water, mass/volume; and MSF = manufacturer's stripping factor, unitless.

For volatile removal, the manufacturer's stripping factor generally ranges from 10 to 15 where treatment of discharge gas from the PTA is not required. In this case using a MSF equal to 12 or greater, the minimum air to water ratio is

$$\left(\frac{A}{W}\right) = \frac{16{,}000}{H_{\mathrm{ATM}}} \tag{9}$$

and NTU is approximated by

$$\mathrm{NTU} = \ln\left(\frac{C_{\mathrm{in}}}{C_{\mathrm{out}}}\right) \tag{10}$$

Example

Design a PTA for stripping trichloroethylene at 60°F and above for a water flow rate of 750 gpm, influent concentration of 0.05 mg/L. Assume that treatment of the discharge gas is not required. Use a 6-ft-diameter column. The packing MSF equals 12.

Solution

Determine Henry's law constant for trichloroethylene at 60°F:

$$T = \frac{5}{9}(60-32) = 15.55°\mathrm{C}$$

Determine H_{ATM} using Eq. (3) with values for A' and B' from Table 7:

$$\log H_{\mathrm{ATM}} = \frac{-1716.16}{273.15+15.55} + 8.59$$

$$\log H_{\mathrm{ATM}} = -5.94 + 8.59 = 2.65$$

$$H_{\mathrm{ATM}} = 446.68$$

Determine the minimum (A/W) ratio from Eq. (9):

$$\left(\frac{A}{W}\right) = \frac{16,000}{H} = \frac{16,000}{446.68} = 36$$

Select the (A/W) ratio equal to 40. Then the air flow rate, A, to PTA is determined:

$$A = 40\left(750\frac{\text{gal}}{\text{min}}\right)\left(\frac{\text{ft}^3}{7.48\,\text{gal}}\right) = 3713\frac{\text{ft}^3}{\text{min}}$$

Select air flow rate equal to 4000 cfm. Because the MSF = 12, NTU is calculated from Eq. (10):

$$\text{NTU} = \ln\left(\frac{C_{\text{in}}}{C_{\text{out}}}\right)$$

$$\text{NTU} = \ln\left(\frac{0.05}{0.005}\right) = 2.3$$

For a 6-ft-diameter column, the hydraulic loading would equal

$$\text{Hydraulic loading} = \frac{750}{\frac{\pi(6^2)}{4}} = 26.5\ \frac{\text{gpm}}{\text{ft}^2}$$

At 30 gpm/ft^2, the HTU for packing is reported by the manufacturer to be 3.4, then from Eq. (5) the height of packing is

$$Z = (\text{HTU})(\text{NTU}) = (3.4)(2.3) = 7.48\ \text{ft}$$

Select a factor of safety of 1.4, then use 10.5 ft.

Example

Design a PTA (degasifier unit) for stripping to remove 90% of H_2S and CO_2 from RO product water, which has the following characteristics:

$$\text{Flow rate} = W = 5.0\ \text{MGD} = 3472\ \text{gpm}$$

$$\text{Water pH} = 6.0$$

$$\text{Water } H_2S \text{ concentration} = C_{\text{in}} = 3.0\ \text{mg/L}$$

$$\text{Water } CO_2 \text{ concentration} = C_{\text{in}} = 14.0\ \text{mg/L}$$

$$\text{Minimum temperature} = 60°\text{F} = 15.55°\text{C}$$

Assume that the discharge gas must be treated. Use a stripping factor, MSF, equal to 10.

Solution

Determine H_{ATM} for H_2S and CO_2 using Eq. (3) with values for A' and B' from Table 7.

Henry's law constant for H_2S:

$$\log H_{\text{ATM}} = \frac{-884.94}{(273.15 + 15.55)} + 5.703$$

$$\log H_{\text{ATM}} = -3.065 + 5.703 = 2.638$$

$$H_{\text{ATM}} = 434.51$$

Henry's law constant for CO_2:

$$\log H_{\mathrm{ATM}} = \frac{-1012.4}{(273.15+15.55)} + 6.606$$
$$\log H_{\mathrm{ATM}} = -3.507 + 6.606 = 3.099$$
$$H_{\mathrm{ATM}} = 1256.02$$

Both H_2S and CO_2 have large constants, so as a result both will be readily stripped. Because the H_2S has a smaller constant, it will govern the design. Determine the (A/W) for H_2S from Eq. (8):

$$\mathrm{MSF} = 0.00075\, H_{\mathrm{ATM}} \left(\frac{A}{W}\right)$$
$$\mathrm{MSF} = 0.00075(434.51)\left(\frac{A}{W}\right)$$

Because MSF = 10, then

$$\left(\frac{A}{W}\right) = \frac{10}{(0.00075)(434.51)} = 30.7$$

Then the air flow rate, A, to PTA is determined:

$$A = 30.7\left(3472\,\frac{\mathrm{gal}}{\mathrm{min}}\right)\left(\frac{\mathrm{ft}^3}{7.48\,\mathrm{gal}}\right) = 14{,}250\,\frac{\mathrm{ft}^3}{\mathrm{min}}$$

Select the air flow rate equal to 15,000 cfm. Because the MSF=10, NTU is calculated from Eq. (7):

$$\mathrm{NTU} = \left(\frac{\mathrm{MSF}}{\mathrm{MSF}-1}\right) \ln \frac{\left[(C_{\mathrm{in}}/C_{\mathrm{out}})(\mathrm{MSF}-1)+1\right]}{\mathrm{MSF}}$$
$$\mathrm{NTU} = \left(\frac{10}{10-1}\right) \ln \frac{\left[(3.0/0.3)(10-1)+1\right]}{10}$$
$$\mathrm{NTU} = 1.11 \ln \frac{[10(9)+1]}{10} = 1.11 \ln(9.1) = 2.45$$

Selecting a 12-ft-diameter column, the hydraulic loading would equal

$$\text{Hydraulic loading} = \frac{3472}{\frac{\pi(12^2)}{4}} = 30.7\ \frac{\mathrm{gpm}}{\mathrm{ft}^2}$$

At 32 gpm/ft^2, the HTU for packing is reported by the manufacturer (3 1/2 in. Tri-Packs by Jaeger Products, Inc) to be 3.7, then from Eq. (5) the height of packing is

$$Z = (\mathrm{HTU})(\mathrm{NTU}) = (3.7)(2.45) = 9.1\ \mathrm{ft}$$

Select a factor of safety of 1.3, then use 11.8 ft.

3.2. *System Design Considerations (4,9,14–17)*

3.2.1. *General*

Packed tower aeration (PTA), also referred to as packed column aeration (PCA), is a waterfall aeration process that trickles water down through and air flow up through plastic packing within a cylinder (tower) to interact the water with air. Packed tower aeration is commonly used to treat raw water to softening plant and treat product water from a reverse osmosis plant. Adding PTA to an existing or new plant will require (1) changes in the staging of the well pumps to increase pumping head to pump the raw water to the top of the tower (30–40 ft) and (2) repumping treated water from the tower discharge wet well to the distribution system or storage tanks. Housing the tower usually is not necessary because the water temperature remains fairly constant throughout the PTA treatment process. Consequently, water rarely freezes during the process. The major process elements of PTA are the column (or tower), water distributor, packing medium, mist eliminator, blower (fan), cleansing system, instrumentation, and booster pump.

3.2.2. Column or Tower

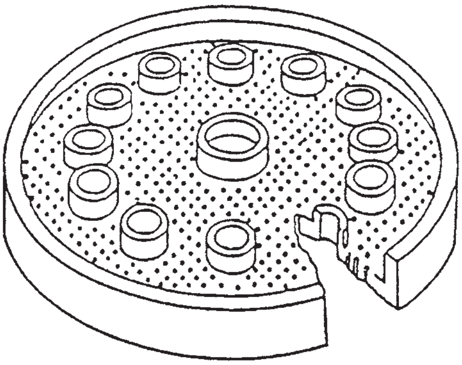
Columns can be constructed from plastic, aluminum, stainless steel, or concrete. Reinforced fiber glass, polyvinylchloride (PVC), and polypropylene (PP) are commonly used plastics because of their relatively lower cost and resistance to chemical deterioration. To take advantage of the benefits of both PVC (chemical resistance) and FRP (fiber reinforced plastic) (strength), PVC vessels are overlaid with FRP. Additionally, these materials have an exterior coating applied to limit light penetration and resist ultraviolet light damage. Limiting light penetration slows down bio-growth fouling of the plastic packing, which allows the PTA to have longer periods between cleaning of the packing. A plastic tower's diameter is usually limited to 12 ft due to shipping restrictions. The inner components for PTA include water distributors, packing, mist eliminators, and miscellaneous components.

3.2.3. Water Distribution System, Packing, and Instrumentation

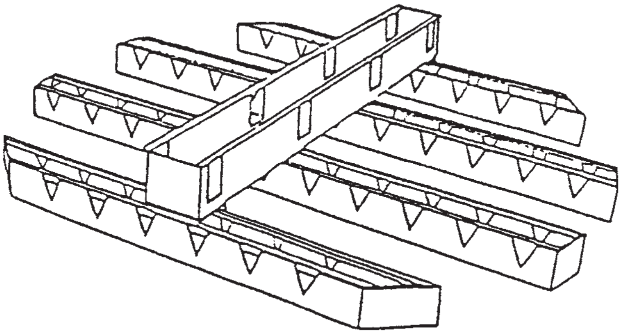
The five primary designs used for water distributors are orifice plate, trough-type distributor, orifice headers, combination of trough and orifices, and spray nozzles (see Fig. 2). These distributors equally dispense the water over the packing causing the water to break into tiny droplets, which increases the air-to-water contact.

The purpose of the packing is to provide a large surface area for the air and water to interact and create sufficient water turbulence to ensure exposure of the water to air. They typically are made from plastic or ceramic, and come in the following forms: super intalox, Tellerettes, Tri-packs, pall rings, berl saddles, and Raschig rings. Additionally, the packing must have large void areas to minimize air headloss through the packing. Therefore, effective packing must provide large surface areas per volume (geometric surface area) and high voids (percentage of void space). Packing geometric surface areas can range from 38 to 85 ft^2/ft^3 and void spaces can range from 90% to 95%.

Other important considerations are weight and strength of packing material. These characteristics determine the height of the packing and how the packing is loaded in the tower. Fragile and heavy material cannot be stacked as high as sturdy and light material. Packing material constructed from PP provides strength, sturdiness and light weight; therefore, it is commonly utilized in PTAs. The bulk density for PP packing ranges from 3.3 to 6.2 lb/ft^3. Other packing materials are compared with PP packing by the use of the bulk density factor. For example, PVC packing may have a bulk density factor of 1.5, which indicates its bulk density is 1.5 times greater than the same packing constructed from PP. In a 12-ft-diameter tower, packing material depth can range from 10 to 12 ft.



Orifice - Type Distributor



Trough - Type Distributor

Fig. 2. Distributor types (US EPA).

Located above the water distributor and prior to the tower air discharge is the mist eliminator. It is designed to prevent water vapor from escaping through the discharge. The eliminators are usually constructed of packing material with higher geometric surface areas that encourage the formation of water droplets on the media. Other appurtenances with the PTA are support grids for the packing material, access hatches (main ways for replacing and removing packing), cleansing system (clean biological growth or mineral deposits off the media), and differential pressure measuring devices. The differential pressure device is used to determine when the packing should be cleaned of biological growth or mineral deposit. The packing should be cleaned before the pressure drop through the tower exceeds the pressure drop when the tower was clean (no fouling) by 50%. The exterior components of PTA are blowers, packing cleaning system, and booster pumps.

3.2.4. Blower, Packing Cleaning System and Booster Pumps

There are two ways that air can be introduced into the PTA—air can be either blown up through the packing (forced-air-type) or pulled up through the packing (induced-air-type). A typical forced-air-type PTA unit is shown in Fig. 3. An induced-air type would allow air to be vented below the packing (plastic media) and the tower air discharge would be ducted to the inlet of the fan. If the PTA is removing hydrogen sulfide or another odorous gas, then the discharge from the tower for forced-type and the

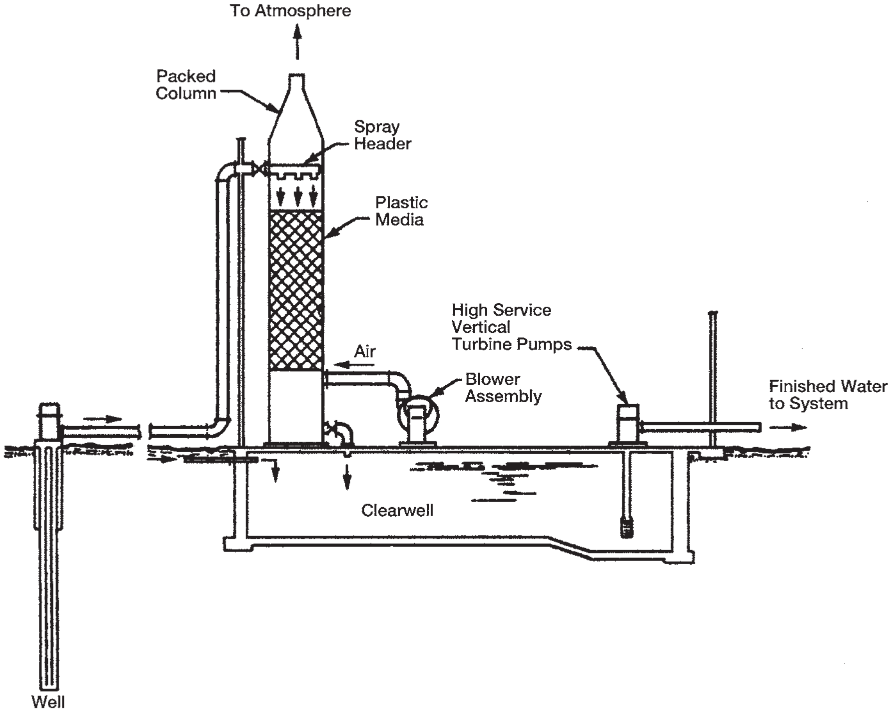


Fig. 3. Packed tower aeration system.

discharge from the fan for induced-type must be directed to an odor control unit (wet-scrubber-type) for the removal of the odorous gas from the air prior to the discharge to atmosphere.

A cleaning system for PTA consists of a spray header located above the mist eliminator, cleaning solution pump, and piping from the sump to the spray. The sump of the packed tower (the lower portion of the tower below the packing and air inlet) is first isolated from the finished pipe. This isolation should include an air gap to prevent contamination of finished water. A cleansing solution is added to the sump and the pump is operated for 4–10 h depending on the extent of the fouling. Depending on the cause of the fouling, the cleansing solution will change as follows:

Mineral fouling caused by the deposit of insoluble carbonates, sulfates, or hydroxides can be removed by preparing the following cleaning solution:

- A 2% sulfamic acid (HSO_3NH_2) water solution can be prepared by dissolving 18 lb of sulfamic acid powder per 100 gal of water.
- A 0.6% solution of hydrochloric acid (HCl) or sulfuric acid (H_2SO_4) can be prepared by adding 2 gal of 30% acid per 98 gal of water.

Biological fouling caused by growth of microorganism (slime) can be removed by preparing a bleach cleaning solution:

- A 2% solution of bleach (NaOCl) can be prepared by adding 16.7 gal of 12% commercial bleach to 83.7 gal of water.

The above solution amounts are based on 100 gal of cleansing solution. To provide a 1-ft depth of cleansing solution in the sump of a 12-ft diameter tower, 846 gal will

Table 8
Typical Air Stripping Parameters for Removal of 13 Commonly Occurring Volatile Organic Chemicals[a] with Unitless Henry's Law Constant Listed (US EPA) (4)

Compound	Henry's law constant	Air-to-water ratio	Air stripper height (ft)[b]	Diameter of packed column (ft)
Trichloroethylene	0.116	29.9	38.03	8.10
Tetrachloroethylene	0.295	11.8	43.77	5.97
Carbon tetrachloride	0.556	6.2	44.88	4.95
1,1,1-Trichloroethane	0.172	20.1	40.06	7.07
1,2-Dichloroethylene	0.023	150.6	33.47	14.89
Dichloromethane	0.048	71.59	28.61	11.12
cis-1,2-Dichloroethylene	0.093	37.10	34.88	8.73
Vinyl Chloride	265.000	0.013[c]	59.58	1.90
Benzene	0.106	32.69	36.25	8.37
Toluene	0.117	29.62	39.04	8.07
m-Xylene	0.093	37.26	40.49	18.34
Chlorobenzene	0.069	50.29	37.60	22.74
1,2-Dichlorobenzene	0.090	38.67	40.45	8.86

[a] Water flow rate, 2.16 MGD (8.17 MLD). Inlet water concentration, 100.0 µg/L. Water treatment objective, 1.0 µg/L. Air-stripper temperature, 50°F (10°C). Air-stripper packing pressure drop, 50.0 (N/m^2)/m packing. Air-stripper packing, 3-in. plastic saddles.

[b] 1 ft = 0.3 m.

[c] Theoretical calculation based on the extremely high Henry's law constant.

be required. Therefore, the amount of chemicals indicated above would be multiplied by 8.46.

3.3. Additional System Design Considerations

Aeration provides a fixed percentage of contaminant removal regardless of influent concentration. To compensate for uncertainty, aeration systems can be designed to incorporate safety factors of two or three times the expected influent contaminant concentrations to ensure compliance with regulatory standards (4).

Aeration system performance is affected primarily by column size and airflow. Increases in airflow and column height improve removal efficiencies. Typical design parameters are provided for 13 common VOCs in Table 8. Design considerations include:

- Type of organic contaminant(s).
- Concentration of contaminant(s).
- Type of packing material.
- Height of packing material.
- Air-to-water ratio.
- Water loading rate.
- Water temperature.

The removal efficiency of a PTA system is affected by the above factors. Figure 4 shows that as packing depth decreases, the air to water ratio *(A:W)* must increase to maintain 95% removal efficiency. Additionally, for VOCs, as the water temperature increases, PTA removal effectiveness increases. As the water temperature increases, the packing depth can be reduced to achieve the same removal efficiency. This effect is

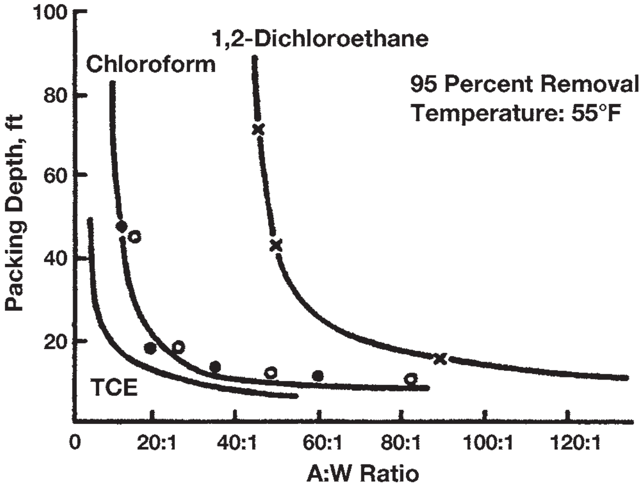


Fig. 4. Effect of compound on packed-column design (US EPA).

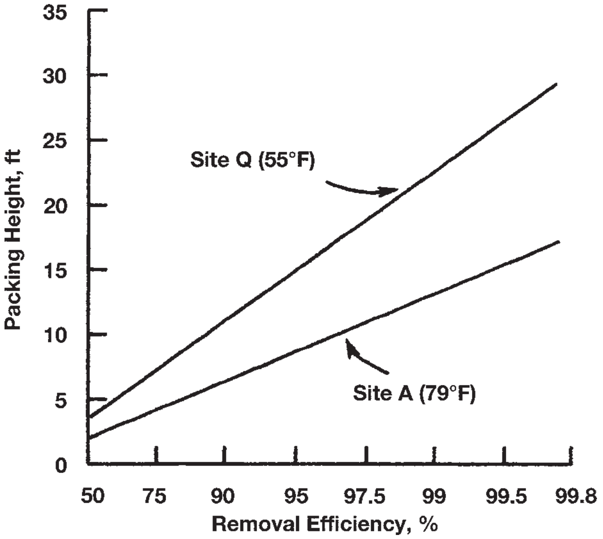


Fig. 5. Packing heights vs removal efficiencies for trichloroethylene (US EPA).

shown in Fig. 5. In most cases, heating water is not cost effective, but in temporary situations of low flow, it has been used effectively.

Different contaminants require different designs to accommodate the particular degrees of volatility and, thus, affinities for aeration. Henry's law constant is used to define this affinity as previously discussed. Packing materials are designed to simultaneously provide a low pressure drop across the material and maximum air–water contact area. The desired contaminant removal level and air-to-water ratio determines the packing material height. The selected column height and design of air intake louvers must comply with local zoning regulations concerning structural height and noise nuisance. These zoning regulations are mostly based on site-specific considerations.

As shown in Eqs. (8) and (9), the minimum air-to-water ratio in a column is a function of Henry's Law constant, pressure, manufacturer's stripping factor and the desired level of contaminant removal. This ratio determines the size of the system's blower, which is the primary component of operating costs for PTA systems. Air-to-water ratios for VOC typically range from 30:1 to 100:1, while for ammonia the ratio typically ranges from 2000:1 to 6000:1. These ranges are temperature dependent and Henry's law constant is adjusted as previously discussed. The water loading rate, the amount of water passing through the column, routinely ranges from 16.9 to 20.4 L/sec/m^2 (25 to 30 gpm/ft^2). The column diameter specification is derived to accommodate the desired water loading on the column.

3.4. *PTA Pilot Testing for VOC Removal*

A pilot PTA can be used to determine the effects of various water loading rates, air flow rates, packing type, and packing material on removal efficiency and/or on the operation of the unit. A schematic of a typical pilot column is illustrated in Fig. 6. Using 8 to 12 column runs, various combinations of design factors can be evaluated. In order to achieve steady conditions, a test run will typically be operated for about 30 min, after which influent and effluent sampling can commence.

To ensure accurate pilot test results, the following precautionary steps should be taken:

- Packing material should be carefully placed into the column to avoid channeling and vacant pockets.
- Pilot column should be level to avoid channeling and wall effects.
- Performance points for sampling should be carefully selected.
- Duplicate samples should be collected and analyzed to verify results.
- To verify laboratory results, split samples can be sent to different laboratory for analysis.

Additional QA/QC steps should be incorporate to ensure accurate results. These include chain-of-custody, field blank, and laboratory blanks (23).

3.4.1. Emission Control

3.4.1.1. VOCs

As a result of using a PTA to remove VOCs from a water supply, the PTA exhaust gas may require treatment for VOC in the gas in order for the emission stream to meet air emission regulations. VOC emissions in lb/hr for PTA units are calculated as the following (4,14):

$$E = \frac{5.004\,V\;(C_1 - C_2)}{1 \times 10^7} \tag{11}$$

where E = emission rate, lb/h; C_1 = influent concentration of the VOC, µg/L; C_2 = effluent concentration of the VOC, µg/L; and V = Water flow rate, gpm.

The calculation emission rate from a PTA must be compared to requirements of applicable air quality standards, which are expressed in terms of either permissible emission rates (lb/day or lb/hr) or projected ground level concentrations (mg/m^3). In addition to air quality standards, PTA emissions should be evaluated for their proximity to residential areas, worker exposure, local air quality, and local meteorological conditions.

When a projected ground level concentration is unacceptable, then the column may be changed to bring the PTA emission into compliance. Dilution of the PTA emissions to an acceptable level is the least costly method and can be accomplished by increasing

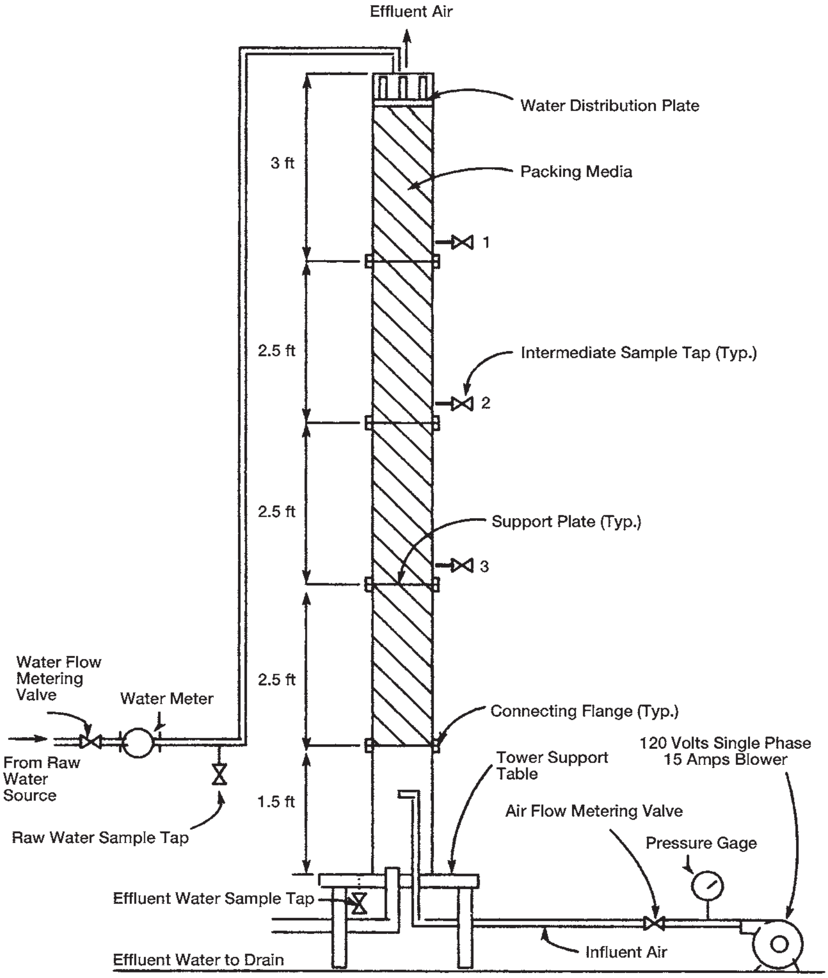


Fig. 6. Schematic of pilot aeration column (US EPA).

tower height, airflow rate, and exhaust gas velocity. If these modifications are unsuccessful or if the PTA emission rate must meet a permissible emission rate, then vapor phase treatment of VOC emission must be considered.

There are four vapor phase treatment processes: (a) thermal destruction, (b) catalytic incineration, (c) ozone destruction with ultraviolet radiation, and (d) granular carbon adsorption (GAC). Processes a–c are not widely utilized due to cost and/or effectiveness of treatment. Thermal destruction is an effective process, but the operating cost is very high due to energy requirements. Catalytic incineration, shown in Fig. 7, has lower energy requirements compared to the thermal destruction process, but it is not effective in eliminating low levels of chlorinated organic compounds. Ozone destruction with an ultraviolet radiation process has limited performance data available; as a result, the performance of this process must be examined in a pilot study for the particular VOC in question in order to determine operational parameters. The most commonly used vapor phase treatment process for VOC is carbon adsorption.

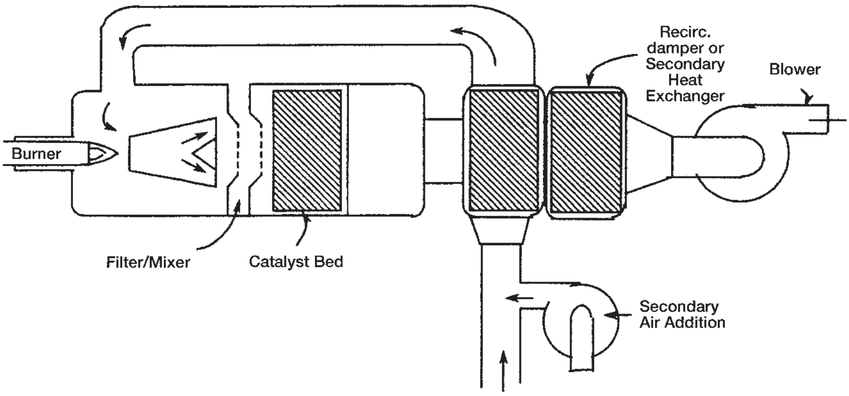


Fig. 7. Schematic of catalytic incineration process (US EPA).

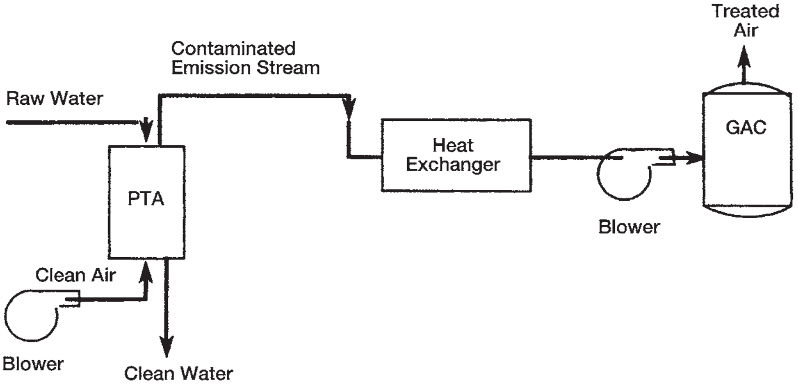


Fig. 8. Vapor-phase carbon system for treatment of aeration exhaust air (US EPA).

Carbon adsorption for control of VOC gases from PTA is accomplished with a vapor phase GAC unit. Currently, GAC is the most frequently used approach to controlling these VOC emissions. The specifications for the GAC gas phase unit depends on operating conditions of the PTA system such as air-to-water ratio, concentration of the VOC in the emission stream, and acceptable level of VOC emissions. Additionally, depending on the characteristics of the emission stream, the GAC unit may require that emission stream to be pretreated. There are three possible pretreatment methods: cooling, dehumidification, and high VOC reduction, which may or may not be needed, prior to the gaseous phase carbon adsorption. Adsorption of VOCs on carbon occurs more favorably at temperatures less than 130°F. At temperatures greater than 130°F, the emission stream temperatures are significant and a heat exchanger may be used to lower the temperature (see Fig. 8). The amount of water vapor in the emission streams from a PTA must be considered for pretreatment. In an activated carbon bed treating the emission stream, the water vapor competes with VOCs for adsorption sites on the activated carbon surface. At a humidity level in excess of 50% (relative humidity) in the emission stream, the efficiency of the adsorption may be limited for a dilute emission stream (lower VOC concentration).

Under conditions when concentration of VOCs exceeds 1000 ppmv, a relative humidity above 50% can be tolerated. Likewise when the VOCs concentration is less than 1000 ppmv, the relative humidity should be reduced to 50% or less (3). Generally, dehumidification of an emission stream is accomplished by either cooling-condensing or by diluting the emission stream. The amount of water vapor in the emission stream can be lowered by cooling and condensing the water vapor in the emission stream. Typically, cooling and condensing of the emission stream can be accomplished by using a shell-and-tube type heat exchanger. Dilution is another alternative available for dehumidification. This alternative can be used when the dilution air humidity is significantly less than the emission stream. The drawback to this alternative is that it increases the air stream flow, which in turn increases the size of the adsorber system. As a result, the dilution alternative may not be cost effective. Another drawback is that the removal efficiency of the carbon adsorber, which is a constant outlet device, will be decreased.

3.4.1.2. Hydrogen Sulfide and Carbon Dioxide

Because CO_2 is an asphyxiant and H_2S is toxic and has a rotten egg odor, the emission stream from a PTA removing these gases from a water source must be treated prior to discharging to ambient air. Wet scrubbers using sodium hydroxide–water solutions at a high pH of 9 and greater are commonly employed to treat the emission stream PTA containing hydrogen sulfide and carbon dioxide. A two-stage wet scrubber is used with the first stage using sodium hydroxide and the second stage using a combination of sodium hydroxide and sodium hypochlorite. Wang et al. (14) state that the efficiency of an absorption process used to remove a pollutant or pollutants from an air flow will depend, in part on

- Solubility of the pollutant(s) in the chosen scrubbing liquor.
- Pollutant(s) concentration in the air stream being treated.
- Temperature and pressure of the system.
- Flow rates of gas and liquid (liquid/air ratio).
- Gas/liquid contact surface area.
- Stripping efficiency of the liquor and recycling of the solvent.

Of the above parameters, the ability to increase gas/liquid contact will always result in higher absorption efficiency in a wet scrubber. If temperature can be reduced and the liquid-to-air ratio increased, then the absorption efficiency will also be improved in the scrubber. The actual design of the tower (diameter, height, depth of packed bed, etc.) will also depend on the given vapor/liquid equilibrium for the specific pollutant/scrubbing liquor. Additionally, the type of tower (packed vs tray, and so on) used will affect this equilibrium. The design of wet scrubbers is not covered in this chapter, but design examples can be found elsewhere in the literature (14).

3.5. Other Types of Tower (4,6)

PTA systems are designed so that water cascades, which imparts the necessary turbulence and air-to-water interface. Tray-type towers impart the turbulence to water by using several layers of slats to mix water with air. Innovations in PTA are reflected in the newest additions to the tower aeration system. Emerging aeration techniques include the catenary grid and Higee systems, which are discussed below.

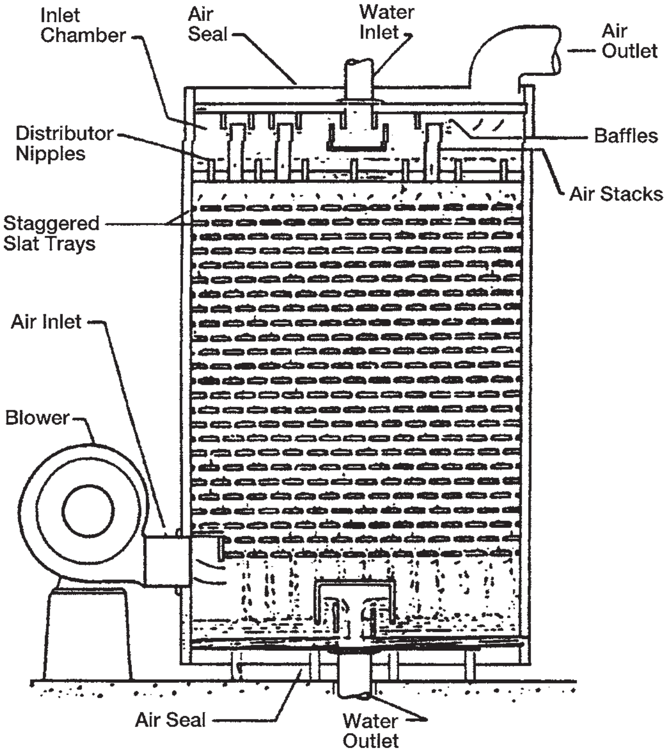


Fig. 9. Schematic of a redwood slat tray aerator (US EPA).

3.5.1. Multiple-Tray Aeration

Water falling and splashing over a series of steps or trays can result in effective aeration. Aeration is mainly achieved by the mixing of air with the falling water in the underlying steps. The creation of turbulence in water is important, because better aeration results are obtained by increasing the water flow to an optimal rate. Cascade aerators do not require inlet heads; thus, relatively large quantities of water can be treated in a comparatively small area, and they are easy to clean. The structure is simple and inexpensive.

The removal of carbon dioxide by cascade aeration is less efficient as compared with other aeration methods. In the transfer of oxygen, there is no substantial difference from other methods. Thus, if raising the oxygen content of the water is the main purpose of aeration, cascade aerators will be very suitable. A reduction of the oxygen deficit by about 30% per step of cascade aerator can be obtained. The aeration of water falling over weirs or dams in streams is a form of cascade aeration. Multiple-tray aeration directs water through a series of trays made of slats, perforations, or wire mesh. Air is introduced from underneath the trays, either with or without added pressure. Figure 9 shows a diagram of a redwood slat tray aerator. Multiple-tray aerators generally consist of a distribution pan or a perforated pipe grid, multiple levels of slated or perforated trays filled with coke or gravel, a collecting pan, an enclosure, and an induced or forced draft ventilation system. Air flows countercurrently with the falling droplets of water in the aerator. Multiple-tray aerators have wide application in the aeration of groundwater for iron and manganese removal and carbon dioxide gas removal. Some efficient multiple-tray aerators use only an atmospheric ventilation system.

The major design considerations for multiple-tray aeration are tray type, tray height, pressurized or unpressurized air flow, and air-to-water ratio. Trays can be constructed from a variety of materials including slat, coke, wood, or plastic and range in stack height from 3.6 to 4.8 m (12 to 16 ft). Utilizing a pressurized air flow system will allow for a higher air flow rate and higher removal compare with an unpressurized system. The air-to-water ratio for a pressurized system is typically 30:1, whereas an unpressurized system may be 10:1 or lower.

3.5.2. System Performance

Slat tray aeration with an air-to-water ratio of 30:1 and a tray height of 3.6 to 4.8 m (12 to 16 ft) has achieved 30–90% reductions of trichloroethylene and 20–85% reductions of tetrachloroethylene.

An atmospheric multiple-tray aerator consists of distribution trays, coke tray, and fine gravel tray. The removal of carbon dioxide by multiple-tray aerator (gravity ventilation system) can be estimated by an empirical equation, developed by Scott (19):

$$P = 100\, e^{-k\, n} \tag{12}$$

where P = percentage of free CO_2 remaining after aeration; n = number of trays; and k = constant ranging from 0.12 to 0.16. The carbon dioxide content is reduced from 13 to about 2 parts per million (ppm); the largest reduction is accomplished by the spray aerator (a distribution pan) and the first tray. The iron content is reduced from 3–5 ppm in passing through the coke trays, while the fine gravel trays below provide a very good filtering effect. The effluent contains only about 0.2 ppm of Fe (depending on the pH and initial iron concentration of the water).

The advantages of multiple-tray aeration units are that they have less surface area that is susceptible to clogging from iron and manganese precipitation compared to packing in a PTA. However, this also becomes a disadvantage because tray aeration is not as effective as PTA in removing carbon dioxide and hydrogen sulfide. Multiple-tray aeration units are generally available as package systems and installed prior to the lime softening process. Another advantage of an atmospheric multiple tray aerator is that there is no fan and therefore no electricity cost. The many disadvantages of multiple-tray aerators (atmospheric ventilation) are (a) carbon dioxide removal will vary seasonally and with changing wind conditions, (b) they show a tendency to clog when the water contains high levels of iron and hinder the trickling of finely divided water droplets, and (c) high expenses for cleaning or replacing the cokes. To cope with these disadvantages, forced or induced draft tray aerators are now more common than the atmospheric-type aerators, and backwashing equipment is used in the new aerators to remove the hydrates. The cleaning system would be similar to those described for PAC.

3.5.3. Catenary Grid

Another type of falling water aeration system is the catenary grid system, in which falling water is directed through a series of parabolic wire screens mounted within the column. The screens cause the water to form droplets and allow air to flow upward through

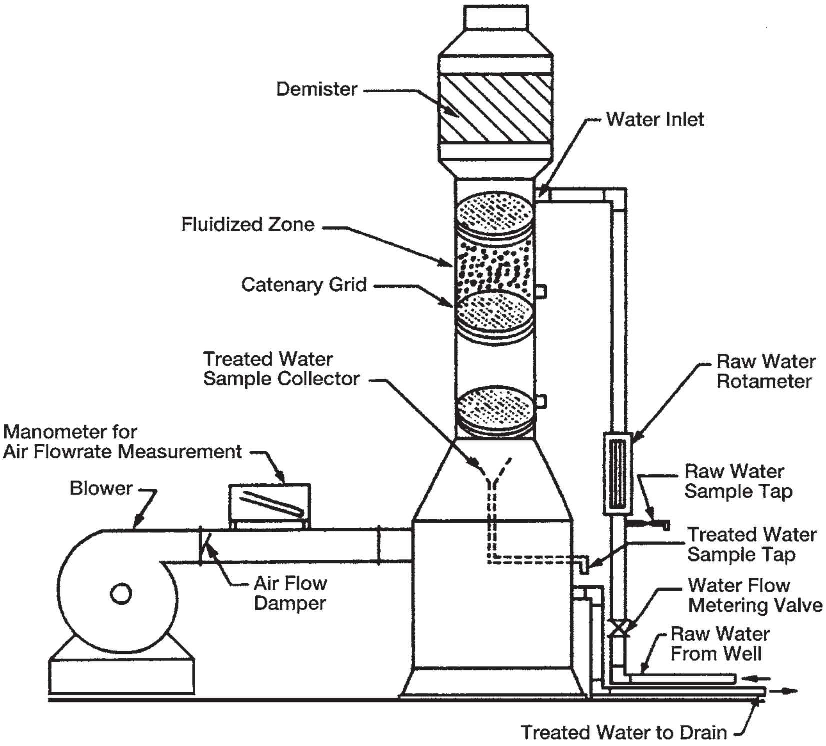


Fig. 10. Catenary grid system (US EPA).

the column. This mixing of the air and water by the grid is similar to the packing materials in PTA systems. The principal design considerations for catenary grid systems are that removal efficiency improves with increases in air-to-water ratios and increasing number of screens in the column. Figure 10 illustrates a forced air catenary grid system.

Compared to PTA, a catenary grid system can achieve comparable VOC removal rates. The catenary grid system requires a higher air-to-water flow ratio than PTA. Additionally, the screens are very thin as compared with packing in a PTA. As a result, the catenary grid system utilizes a smaller diameter column and shorter columns than PTA, resulting in a more compact design and a lower capital cost relative to PTA. A disadvantage of the catanery grid system is that higher air flow for the system results in a higher energy requirement than PTA. Another disadvantage of this system is that there are application limitations due to the limited amount data available on removal efficiency for different organic compounds. As a result, pilot plants would be required to determine design parameters and the effectiveness of the system. These design parameters include air-to-water ratio, number of screens, and hydraulic loading rate. An additional disadvantage of the catenary grid system is that the procedure for scaling systems up from pilot plants to full-scale operations is not fully developed.

3.5.4. Higee Aeration

Another variation of the PTA process is the Higee aeration system. To achieve the necessary air and water mix, water pumped into the center of a spinning disc of packing material and air is pumped countercurrently toward the center from the outside of

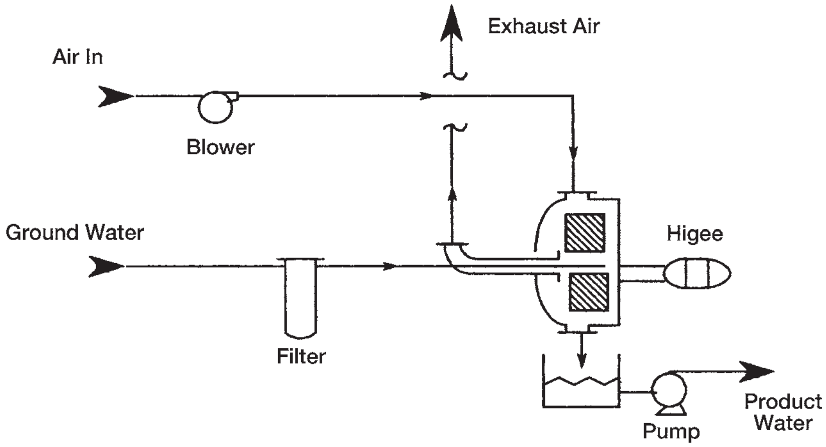


Fig. 11. Schematic of Higee system (US EPA).

the spinning disc. Simultaneously, water flows from the center of the disc and mixes with the air. Like packing used by a PTA system, the packing material used for the disc has a large surface area per unit volume. A schematic of the Higee aeration is shown in Fig. 11.

The advantage of the Higee aeration system is that it requires less packing material than PTA units to attain equivalent removal efficiencies. Additionally, the system utilizes smaller air volumes and can process high water flows in a compact space. As a result, the units used for the Higee aeration system are compact in size as compared to PTA. This allows the Higee aeration system to be used in applications within constrained spaces and heights. Because limited data are available concerning the organic compound removal efficiencies and reliability of the of Higee systems, they are best suited for temporary applications of less than 1 yr, and where space is limited and the capacity required is less than and equal to 6.3 L/sec (100 gpm).

4. DIFFUSED AERATION (4,6)

Another aeration method for the removal of VOCs is the diffused aeration system (4,6). This system utilizes a blower (centrifuge or positive displacement type) and air diffusers, which bubbles air through the water in a contact chamber for aeration. The blowers supply air under pressure to the diffusers, which are located near the bottom of the contact chamber. Most of the pressure requirements are to overcome the static pressure of the water over the diffusers. Additional pressure requirements are for minor losses including friction losses in piping and friction losses through the orifices in the diffusers. The diffusers are used to create fine bubbles that impart water–air mixing turbulence as they rise through the chamber. Figures 12 and 13 show illustrations of diffused aeration systems used for an onsite home well system and water treatment plant (WTP), respectively. The ability to adapt is the main advantage of the diffused aeration system. It can be installed in existing structures such as storage and contact tanks. Because diffused aeration system is less effective than PTA, it is usually utilized only when it can be installed in an existing structure. Another disadvantage of the system is that it consumes more energy than PTA.

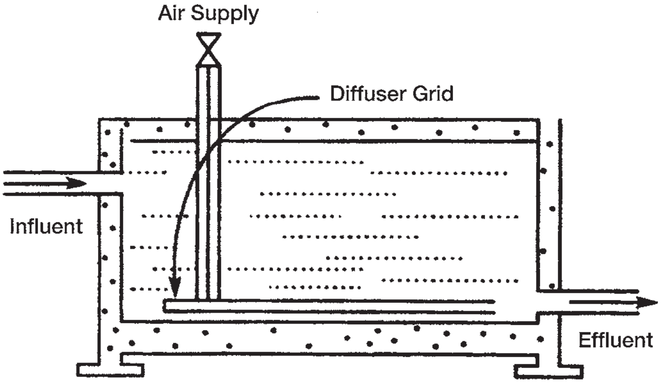


Fig. 12. Schematic of a plant-scale diffused aeration process (US EPA).

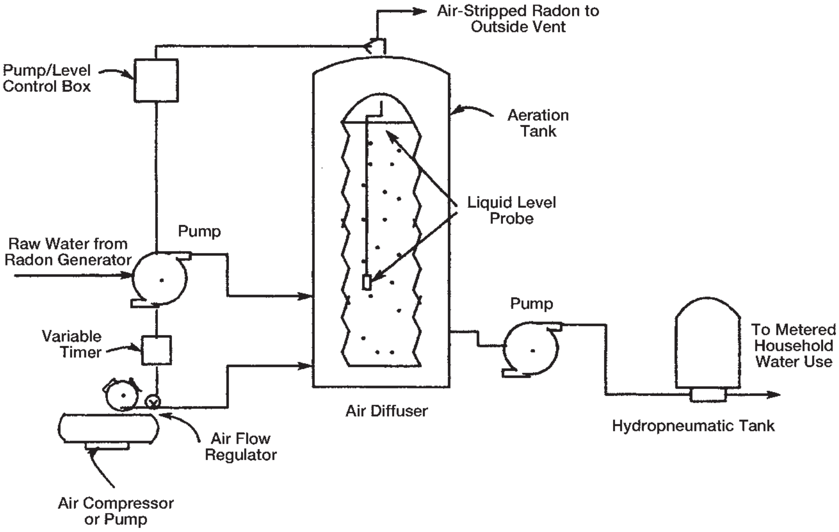


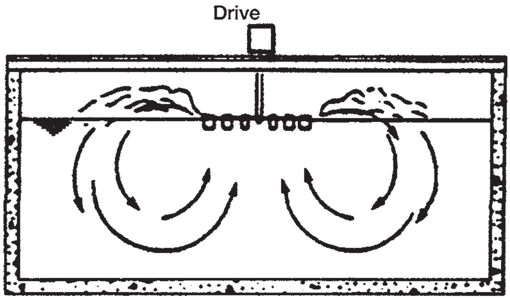
Fig. 13. Home diffused aeration system (US EPA).

4.1. Design Criteria

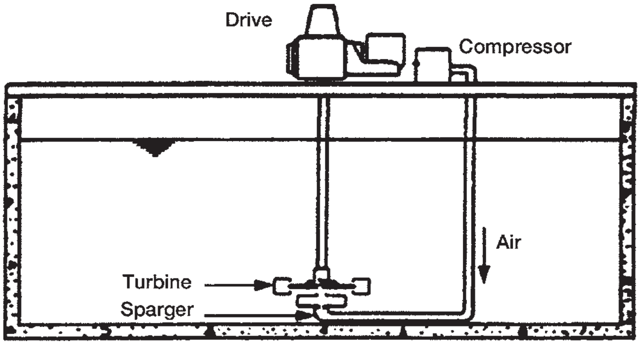
Design considerations for a diffused aeration system are

- Depth of contact tank: 1.5–3 m (5–10 ft)
- Air : water ratio: 5:1 to 15:1
- Detention time: 10–15 min

Other major design considerations are the diffuser and the contact tank hydraulics. The diffusers are porous plates or diffuser tubes that are installed near the bottom of the tank with minimal spacing to ensure maximum water–air mixing turbulence as the bubbles rise up through the water. The shape of the contact tank will also ensure the water–air mixing turbulence. A long and narrow tank creates a plug flow regime and prevents short circuiting around the water–air mixing turbulence. Installing baffling in the tank can help achieve plug flow.



Mechanical Surface Aerator



Submerged Turbine Aerator

Fig. 14. Schematic of mechanical aeration process (US EPA).

5. MECHANICAL AERATION

Mechanical aerators (4,6) can effectively remove VOCs and are commonly used in wastewater treatment, not water treatment. The aerators use surface or subsurface mechanical stirring mechanisms to create water–air mixing turbulence. Figure 14 illustrates a surface and subsurface aerator installations.

Mechanical aerators are easier than PTAs to maintain because they do not contain packing that requires cleaning of biological growth and mineral deposits and they can be added to existing contact tanks. Like diffused aeration, mechanical aeration units require large amounts of space because they demand long detention times for effective treatment. High flow installations require open air design, which may be susceptible to freezing problems in very cold climates. Mechanical aerators also have high energy consumption.

6. SYSTEM PERFORMANCE

Aeration systems are used in removing organic compounds from contaminated groundwater sources (4,6). As previously discussed, most VOCs because of their high and very high Henry's law constants, are effectively removed using aeration systems. PTAs, multiple-tray aerators, and tray aerators can be utilized on small and large WTPs as standalone processes. To make them more practical, other aeration processes such as diffused aeration and mechanical aeration, must be installed in existing tanks. The effectiveness of PTAs, multiple-trays, tray aerators, and other aeration processes in removing trichloroethylene

Table 9
Examples of Removal Efficiencies for PTA Systems (US EPA) (4)

TCE

- A full-scale redwood tray aeration plant with a 3.8 MGD capacity at an air-to-water ratio of 30:1 achieved 50–60% reductions from initial TCE influent concentrations of 8.3 to 39.5 µg/L.
- A full-scale multiple-tray aeration unit with a 6 MGD capacity achieved 50% reductions from initial TCE influent concentrations of 150 µg/L
- A full-scale packed tower aeration column plant using groundwater at an air-to-water ratio of 25:1 achieved 97–99% reductions from initial TCE influent concentrations ranging from 1500 to 2000 µg/L.

Vinyl chloride

- A pilot packed tower aerator with 9°C influent, achieved up to 99.27% removal of vinyl chloride.
- A spray tower aeration unit removed vinyl chloride from groundwater with VOC concentrations of 100–200 µg/L.
- An in-well aeration unit with an air-lift pump achieved 97% removal of vinyl chloride.

Aldicarb

- Aeration was found to be ineffective in reducing levels of aldicarb because of its low Henry's law constant.

VOCs

- A four-stage aeration design with four shower heads and a pressure drop of 10 psi achieved 99.9% VOC removal.

(TCE), vinyl chloride, aldicarb (pesticide), and VOCs are listed in Table 9. The removal performances of a diffused aeration system for several organics (VOCs and carbofuran) are listed in Table 10. PTAs and multiple-tray aerators are effective in removing hydrogen sulfides and carbon dioxide in the range of 90–95%. Comparison of removal efficiencies for PCA (PTA) and diffused aeration is shown in Table 3. As this shown in this table, PCA is more efficient than diffused aeration, but diffused aeration can achieve a comparable removal of trans-1, 2 dichloroethylene and TCE.

7. SYSTEM COSTS

Table 11 compares various aeration systems such as PTA, diffused aeration, multiple-tray aeration, mechanical aeration, catenary grid, and Higee aeration for operations, maintenance, and energy consumption (4,6,15–18,20). All aeration systems do not require high operational skills, but the major difference in these systems is in energy consumption. Multiple-tray and mechanical aeration require the lowest level of operational skill, maintenance, and energy consumption; therefore, for small systems these two aeration systems will have the lowest operational cost.

In the United States, the cost for water treatment and delivery is generally in the range of \$1.00–1.50 per 1000 gal. The additional cost for removing organics, hydrogen sulfides, and carbon dioxides with PTA are within this cost but can significantly increase this cost for water. The costs for PTAs are presented in Table 12 for treatment of dibromochloropropane, trichloroethylene, vinyl chloride, and radon. As shown in this table, the additional costs per 1000 gal for flows of 0.1, 0.5, 1.0, and 10.0 MGD are within the

Table 10
Typical Performance of Diffused Aeration (US EPA) (4)

Compound	% Removal
VOCs	
Trichloroethylene	53–95
Tetrachloroethylene	73–95
1,2-Dichloroethane	42–77
1,1-Dichloroethylene	97
1,1,1-Trichloroethane	58–90
SOCs	
Carbofuran	11–20
1,2-Dichloropropane	12–79
cis-1,2-dichloroethylene	32–85
trans-1,2-Dichloroethylene	37–96
o-Dichlorobenzene	14–72
Ethylbenzene	24–89
Monochlorobenzene	14–85
Toluene	22–89
Xylenes	18–89

Table 11
Comparison of Operation Skills, Maintenance Requirements, and Energy Usage for Small Aeration Treatment Technologies (18)

Aeration technology	Level of operational skilled required	Level of maintenance required	Energy requirement
Packed tower aeration	Low	Low	Varies
Diffused aeration	Low	Low	Varies
Multiple-tray aeration	Low	Low	Low
Mechanical aeration	Low	Low	Low
Catenary grid	Low	Low	High
Higee aeration	Low	Medium	High

cost range of water, but at the lowest flow the cost for a PTA can increase the cost of the water by 290% and at the highest flow it will only increase the costs by 120–160%. These costs also show, like most unit processes, that there is economy in size.

Vinyl chloride is easy to remove with PTA, because it has the largest Henry's law constant and it is the least costly, while dibromochloropropane is most difficult to remove with PTA, because it has the smallest Henry's law constant and it is the most costly. The removal of radon with a PTA is similar in efficiency as removing vinyl chloride; therefore, the costs for radon removal with PTA are shown to be the same as for vinyl chloride. The cost of radon treatment is presented below.

Table 13 shows preliminary cost estimates for removing radionuclides that were developed by US EPA. The cost for radionuclide treatment ranges from $0.10 to $0.75 per 1000 gal. The cost per 1000 gal for removing radon (Rn) with PTAs for population serving 100–500 persons, 3,300–10,000 persons and 75,000–100,000 persons are

Table 12
Cost ($1998) for Percent Removal of Several VOCs and Radon Using Packed Tower Aeration (US EPA) (4)

	Costs by system size			
System capacity (MGD)	0.1	0.5	1.0	10.0
Average daily flow (MGD)	0.032	0.22	0.4	4.32
Population served	500	1,500	3,000	22,000
Dibromochloropropane				
Capital Cost	106,000	420,000	636,000	5,700,000
Annual O&M Cost	4,500	25,000	50,000	460,000
Total Cost ($/1000 gal)[a,b]	1.90	0.90	0.85	0.60
Cost/Home/Year[c]	175	165	160	155
Trichloroethylene				
Capital Cost	85,000	210,000	318,000	2,100,000
Annual O&M Cost	2,700	10,800	21,200	201,000
Total Cost ($/1000 gal)	1.10	0.45	0.40	0.30
Cost/Home/Year	75	70	65	60
Vinyl Chloride/radon				
Capital Cost	54,000	148,000	210,000	1,484,000
Annual O&M Cost	1,600	6,800	16,700	106,000
Total Cost ($/1000 gal)	0.70	0.30	0.25	0.20
Cost/Home/Year	50	45	40	35

[a] Total cost is calculated on amortizing the capital cost over 20 yr at 10% interest rate, adding the annual O&M cost, and dividing by the total annual flow.

[b] 1000 gal = 3.78 m^3.

[c] Cost per home per year is calculated based on total cost per year divided by the number served using 3.0 people per home.

Table 13
Radionuclide Process Treatment Costs (US EPA) (4)

Process	Range of costs of removal process (dollars/1000 gallons of water)
Coagulation/Filtration[a]	0.07–0.28[b]
Lime softening[a]	0.10[b]
Aeration	0.10–0.75[c]
Ion exchange (cationic)	0.30–0.80[c]
Ion and manganese treatment	0.30–1.10[c]
Lime softening (new)	0.50[b]
Ion exchange (anionic)	1.60–2.10[b]
Reverse osmosis	1.60–3.20[c]

1000 gal = 3.78 m^3.

[a] Adding to an existing facility.

[b] 1982 dollars.

[c] 1987 dollars.

shown in Table 14, where lower treatment cost for larger systems reflect economies of scale for the aeration process. Table 15 compares packed column aeration and GAC for treating three different levels of radon in effluent. Aeration is more expensive but more

Table 14
Costs for Removing Radon from Drinking Water by Packed Tower Aeration (US EPA) (4)

	Population served		
	100–500	3300–10,000	75,000–100,000
Total capital cost ($1000)	67	250	2200
Operations and maintenance cost ($1000 per year)	1.2	15	230
Cost (cents/1000 gal)	75	14	9

1000 gal = 3.78 m^3.

Table 15
Costs of Radon Treatment at the Plant Scale (200 gpd) for GAC vs Aeration (US EPA) (4)

Influent concentrations (pCi/L)	Effluent concentrations (pCi/L)		Capital costs in dollars		Operating costs in dollars	
	I[a]	II[b]	I	II	I	II
15,000	1350–3300	750	430–760	900	20	60
30,000	2700–6600	1500	430–760	900	20	80
150,000	1200	67,500	1500	1000	40	80

[a] I = GAC process.
[b] II = Aeration process.

effective than GAC for radon influent levels from 15,000 to 30,000 pCi/L. On the other hand, GAC is more expensive and more effective than aeration for high radon influent levels of 150,000 pCi/L.

The capital costs for the PTA include the tower or column, internal column parts, packing material, blower(s), clear well, booster pump(s), and any associated piping. Variation in capital cost will be due to site-specific conditions including the raw water holding tank, restaged well pump, blower building, chemical facility, noise control installation, and air emission control. Sound attenuation on the blower (fan) can be accomplished by installing fiberglass silencers on the blower inlet. These silencers (Vibroacostics and Aeroacostic) are low cost and only slightly increase the head loss. The equipment cost for a silencer on a 10,000 cfm blower will range from $2500 to $5000, which depends on material (steel or stainless steel) used to construct the house unit for silencer. By contrast, the cost for air emission control for VOC with vapor phase GAC will strongly influence plant design and total costs. US EPA research has shown that emission control with a vapor phase carbon adsorption systems will double the costs of a PTA system. Carbon adsorption systems have significant capital and operation and maintenance costs for carbon contactors, activated carbon material, and gas dryer systems. Also, the cost to control odor (hydrogen sulfide) of the emission stream from a PTA can be significant. The capital cost for a wet scrubber system can be as much as 133% of the cost for PTA. It has been reported that two 15,000 cfm/6.0 MGD PTA units

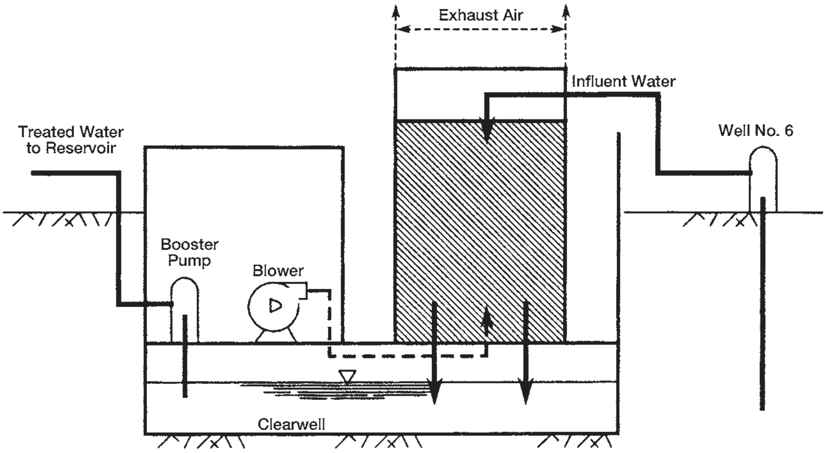


Fig. 15. Schematic diagram of a Scottsdale packed column (US EPA).

have equipment costs of $450,000 and the two 15,000 cfm wet scrubber units have equipment costs of $600,000.

8. CASE STUDY OF PACKED TOWER AERATION

8.1. Scottsdale, AZ

In Scottsdale, AZ (4), two wells of a 24-well system were found to be contaminated with TCE at levels of 18–200 μg/L and 5–43 μg/L, respectively. Prior to selecting PTA as the treatment unit, a cost comparison was done between it and GAC treatment unit. It was estimated that the GAC treatment unit would cost from $0.04 to $0.10/m^3 ($0.17 to $0.38/1000 gal), while PTA would cost only $0.02/m^3 ($0.07/1000 gal). As a result of the lower cost, the PTA was selected.

Figure 15 contains a schematic diagram of this PTA treatment facility, which treated a flow of 75.7 L/s (1200 gpm) by utilizing 3.6 m (12 ft) of packing material in a column diameter of 3 m (10 ft). The PTA used an air-to-water ratio of 50:1. As a result of this design, the PTA achieved over 98% reduction from the initial influent levels, producing effluent levels of TCE ranging from 0.5 to 1.2 μg/L. The system's capital cost was $300,000, and its operation and maintenance costs averaged $25,000 annually.

8.2. Naples, FL

PTA systems were installed as posttreatment of product water from 8 MGD reverse osmosis (RO) water treatment and pretreatment multiple-tray aerators of raw water for a 12 MGD lime softening (LS) water treatment. The Collier County South Water Treatment Plant (WTP) in Naples, FL (15,17), consists of two treatment plants: a reverse osmosis (RO) treatment plant treating brackish water (1500 mg/L of sodium and 3050 mg/L of chloride) from Hawthorn Aquifer and a lime softening (LS) treatment plant treating hard water (total hardness of 325 mg/L as $CaCO_3$ and calcium hardness of 275 mg/L). The existing RO WTP is being expanded from 8 to 20 MGD. The existing multiple-tray aerators on the LS WTP are being replaced with PTAs. The capacity of PTAs for the LS WTP will have a future flow of 20 MGD. Figure 16 illustrates the flow schematic of the existing (dashed) and the proposed (solids) degasifier units and odor control units.

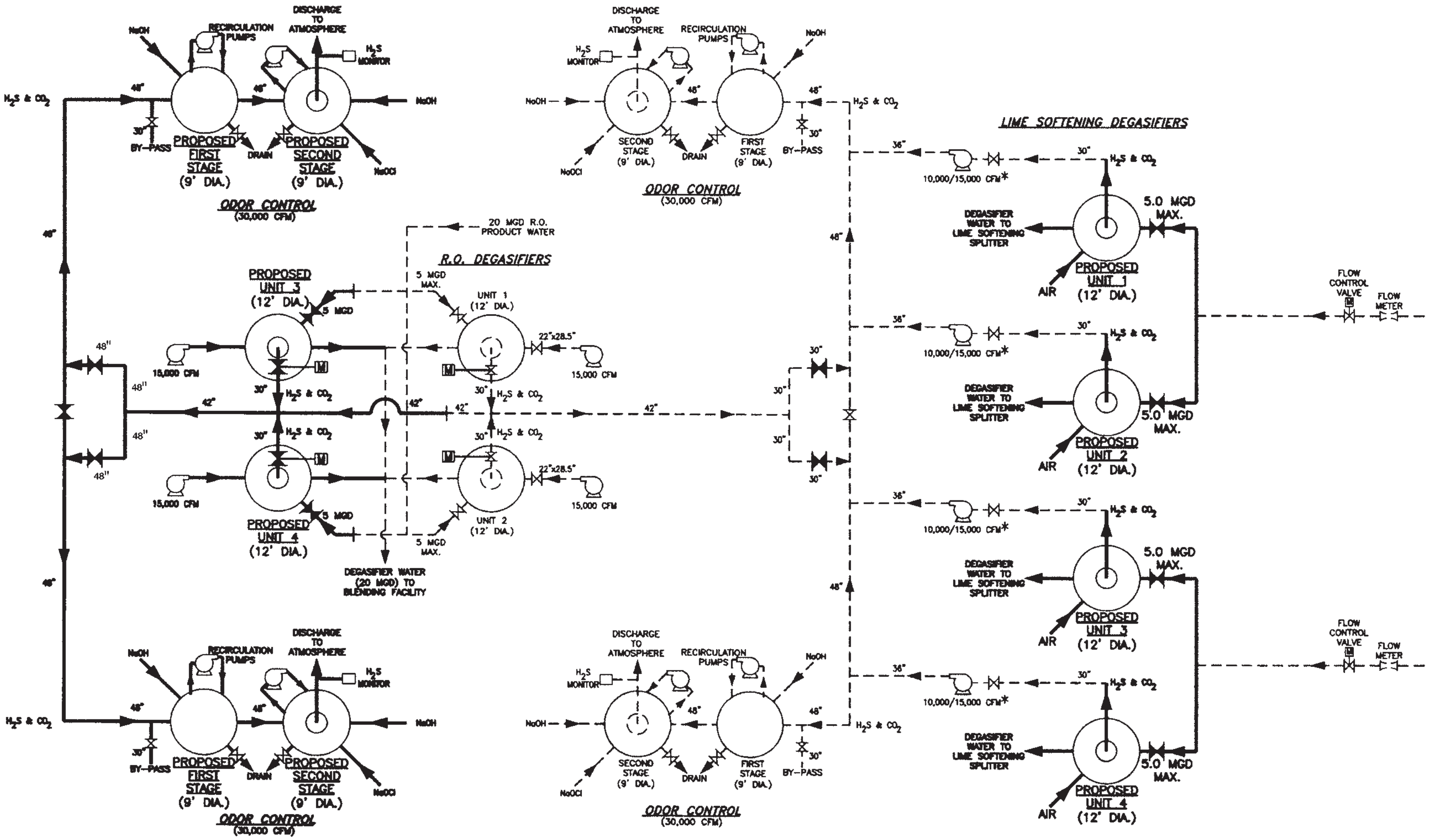


Fig. 16. Flow schematic for proposed improvements at Collier County South WTP, Naples, FL (Hole Montes, Inc.).

Table 16
Equipment List for the Proposed Degasifier Units (PTA) for Collier County South Water Treatment Plant, Naples, FL (15)

Vessel	
Nominal vessel diameter	12 ft
Height of vessel	29 ft-5 in.
Sump height/height to air inlet	8 ft/5 ft
Flooded packing weight	13,564.8 lb
Material	1/4 in. min Type 2 Grey PVC
Liquid flow rate	3470 gpm
Air flow rate	15,000 cfm
Air velocity	2.2 fps
Pressure drop	1.5–2.5 in. water column
Vessel Packing	
Manufacturer	Jaeger Product, Inc.
Volume (Required)	1266.7 ft^3
Height	11.2 ft
Material	Polypropylene
Diameter	3 1/2 in.
Demister Packing	
Manufacturer	Jaeger Product, Inc.
Volume (Required)	108.4 ft^3
Height	11.5 in.
Material	Polypropylene
Diameter	2 in.
Fan (only RO)	
Capacity	15,000 cfm
SP	12 in. water column
Fan speed	2276 rpm
Brake horsepower	42
Motor (only RO)	
Rated horsepower	50
Synchronous speed	1780 rpm
Electrical	230/460V three-phase 60 Hz
Enclosure	TEFC

The hydrogen sulfide and carbon dioxide levels in product water from the RO WTP were 5.0 and 14 mg/L, respectively. The pH of the raw water to RO WTP was lowered to 6.5 with sulfuric acid. The hydrogen sulfide and carbon dioxide levels in raw water to LS WTP are 3.8 and 14 mg/L, respectively. The equipment list for the proposed PTAs is presented in Table 16. Each PTA will have the capacity to treat 5 MGD.

The preliminary equipment cost for the two PTA (12 MGD RO WTP) with blowers was estimated to be $450,000, with an estimated total construction cost of $1 million. Included in the total construction cost are costs for 20 and 30 in. diameter stainless-steel inlet and discharge piping and valving, 30 and 42 in. diameter reinforced fiber glass ducts, 6 in. diameter PVC drain pipes, 2–14 ft diameter concrete pad for the vessels, electrical, instrumentation, and controls. The preliminary equipment cost for the four PTA (20 MGD LS WTP) without fans is $825,000 and the estimated total construction

Table 17
Equipment List for the Proposed Wet Scrubber Units-Odor Control System for Collier County South Water Treatment Plant, Naples, FL (15)

Vessel	
Number of Stages per unit	2
Empty weight	8.5 kips
Service weight	25.0 kips
Vessel body	Filament Wound FRP
Diameter	9 ft
Vessel height/height w stack	27 ft-9 in./40 ft-3 1/2 in.
Water sump height	8 ft
Air velocity at 30,000 cfm	7.86 fps
Recirculation pumps	2
Wetted parts	Glass-reinforced polymer
Operation conditions	450 gpm/60 ft TDH/1155 rpm
Primary efficiency	73%
Design hp	9.4
Maximum hp	9.7
Chemical connection diameters	1 in. NaOH Stages 1 & 2 1 in. NaOCl Stage 2
Packing	
Manufacturer	Jaeger Products, Inc.
Material	Polypropylene
Aerator diameter/height	3 1/2 in. (No. 2)/10 ft
Demister diameter/height	2 in. (No. 1)/1.0 ft
Chemical feed tanks	
Tank service	15% NaOCl
Rated volume	8500 gal
Tank outside diameter/height	11 ft 11 in./14 ft-7 in.
Inner and outer tank material	Polyethylene cross link
Tank service	50% NaOH
Rated volume	8500 gal
Tank outside diameter/height	11 ft 11 in./14 ft-7 in. (w/insulation & heater)
Inner and outer tank material	Polyethylene cross linked
Chemical feed pumps	Positive displacement reciprocating (diaphragm)
Number	Four NaOH & two NaOCl
Motor enclosure/frame	TEFC/56C
Hp/rpm	0.75/1750
Electrical	115 v/60 Hz/single phase
Rated capacity	55 gph @150 psig

cost is $1.7 million. Included in the total costs is 20 in. diameter ductile iron piping and valving and 30 in. diameter reinforced fiber glass ducts. The proposed odor control unit (wet scrubber type) for the 20 MGD RO WTP has an equipment cost of $760,000 and a total construction cost of $1.6 million. The total construction for the scrubber includes costs for 50 × 30 ft reinforced concrete slab for the scrubber units, four 11 ft diameter concrete pad for the vessels, electrical, instrumentation, and controls. See Table 17 for a list of equipment for the odor control system.

NOMENCLATURE

A	air loading rate, cfm
a	area, ft^2 or m^2
A'	empirical constant, unitless
B'	empirical constant, unitless
C_1	influent concentration of the VOC, μg/L
C_2	effluent concentration of the VOC, μg/L
C_{in}	concentration of contaminant in the inlet water, mass/volume
C_{out}	concentration of contaminant in the discharge water, mass/volume
E	emission rate, lb/h
H	Henry's law constant, atm m^3/mole
H_{ATM}	Henry's law constant, atm
H_{unitless}	Henry's law constant, dimensionless
HTU	height of transfer unit, ft or m
k	constant for tray aerator, unitless
K_{La}	volumetric mass transfer, s^{-1}
L	liquid loading, mole of water
M	the molecular weight of the solute
MSF	manufacturer's stripping factor, unitless
n	number of trays
NTU	number of transfer units,
P	free CO_2 remaining after aeration, %
R	universal gas constant, 0.000082057 atm m^3/mole-K
S	solubility, mg/L
T	temperature, Kelvin (K)
V	water flow rate, gpm
VP	the vapor pressure expressed, mm
W	water loading rate, cfm
Z	packing height, ft or m

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Air Stripping

Ju-Chang Huang and Chii Shang

CONTENTS

1. INTRODUCTION

Air stripping is a process by which a liquid, usually water or wastewater, is brought into intimate contact with a gas, usually air, so that some undesirable substances present in the liquid phase can be released and carried away by the gas.

In the past, the major objectives of wastewater treatment were the removal of SS (suspended solids), BOD (biochemical oxygen demand), and coliform bacteria. It is only very recently that the removal of inorganic nutrients, such as nitrogen and phosphorus, has been brought into focus. This is because it has been realized that the discharge of these nutrients into surface waters can result in excessive growths of algae and other aquatic plants, a phenomenon commonly referred to as "eutrophication."

Municipal wastewater and many industrial wastes are among the principal contributors of these nutrients to surface waters. For example, the average concentrations of nitrogen and phosphorus in typical domestic wastewater are, respectively, about 35–45 mg/L as N and 10–15 mg/L as P. Yet, nutrient concentrations of as low as 0.3–0.5 mg/L of nitrogen and 0.01–0.05 mg/L of phosphorus have been reported to cause eutrophication. Therefore, to eliminate this problem, a high efficiency of nutrient removal in the waste treatment process must be achieved. Conventional waste treatment processes are effective in

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removing only about 40–50% of the nitrogen and 25–30% of the phosphorus. Therefore, new treatment technologies must supplement conventional methods in order to improve the nutrient removal efficiencies.

In typical domestic wastewater, ammonia nitrogen represents about 55–60%, organic nitrogen about 40–45%, and nitrates plus nitrites together about 0–5% of the total nitrogen. Within a waste treatment plant, organic nitrogen is easily converted into ammonia species through hydrolysis, which can take place in various treatment units. A portion of ammonia is then utilized by bacteria for cell synthesis, and the remaining ammonia usually leaks out in the final plant effluent as residual ammonia nitrogen. In some situations, active biological nitrification may take place in the aeration tank. In such a case, most of the excess ammonia will be converted to nitrates.

The discovery of chlorinated hydrocarbons in remote global environments prompted researchers to re-examine the rates of evaporation of these compounds. These compounds, usually of high-molecular-weight and low vapor pressure, exhibit unexpectedly high evaporation rates due to their high equilibrium vapor partial pressures (1,2).

The presence of organic compounds that are potentially hazardous or toxic in water bodies is made increasingly evident by advances in analytical methods. This has resulted in the development of new technologies for the removal of these compounds from raw potable surface and groundwater supplies, as well as from process stream wastewater and effluent from groundwater remedial activities.

The removal of substances having reasonable equilibrium vapor pressures at ambient temperatures, including ammonia, carbon dioxide, hydrogen sulfide, and many VOCs (volatile organic compounds), by any of the processes known as air or gas stripping has proven to be efficient and cost effective. The Henry's law constant is a primary indicator of a compound's potential for removal by air stripping.

The countercurrent packed-tower type air stripper offers greater interfacial surface area for mass transfer of volatile compounds than do other gas-stripping processes. This method therefore offers significant advantages in efficiency and overall cost when used for the removal of volatile compounds from potable or wastewater streams. Equations have been developed to optimize system design for removal of specific compounds. In addition, a pilot study, scaled appropriately to the magnitude and sensitivity of the removal requirements of the air-stripping project, is recommended to enable the correct design specifications and overall cost estimates to be prepared. Secondary factors may affect the cost-effectiveness and removal efficiency of air-stripping processes, and therefore will require consideration. Cost modeling and system design to minimize power requirements should also be included in the design process.

2. HENRY'S LAW AND THE MASS-TRANSFER COEFFICIENT

Such processes as mechanical surface aeration, diffused aeration, spray fountains, spray or tray towers, open-channel cascades, and countercurrent packed towers are encompassed by the term air stripping. These procedures produce a condition in which a large surface area of the water to be treated is exposed to air, which promotes transfer of the contaminant from the liquid phase to the gaseous phase. This occurs because under normal conditions the concentration of the contaminant in ambient air is much lower than the concentration in contaminated water.

The ratio of the contaminant at equilibrium in the liquid phase, C_L, to the contaminant in the gaseous phase, C_G, is a relationship known as Henry's law:

$$H_c = \frac{C_G}{C_L} \tag{1}$$

where H_c is Henry's constant. Henry's constant is a property of the solute/solvent system and the temperature, and follows Van't Hoff's relationship (3).

$$\log H_c = \left(\frac{-H^\circ}{RT} \right) + k \tag{2}$$

where H° = enthalpy change resulting from the dissolution of the compound in water; R = the universal gas constant; T = the absolute temperature; and k = a compound-dependent constant.

The general form of the equation for the rate of mass transfer across the gas/liquid interface in a gas stripper is (4)

$$\frac{1}{V}\frac{dm}{dt} = -K_L a\left(C_L{}^* - C_L\right) \tag{3}$$

where V = the liquid volume, m^3; m = the mass of the solute, kg; t = time, s; K_L = the overall liquid mass transfer coefficient, m/s; a = the specific interfacial area, m^2/m^3; C_L = the bulk average concentration in the liquid phase, kg/m^3; $C_L{}^*$ = the liquid concentration in equilibrium with the gas phase concentration, C_G, kg/m^3; and $K_L a$ = the transfer rate constant.

Several models exist for the characterization of gas transfer across the gas/liquid interface (5). According to the two-film model (6), laminar films exist at the gas/liquid interface. The resistance to the rate of mass transfer is given by R_T, and is estimated by summing the resistances offered by the liquid- and gas-phase boundary layers, R_L and R_G, respectively (4):

$$R_T = \frac{1}{K_L a} = R_L + R_G \tag{4}$$

The rate constants for the local liquid and gas phase transfers, k_L and k_G, respectively, are related to the overall transfer rate constant by

$$K_L a = \left(\frac{1}{k_L a} + \frac{1}{k_G a \cdot H_c} \right)^{-1} \tag{5}$$

For extremely volatile compounds, with high Henry's constants, the overall rate of transfer would therefore be controlled by the transfer rate at the liquid-phase boundary.

3. ANALYTICAL REQUIREMENTS FOR AN AIR-STRIPPING PROGRAM

An analytical program must be established, capable of identifying and quantifying contaminants in a water source to be treated, in order to assess remedial technologies. MCLs (maximum contaminant levels) for volatile organic pollutants in micrograms per liter have been prescribed by the US EPA (US Environmental Protection Agency), based on continual improvements in detection techniques.

US EPA published its initial list of 187 organic compounds found in US drinking water in 1975. Analyses were performed using GC-MS (gas chromatography with mass spectroscopy) and a packed column to separate organic compounds. Present-day analyses using a capillary column to separate compounds have increased the resolution of GC-MS detection several fold (7).

Multiple goals must be achieved by analytical methods intended to assess contaminated water bodies, particularly where treatment levels and options will be considered. Objectives must include at least the following (8):

1. Analytical programs must determine the types and concentrations of compounds present in order to allow the evaluation of various treatment methods. The relative economy of a particular technology is often dependent on the levels of contaminants to be treated.
2. The variability of contaminant levels in the water supply must be considered. Groundwater, surface water, and industrial wastewater may all show variations in quality with time due to the effects of pumping, recharge, or process flow. A potential system must be capable of treating the range of influent water qualities encountered to acceptable limits.
3. The concentrations of the contaminants in water immediately prior to and following treatment must be determined to allow analysis of the efficiency of the system. Pilot-study programs designed to determine the effects of varying system parameters are based on reliable water-quality analyses. Where rapid reporting of sampling results is a benefit, the portable GC instrument has found application.

For any analytical program selected, an appropriate quality assurance program must be implemented to minimize errors during the sampling and analysis process. The Federal Register contains the appropriate procedures for US EPA priority pollutants.

4. FEATURES AND DESIGN

4.1. Features of the Countercurrent Air Stripper

A countercurrent packed-tower air stripper has two major components (Fig. 1):

1. A vertical cylindrical tower, whose dimensions range from 6 in. (17 cm) to 9 ft (3 m) or larger in diameter, and from several feet (2 m) to 45 ft (15 m) or more in height. The tower contains a large number of packing elements whose surfaces provide the interface for mass transfer of volatile compounds from the aqueous to the gaseous phase. An aeration nozzle or liquid distributor at the top of the tower evenly distributes the influent water over the packing material in a fine spray. The shell of the tower is commonly made of FRP (fiberglass-reinforced plastic), aluminum, or stainless steel.
2. A high capacity blower forces ambient or heated air into the bottom of the air stripper where the volatile compounds are removed from the water covering the packing elements. The air continues to remove volatile constituents from the water as it is forced up through the column. A demister element at the top of the column prevents the escape of large amounts of water vapor with the exiting air.

The hydraulic head necessary to pump the influent water up to and through the aeration nozzle may be supplied by existing treatment or supply well pumps, or an additional water pump may be supplied.

4.2. Air-Stripper Design Parameters

Four key factors determine the efficiency with which volatile compounds may be removed from the liquid phase in an air stripper. Air-stripper design must include

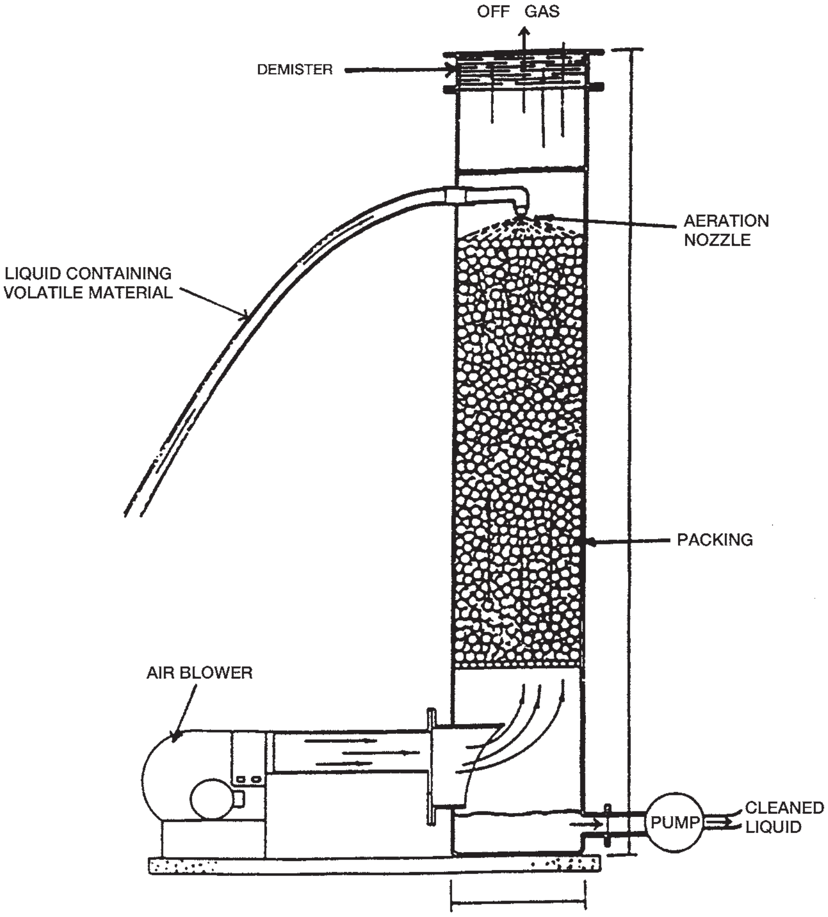

Fig. 1. Diagram of an air-stripping tower.

each of these factors and balance them with operational power requirements to optimize costs.

1. The ratio of air-to-water flow through the air stripper will control the removal rate of the contaminant. The ratio of air-to-water required to produce a desired removal efficiency is determined by the concentration and potential for removal of the contaminant by air stripping, indicated by the Henry constant. An increase in the air-to-water ratio will usually result in greater removal rates, up to a point at which entrainment of the liquid by the air flow occurs, resulting in a sharp increase in the air pressure drop through the stripping column. This phenomenon is known as flooding. The opposite condition occurs when the liquid flow rate is increased until the tower begins to fill with liquid. This is also referred to as flooding. Controlling the air pressure drop through the stripping tower will significantly reduce blower operation costs.
2. The height of the packed tower will also affect the removal efficiency of the contaminant. An optimum balance between the air-to-water ratio and the tower height results in acceptable removal efficiencies at the lowest combination of capital and operational cost.
3. The desired rate of flow of the liquid to be treated will determine the diameter of the air-stripping column.

4. The type of packing material will have an impact on the mass transfer rate, because the surface area of the packing provides the air-to-water interfacial area.

The size of the packing also affects the air pressure drop through the tower. Smaller size packing material offers more surface area than larger materials, but also offers more resistance to the air flow. The ratio of column diameter to nominal packing size should be greater than 12 to prevent channeling of the water along the walls of the air stripper (9).

Henry's constant, H_c, is an indication of how readily a compound will evaporate from a water body, and hence its potential for removal by air stripping. Although Henry's constants for many volatile organic compounds have been presented in the literature (4,8–10), it may be necessary to calculate the constant for compounds for which sufficient data do not exist. Application of regression analysis to equilibrium headspace concentrations of liquid samples of known concentration has been described as a method for empirically determining Henry's constant (8,9). Kavanaugh (9) demonstrated the van't Hoff effect, finding that for many volatile organic compounds Henry's constant increased approximately threefold for every 10°C rise in temperature.

It is the overall mass transfer coefficient, however, that ultimately controls the rate of removal of a substance by air stripping. For example, dichloroethane, which has a lower Henry's constant than trichloroethylene, has been found easier to remove by air stripping, owing to its higher mass transfer coefficient (10). The mass transfer coefficient for a specific substance in a specific air-stripping system may be calculated by (9):

$$K_L a = k_L a = \alpha \left(\frac{L_M}{U_L} \right)^{1-n} \left(\frac{U_L}{\rho_L D} \right)^{0.5D} \tag{6}$$

where L_M = the liquid mass flux rate, kg/m^2-h; α and n = constants specific to the packing type; U_L = the liquid viscosity; ρ_L = the liquid density; and D = the molecular diffusion coefficient of the compound in water.

Information provided by the packing manufacturer is needed to apply Eq. (6) to calculate the mass transfer coefficient.

A quantity termed HTU (the height of a transfer unit) (9) characterizes the efficiency of mass transfer from water to air:

$$\text{HTU} = \frac{L}{K_L a \cdot C_o} \tag{7}$$

where L = the molar flux rate of the contaminant in the liquid phase, kmol/m^2-s, and C_o = the molar density of water (55.6 kmol/m^3). Analytical error may be introduced in the calculation of HTU due to uncertainties in various factors used to calculate the mass transfer coefficient. Commonly, existing field data are used for this design parameter. If such data are nonexistent for the contaminant to be removed, pilot study data may be analyzed to yield dependable mass transfer coefficient data suitable for final, full-scale design.

A design factor termed NTU (the number of transfer units) was also introduced by Kavanaugh (9) to characterize the difficulty of removing the contaminant from the liquid phase:

$$\mathrm{NTU} = \left(\frac{S}{S-1}\right)\ln\left[\frac{C_{\mathrm{inf}}(S-1)}{C_{\mathrm{eff}}} + \frac{1}{S}\right] \tag{8}$$

where C_{inf} = the concentration of the contaminant in the influent water; C_{eff} = the concentration of the contaminant in the effluent water; and S = a concept known as the stripping factor. The stripping factor (4) is crucial in determining the ability of an air stripper to remove a specific contaminant. Theoretically, if $S > 1$, complete removal of the contaminant could be achieved by increasing the height of the packed tower to infinity. Conversely, if $S < 1$, the removal rate would have an upper limit despite further limits in tower height. It is necessary to design for a stripping factor greater than 1. Therefore, the stripping factor, S, is determined by

$$s = \frac{G'}{L'}H_c \tag{9}$$

where G'/L' = the volumetric air-to-water ratio. Thus, it may be seen that contaminants with lower Henry's constants will require higher air-to-water ratios to achieve successful removal rates.

A graphic comparison of the stripping factor *(S)* and the number of transfer units (NTU) shows that beyond $S = 4$–5, little additional contaminant removal occurs (9), as shown in Fig. 2. A stripping factor of 3 is suggested for most calculations of the required air-to-water ratio. NTU for air-stripper design can be calculated by substituting the desired removal efficiency into Eq. (8). The product of the HTU and the NTU yields the packed column height necessary to effect the desired removal of the contaminants:

$$Z = \mathrm{HTU} \times \mathrm{NTU} \tag{10}$$

where Z = the height of the packed column, m. A safety factor of 1.5 is recommended when implementing the tower height calculated by this method (9).

Air-stripping tower diameter is selected as a function of the liquid loading rates necessitated by the required design flow capability. The optimum tower diameter may be determined with the use of pressure-drop curves developed by Eckert (11) as shown in Fig. 3. The volumetric air-to-water ratio, calculated by Eq. (9), is converted to a weight-to-weight ratio and plotted on the abscissa in the form:

$$X = \left(\frac{L'}{G'}\right)\left(\frac{\rho_G}{\rho_L - \rho_G}\right)^{0.5} \tag{11}$$

where L'/G' = the volumetric water-to-air ratios and ρ_G and ρ_L = the densities of air and water, 1.205 kg/m^3 and 998 kg/m^3, respectively.

The ordinate value, corresponding to the intersection of the abscissa value with the appropriate pressure-drop curve (as supplied by the packing manufacturer), allows the determination of the allowable gas-flow rate from

$$Y = \frac{G'^2 C_f^{\,0.1}}{\rho_G(\rho_L - \rho_G)} \tag{12}$$

where G' = the optimum gas flow rate and C_f = the packing factor. From the volumetric ratio, the optimum liquid loading rate may also be determined.

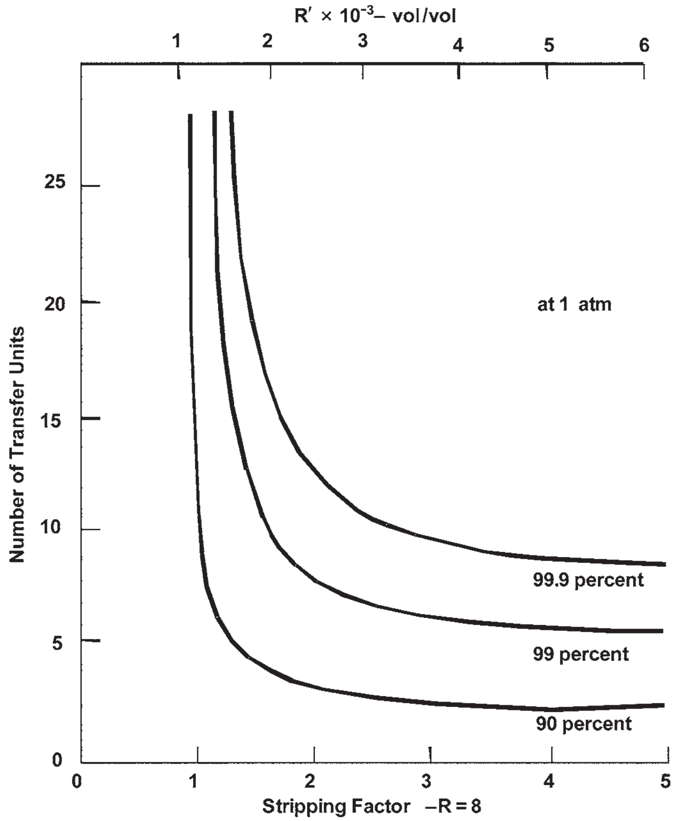

Fig. 2. General relationship between stripping factor and NTU.

The tower diameter may then be determined by:

$$\Phi = \left(\frac{4}{\pi} \frac{Q_L \rho_L}{L'} \right)^{0.5} \tag{13}$$

where Φ = the tower diameter, m; Q_L = the design flow, m^3/s; and L' = the liquid loading rate, kg/m^2-s.

Typically, the air-stripper manufacturer will supply liquid flow ranges acceptable for a particular tower. Selecting an air stripper for which the design flow is at the lower end of the tower's rated capacity will produce high contaminant removal rates, but may not optimize power requirements. For large-scale systems where significant operational costs may be incurred by overdesigning the system, the use of pressure-drop curves and calculations such as Eqs. (1)–(13) are required.

4.3. Packing Material

The function of the packing material in an air stripper is to provide a large wetted surface area for mass transfer of contaminants to the gas phase, or ambient air. Several shapes and sizes are available, such as rings, saddles, and spheres. The packing material is commonly manufactured from polypropylene, PVC, or ceramic.

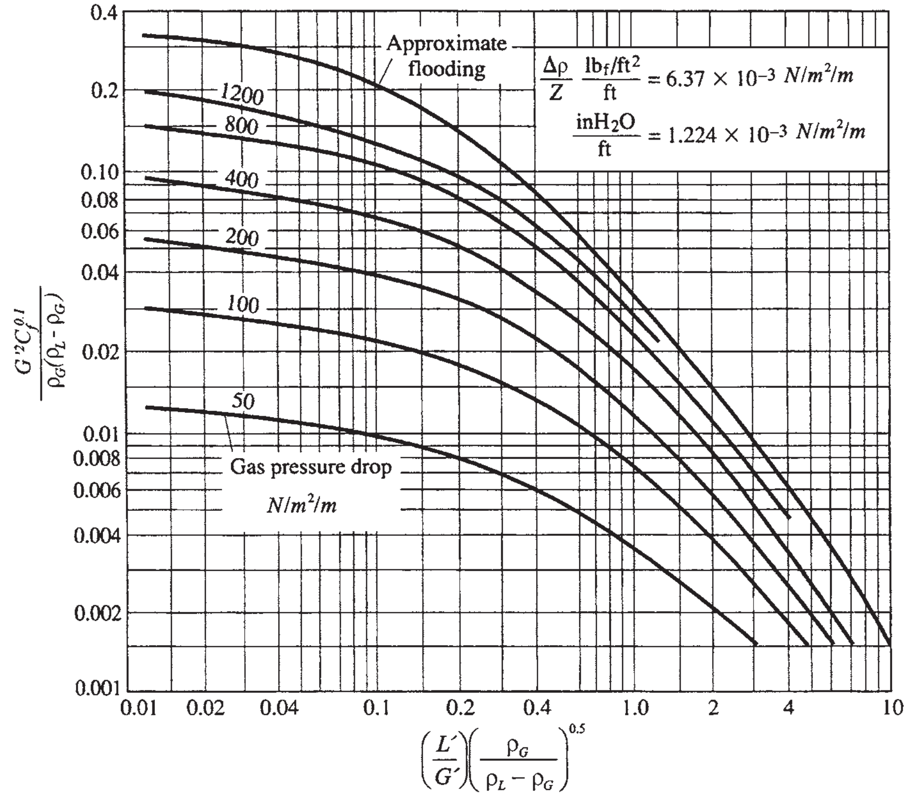

Fig. 3. Flooding and pressure drop correlations for packed towers.

When selecting a packing material, several factors must be balanced. A packing material that offers a large surface area for mass transfer will usually present more resistance to countercurrent air flow, causing a higher gas pressure drop. Different materials offer better resistance to corrosivity, encrustation, or unfavorable water conditions. Hand et al. (8) suggest an initial packing material selection offering a very low gas pressure drop, allowing the engineer to increase removal efficiency, if necessitated at some future time, by replacing the packing with a smaller or different-type packing material with more surface area.

5. PILOT STUDIES

The mass-transfer coefficient is sensitive to several factors, including Henry's constant of the contaminant, the packing factor, and the temperature of the ambient air and water to be treated. An HTU value, calculated at 20°C from Eq. (7), would require a fivefold increase if ambient water and air temperatures of 5°C and –12°C, respectively, were encountered (9). Therefore, the equations presented are recommended for initial design work and evaluation of pilot studies or field data. Data from pilot studies are required to provide dependable values for the mass-transfer coefficient and the effects on removal efficiencies produced by varying system parameters. An analytical program capable of accurately indicating contaminant species and concentrations in influent and effluent water must also be employed.

A pilot study was performed by Bilello and Singley (3) using a 15 in. (38.1 cm) diameter PVC column, scaled up from a 6 in. (15.2 cm) column used in earlier studies. The effects of varying the air-to-water ratio, tower height, packing material, and temperature were studied. Good correlation between data obtained by each column was observed.

Prior to installation of a 9 ft (2.7 m) diameter packed column for removal of TCE (trichloroethylene), DIPE (diisopropyi ether), and MTBE (methyl tertiary butyl ether) from a municipal well water supply, a pilot study was performed using a 12 in. (30.5 cm) packed column. Packing material, liquid and air flow rates, and removal efficiencies were evaluated for the compounds present. In the pilot study, TCE, which has a higher Henry's constant than DIPE, was found to be more readily removed. Based on these findings, a full-scale design resulting in 99.9% removal of DIPE was implemented.

Air-stripper manufacturers and suppliers have assembled data banks based on similar pilot studies. For smaller-scale projects involving common volatile organic compounds, these existing data may be sufficient to specify air-stripper requirements based on the design engineer's experience with such systems and the provision of some system overcapacity. A pilot-scale program is required where it is uncertain that adequate removal of a contaminant may be achieved by existing designs, or where, owing to the economics of large-scale installations, incorrect specifications may later present unacceptable additional capital or operating expenses.

Example 1

A manufacturer of protective coatings (roof coatings, driveway sealers, and automotive undercoatings) uses 45 gpm (170 L/min) of groundwater, pumped from a well on the facility's property, for non-contact cooling purposes. The groundwater is contaminated with 5700 ppb of TCE (trichloroethylene), and therefore cannot be discharged to the local sewage treatment plant in accordance with the facility's NPDES permit, which specifies a maximum limit of 100 ppb TCE. Design an air stripper to reduce the TCE to within acceptable discharge limits.

1. A pilot study was performed by an air-stripper manufacturer using a pilot tower with the following specifications:
   Diameter, 2 ft (0.61 m)
   Packed height, 8.5 ft (2.59 m)
   Air-to-water ratio, 160:1 (volumetric)
   Henry's constant, 0.415 (from previous studies)
   Packing material, #1 Tri-pack
   During the pilot study the influent concentration of 2300 ppb TCE was reduced to 190 ppb in the effluent.

2. A value for HTU was calculated from the pilot test data:

$$\begin{aligned} S &= \frac{G'}{L'} H_c \qquad \text{(Eq. 9)} \\ &= 160 \times 0.415 \\ &= 66.4 \end{aligned}$$

$$\begin{aligned} \text{NTU} &= \left(\frac{S}{S-1}\right)\ln\left[\frac{C_{\text{inf}}(S-1)}{C_{\text{eff}}}+\frac{1}{S}\right] && \text{(Eq. 8)} \\ &= \left(\frac{66.4}{66.4-1}\right)\ln\left[\frac{2300\times(66.4-1)}{190}+\frac{1}{66.4}\right] \\ &= 2.52 \end{aligned}$$

$$\begin{aligned} \text{HTU} &= \frac{Z}{\text{NTU}} && \text{(Eq. 10)} \\ &= \frac{2.59}{2.52} \\ &= 1.03 \text{ m} \end{aligned}$$

3. A production 2 ft (0.61 m) diameter tower has a packed height of 19 ft (5.49 m) and a rated flow of 15–60 gpm (56.8–227 L/min). The blower capacity of the stripper is 600 ft^3/min (17 m^3/min):

$$S = \frac{G'}{L'}H_c \qquad \text{(Eq. 9)}$$

Using an in-between flow value of 45 gpm (0.17 m^3/min),

$$\begin{aligned} S &= \frac{17}{0.17}\times 0.415 \\ &= 41.5 \end{aligned}$$

$$\begin{aligned} \text{NTU} &= \frac{Z}{\text{HTU}} && \text{(Eq. 10)} \\ &= \frac{5.49}{1.03} \\ &= 5.33 \end{aligned}$$

$$\begin{aligned} \text{NTU} &= \left(\frac{S}{S-1}\right)\ln\left[\frac{C_{\text{inf}}(S-1)}{C_{\text{eff}}}+\frac{1}{S}\right] && \text{(Eq. 8)} \\ 5.33 &= \left(\frac{41.5}{41.5-1}\right)\ln\left[\frac{5700\times(41.5-1)}{C_{\text{eff}}}+\frac{1}{41.5}\right] \end{aligned}$$

Solving for the effluent concentration,

$$C_{\text{eff}} = 30.2 \text{ ppb}$$

$$\begin{aligned} \%\,\text{Removal} &= \frac{5700-30.2}{5700}(100) \\ &= 99.47 \end{aligned}$$

The calculations show the concentration of TCE would be reduced well below the permitted limit.

The value for the stripping factor, *S*, appears to be high in view of pressure-drop considerations. A reduction in the size of the blower would produce energy savings and still achieve an acceptable reduction in TCE.

The tendency with production units is to provide blowers of sufficient capacity to allow satisfactory removal of a wide range of compounds, many with Henry's constants much lower than that of TCE. Frequently, a sliding gate valve is provided as a means of reducing the air flow, but unless the blower capacity is reduced, little power savings will result. For modest systems such as the example problem, the small power saving realized by down-sizing the blower is usually outweighed by the advantages of having excess capacity to handle colder temperatures, decreases in regulated discharge limits, or increases in influent contaminant levels.

6. AMMONIA STRIPPING

In addition to the volatile organic compounds found in water, ammonia is an inorganic compound that may occur in drinking water supplies and is frequently present in wastewaters. Ammonia nitrogen exists in both the dissolved gas form (NH_3) and in true solution (NH_4^+). These two species are present in a dynamic equilibrium according to the equation:

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

This equilibrium is controlled by the solubility product which varies with temperature. Therefore, the relative concentrations of these two species depend on both the pH of the solution and the temperature. In general, at a temperature of 20°C and a pH of 7 or below, only ammonium ions are present. As the pH increases above 7, the chemical equilibrium is gradually shifted to the left in favor of the ammonia gas formation. At a pH of about 11.5–12, only the dissolved gas is present. Figure 4 shows this relationship at 0, 20, and 40°C.

In addition to converting all the ammonia to the dissolved gas phase, efficient ammonia stripping requires proper conditions to facilitate a rapid transfer of the dissolved gas from the liquid phase to the air. This can be achieved by the creation of numerous small water droplets in conjunction with an ample supply of air flow. This is because the surface tension at the air–water interface is at a minimum when the water droplets or surface films are being formed, and transfer of dissolved gas from the liquid phase to the air flow is at a maximum at this instant. An ammonia stripping tower, similar to a conventional cooling tower, is normally used for ammonia removal (12).

The efficiency of an ammonia stripping operation depends primarily on five factors:

1. **pH.** As shown in Fig. 4, the relative distribution of the dissolved NH_3 gas vs the NH^{4+} ions in true solution depends greatly on pH. Because only the dissolved gas can be removed from solution, it is important to raise the pH to a value of 11 or higher so that at least 95% of the ammonia nitrogen is converted to the gas form. In full-scale operation, lime is usually the most economical, and thus is the most commonly used material for raising the pH. The amount of lime required to raise the pH depends on the characteristics of the water, primarily its bicarbonate concentration. Figure 5 illustrates the quantities of lime needed to raise the pH of two different domestic sewage samples. This must be determined for each situation.
2. **Temperature.** The liquid temperature can affect the ammonia stripping efficiency in two different ways. First, at a given pH, the percentage of ammonia nitrogen present as a dissolved gas increases with temperature as shown in Fig. 4. For example, at pH 10, at a temperature of 40°C about 95% of the ammonia nitrogen is present as the gas, but at 0°C only about 50% is present in the gaseous form. Second, the solubility of ammonia gas in water increases with decreasing temperature. The greater the solubility, the greater the amount of air required to remove a given amount of ammonia gas.

   Theoretically, the rate of ammonia stripping should be proportional to the difference in the partial pressures of ammonia between the liquid and the gaseous phases. Because a decrease of every 10°C in the process water would result in about a 40% decrease in the

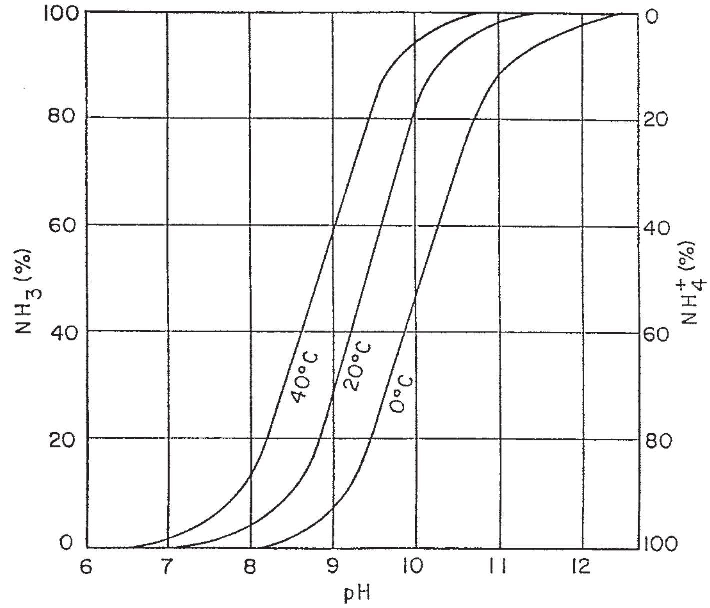

Fig. 4. Effects of pH and temperature on the distribution of ammonia and ammonium ion in water.

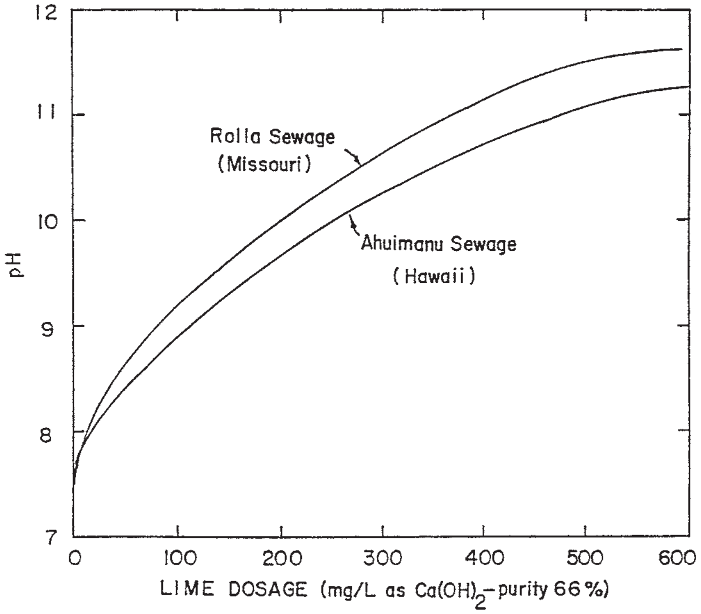

Fig. 5. Amounts of lime required to raise the pH of two sewage samples to various levels.

difference of the partial pressures, the rate of ammonia stripping can be expected to decrease in the same proportion. Therefore, if the operating efficiency must be maintained as high in the winter as in the summer, a substantial increase of air flow must be provided in order to reduce the ammonia partial pressure in the air stream and thus maintain a sufficient partial pressure difference between the liquid and the gaseous phases. If the ambient air temperature drops below 0°C, freezing problems may occur, severely hampering the stripping operation. Even if icing and fogging do not occur at this temperature, the drastic decrease in removal efficiency, reported to be less than 30% (13), would make the ammonia stripping operation impractical and non-economical.

3. **Rate of Gas Transfer.** In order to remove ammonia from water, the dissolved NH_3 molecules must first move from the bulk liquid solution to the air–water interface, and then from the interface to the stripping air flow. Therefore, there are two factors that affect the rate of ammonia gas transfer from the liquid to the surrounding atmosphere.
   a. Transport of the NH_3 molecules from the bulk liquid solution to the air–water interface. This is accomplished by molecular diffusion, but turbulent mixing is much more effective. If the distance of the transport is relatively short, such as that existing within a small water droplet, the rate of gas transport would seldom become a limiting factor governing the overall ammonia release rate.
   b. Transfer of the ammonia molecules from the air–water interface to the gaseous phase. The maximum rate of the interfacial gas transfer takes place when the surface tension is at a minimum, which normally occurs when the water droplets are being formed. Once the water droplets are formed, the interfacial gas transfer becomes quite difficult. Therefore, by maintaining a condition in which there are repeated formations of water droplets of small size, the gas transfer rates within the droplets as well as on the droplet surfaces can both be maintained at the maximum rate. This is a fundamental necessity for the design of an ammonia stripping tower.

   Besides the surface tension, the difference in the ammonia partial pressures between the liquid and the gaseous phases is actually the driving force causing the interfacial gas transfer. The maximum transfer rate will occur when there exists a maximum difference in the partial pressures. With a given ammonia concentration, the partial pressure in the liquid phase is constant. The ammonia partial pressure in the gaseous phase can be minimized by supplying an ample amount of air flow to dilute the concentration of the ammonia released into the gaseous phase. Therefore, the amount of air supply also affects the gas transfer rate.

4. **Air Supply Rate.** Because the difference in the ammonia pressures between the liquid and gaseous phases is the force for ammonia to transfer from the liquid to the air flow, an ample supply of air flow through the ammonia tower will dilute the concentration of the ammonia released thereby reducing its partial pressure in the gaseous phase and maximizing the ammonia release rate. The amount of air that is required to achieve a given degree of ammonia removal can be determined from the following analysis of the material balance (14):

$$L_q(x_1 - x_2) = G(y_1 - y_2) \tag{14}$$

   where L_q = liquid flow through the stripping tower, moles water/unit time; x_1 = inlet water ammonia concentration, moles ammonia/mole water; x_2 = outlet water ammonia concentration, moles ammonia/mole water; G = air flow rate through the stripping tower, moles air/unit time; y_1 = outlet air ammonia concentration, moles ammonia/mole air; and y_2 = inlet air ammonia concentration, moles ammonia/mole air.

   If it is assumed that the water leaving and the air entering the stripping tower have a zero ammonia concentration, then Eq. (14) can be rewritten as

$$L_q x_1 = G y_1 \quad \text{or} \quad \frac{G}{L_q} = \frac{x_1}{y_1} \tag{15}$$

   That is, the amount of air requirement per unit volume of water, G/L_q, is equal to x_1/y_1, or the concentration of ammonia in the inlet water (mole/mole) divided by the ammonia concentration in the outlet air.

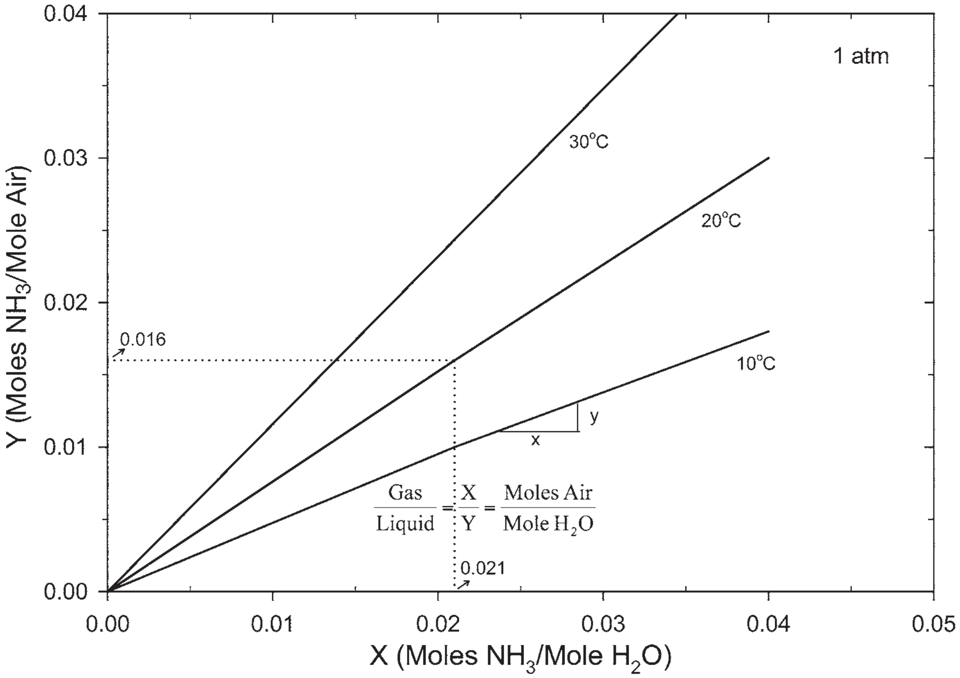

Fig. 6. Equilibrium distribution of ammonia in air and water under one atmospheric condition.

At a given temperature and atmospheric pressure, the molar ratio of ammonia saturated in the outlet air and in the inlet water can be assumed to remain constant according to Henry's law, which can thus be used to determine the respective moles of ammonia in a mole of air as a function of the moles of ammonia in a mole of water. Tchobanoglous (14) has prepared a set of curves showing the equilibrium distribution of ammonia in air and water at various temperatures under the condition of atmospheric pressure (Fig. 6). Using Eq. (15) and Fig. 6, the theoretical requirement of air for the ammonia-stripping operation at 100% efficiency can be calculated. For example, at a water temperature of 20°C and an influent ammonia concentration of 20 mg/L, the theoretical air requirement is calculated as follows:

$$\text{Inlet water NH}_3\text{ conc.} = 20\text{ mg/L} = 20 \times 10^{-3}\text{ g/100g}$$

$$= \frac{20\times10^{-3}}{17} \div \frac{1000}{18}$$

$$= 0.021 \times 10^{-3}\text{ mole NH}_3\text{/mole H}_2\text{O}$$

From Fig. 6, this corresponds to an ammonia concentration of 0.016×10^{-3} moles/mole in the outlet air when it is in complete equilibrium with the ammonia concentration in the influent water. Using Eq. (15), the theoretical air requirement becomes:

$$\frac{G}{L_q} = \frac{x_1}{y_1} = \frac{0.021\times10^{-3}}{0.016\times10^{-3}}$$

$$= 1.315\text{ mole air/mole water}$$

and 1.315 moles air × 22.4 liters/mole × 1 ft^3/28.3 L

$$= 1.04\text{ ft}^3$$

also, 1.0 mole water × 18 gal/mole × 1 lb/454 g × 1 gal/8.34 lb

$$= 0.00475 \text{ gal},$$

so

$$\frac{G}{L_q} = \frac{1.04 \text{ ft}^3}{0.00475 \text{ gal}}$$

$$= 219 \text{ ft}^3 \text{ air/gal water}$$

Because all the curves in Fig. 6 are straight lines, and because the ratio of X/Y is a constant at a given temperature, regardless of the ammonia concentration in the influent water, the theoretical air requirement is dependent on only the water temperature and not on the influent ammonia concentration. This calculation of the theoretical air requirement is based on an operating efficiency of 100%, which is not achievable in actual practice. Therefore, for actual design, to obtain more than 90% ammonia-stripping efficiency it has been recommended that the design air requirement be 1.5 times the theoretical value (14). Another design approach is to use some empirical data or curves relating to the tower packing characteristics based on the concept of the height of a transfer unit vs the G/L_q ratio. These data can be obtained from the manufacturer.

5. **Hydraulic Loading Rate.** The hydraulic loading rate on the stripping tower can affect the ammonia removal in two ways. First, for a fixed tower depth, the larger the hydraulic loading rate, the shorter is the air–water contact period. Below a certain critical contact time the ammonia-stripping efficiency will be reduced drastically. Second, for a given internal packing configuration, if the hydraulic loading rate is too high, it may cause sheeting of the water, which reduces the intensity of droplet formation, thus decreasing the ammonia-stripping efficiency. For most ammonia-stripping operations, using a 6–7 m (20–24 ft) tower with an internal packing of 3.8 × 5 cm (1.5 × 2 in.), a hydraulic loading rate between 0.04 and 0.12 $m^3/min/m^2$ (1 and 3 gpm/ft^2) is recommended.

   Using Eq. (15) and Fig. 6 will give only a theoretical value for the air requirement for a given ammonia removal based on the assumption that the ammonia concentration in the outlet air is in absolute equilibrium with that present in the influent wastewater. This is rarely true in actual practice. Therefore, actual design calculations are somewhat more complicated.

Smith (15) has presented a practical ammonia-stripping tower design based on the concept of the height of transfer unit vs the gas/liquid ratio for a given type of tower packing. He has provided a sample design problem.

A. Design Information

1. Feed stream characteristics
   a. average water flow, Q, MGD
   b. peak water flow, Q_{max}, MGD
   c. water temperature, T, °F
   d. ammonia nitrogen concentration in water, X_1, mg/L
   e. pH of water
   f. wet bulb temperature, °F

2. Required effluent characteristics
   a. ammonia nitrogen concentration in water, X_2, mg/L

3. Design decisions
   a. liquid loading rate, L_q, lb H_2O/h-ft^2
   b. gas loading rate, G, lb air/h-ft^2

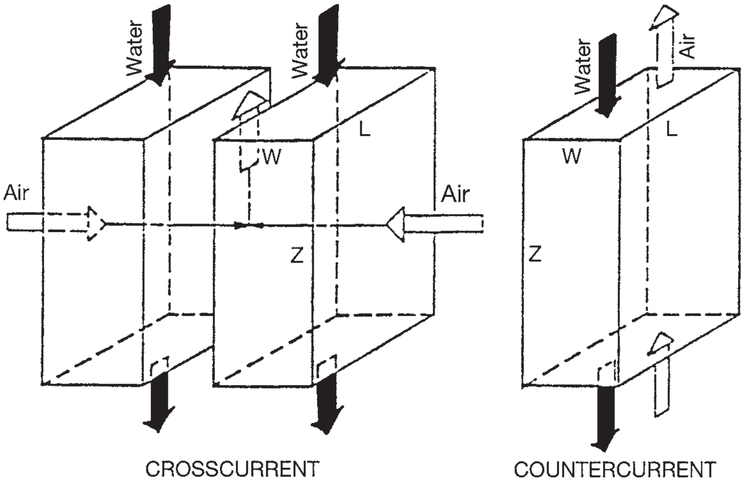

Fig. 7. Configuration of crosscurrent and countercurrent ammonia-stripping towers.

   c. tower width, *W*, ft
   d. excess capacity factor

4. Packing characteristics (can be obtained from manufacturer)
   a. ammonia-stripping height of a transfer unit (ft) vs gas/liquid ratio
   b. height of a transfer unit (ft) for cooling vs gas and liquid loading rates
   c. pressure drop characteristics as a function of gas loading

B. Design Procedure

1. *Selection of a Pretreatment Method:* This includes the determination of the chemical to be used for raising the liquid pH and also the level to which it must be raised. In general, lime is the cheapest chemical to raise the pH. If the pretreatment is also intended for removing both phosphorus and suspended solids, the pH should be raised to between 10.5 and 11.0, which normally requires a hydrated lime dosage of about 400 mg/L for domestic sewage, as shown in Fig. 5.
2. *Determination of the Ammonia Removal Efficiency Required:* Design is generally based on the average concentration of ammonia nitrogen present in the tower effluent. This value is normally dictated by the required regulation.
3. *Selection of Tower Type, Geometry, and Areal Loading Rate:* The first design decision is whether to use crosscurrent or countercurrent flow, which are illustrated in Fig. 7. Next, the liquid loading rate must be fixed in the general range of 500–1000 lb H_2O/h-ft^2. The gas/liquid loading ratio, G/L_q [(lb air/h-ft^2)/(lb water/h-ft^2)], is selected next with a normal value between 2 and 4. For countercurrent towers, the G/L_q ratio will determine the maximum percentage removal possible. The tower width must also be selected by the designer. In general, the wider the tower, the less efficient is the stripping operation for the crosscurrent tower. However, for the countercurrent tower, the effectiveness is independent of the tower width. Both the ammonia concentration and the flow are likely to vary diurnally and seasonally. The design can be based on either the average (usually) or the peak conditions depending on the nature of the effluent requirement. In any case some excess or duplicate capacity should be provided for shut-down and repair or cleaning.
4. *Determination of Packing Characteristics:* The packing characteristics are normally obtained from the tower manufacturer. Figure 8 illustrates the relationship between the height of a transfer unit for ammonia stripping and the G/L_q ratio for one type of packing

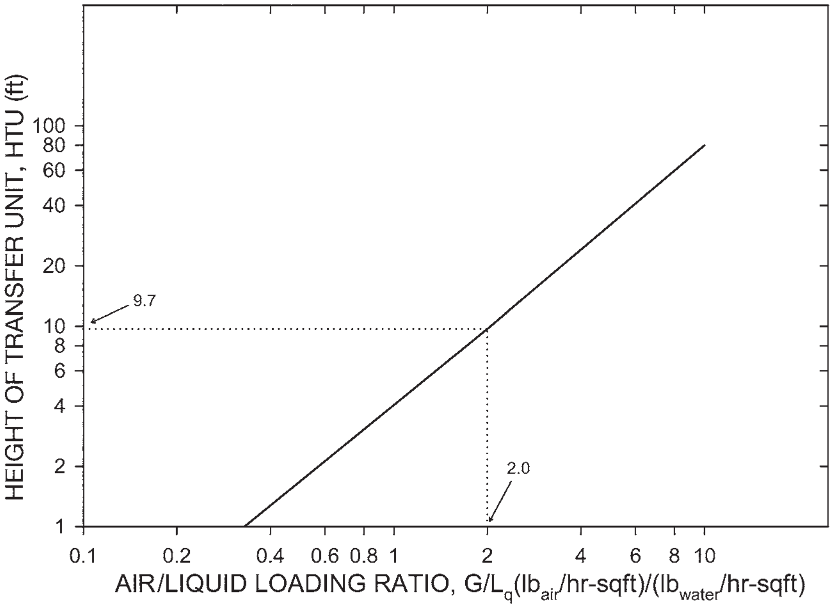

Fig. 8. Typical relationship between the height of transfer unit and the gas/liquid ratio for one type of packing for crosscurrent tower (15).

used in the crosscurrent operation (15). The use of this relationship in the actual stripping tower design is explained in the following example. It must be noted that these data must be obtained from actual test observations for a specific packing.

5. *Sizing of Countercurrent Towers:* The cross-sectional, or plan, area of the tower must be calculated first. For this, the liquid loading rate for the tower, Q_w, lb/h, is determined from the flow rate, Q, MGD, by the equation:

$$Q_w = Q \times \left(\frac{8.34}{24}\right) \times 10^6 \tag{16}$$

where 8.34 is the water density in lb/gal and 24 converts days to hours.
Using the liquid loading rate, L_q, (lb/h-ft^2) selected in step 3, the plan area can be calculated using

$$\text{Plan area} = \frac{Q_w}{L_q} \tag{17}$$

The length and width of the tower can be selected in any way that gives the required plan area (referring to standard manufacturers' equipment design).
Based on the plan area, the height of the tower required to give the desired degree of ammonia removal can be calculated. For a countercurrent tower assuming a constant water temperature throughout the towers:

$$Z = \frac{\text{HTU}}{A-1} \ln\left[\frac{(A-1)X_1 + X_2 - (G_m/L_q)Y_2}{(A-1)X_2 + X_2 - (G_m/L_q)Y_2}\right] \tag{18}$$

where Z = countercurrent tower height, ft; HTU = height of a transfer unit, ft; $A = H_c G_m / L_m$ or $H_c(G/29)/(L_q/18)$, where H_c is Henry's constant = $0.1117e^{0.02612T}$, T is the temperature,

°F, G_m is the gas loading rate, lb-moles/ft^2-h, L_m is the liquid loading rate, lb moles/ft^2-h; X_1 = ammonia concentration in the inlet water, mg-N/L; X_2 = ammonia concentration in the outlet water, mg-N/L; Y_1 = ammonia concentration in the outlet air, mg-N/L; Y_2 = ammonia concentration in the inlet air, mg-N/L (normally considered to be zero).

6. *Calculation of Pressure Drop through the Tower:* The electrical power requirement for the fan is determined by the pressure drop through the tower packing. The pressure drop is directly proportional to the air velocity head, $(1/2p)v^2$. Concentration of mass can be expressed as $Q = \rho A v$, where Q is lb air/h; A = area, ft^2; v is air velocity, ft/h; and ρ is the air density, lb/ft^3. The gas loading rate, G, in units of lb/h-ft^2 is, therefore, equal to ρv. The pressure drop through the tower will therefore be expressed as a constant times G^2/ρ. The constant is a characteristic of the packing and must be obtained from the manufacturer of the packing.
7. *Sizing of Crosscurrent Towers:* Crosscurrent towers are normally built in two identical sections as shown in Fig. 7 so that the air can flow into a common central channel between the two sections and out the top of the tower. For a crosscurrent tower, the liquid loading rate is selected first. The total flow through the tower is divided by 2 and this flow is used to size one of the two sections. Therefore, the plan area of each section is computed as follows:

$$\text{Area of each section} = \frac{Q}{2L_q} \times \frac{8.34}{24} \times 10^6 \tag{19}$$

The width of the tower must be selected by the designer. Because the plan area of one section has been computed by Eq. (19), the length equals the plan area divided by the tower width. Both sections have the same height, Z, and the procedure for finding height is as follows. For a tower of infinitesimal width, the removal of ammonia nitrogen down the tower can be represented by:

$$X = X_1 \exp\left[\frac{-(H_c G_m) \times Z}{L_m \times \text{HTU}}\right] \tag{20}$$

where Z = tower height, ft and X = ammonia concentration at Z ft down the tower, mg-N/L and all other terms the same as for Eq. (18).

Because the term $H_c G_m / L_m$ is a constant based on the temperature and the preselected air/liquid loading, X/X_1 vs Z/HTU should plot as a straight line on semi-log paper as shown in Fig. 9. Various plots will result depending on the temperature and the G/L_q ratio. Therefore, if X/X_1 is known and HTU has been determined as a function of the G/L_q ratio in Fig. 8, the value of Z/HTU can be selected from Fig. 9. Subsequently, the tower height, Z, can be calculated as

$$Z = \text{HTU (from Fig. 10)} \times Z/\text{HTU (from Fig. 9)}$$

The difficult part of the design is developing the plot of X/X_1 vs Z/HTU (Fig. 9). Because the plot is known to be a straight line, only two points need to be determined to obtain the desired plot. One point can be at the top of the tower where Z/HTU = 0 and X/X_1 = 1.0. Therefore, only one other point needs to be calculated to establish the desired line. It has been found by means of computation that the value of X/X_1 at the Z/HTU = 1.0 level from the top of the tower can be correlated to W/HTU as shown in Fig. 10. Therefore, Fig. 9 can be obtained by selecting a G/L_q ratio, obtaining an HTU value from Fig. 8, selecting a width, calculating W/HTU, and determining X/X_1 from Fig. 10. At the selected G/L_q ratio and temperature, the value of X/X_1 can be plotted vs Z/HTU = 1 to obtain Fig. 9. This design relationship holds over a range of influent ammonia concentrations from 20 to 2000 mg-N/L.
8. *Costs of Installing and Operating the Tower:* The capital and operating costs of the ammonia-stripping tower will depend on the design, but reliable cost information must be obtained

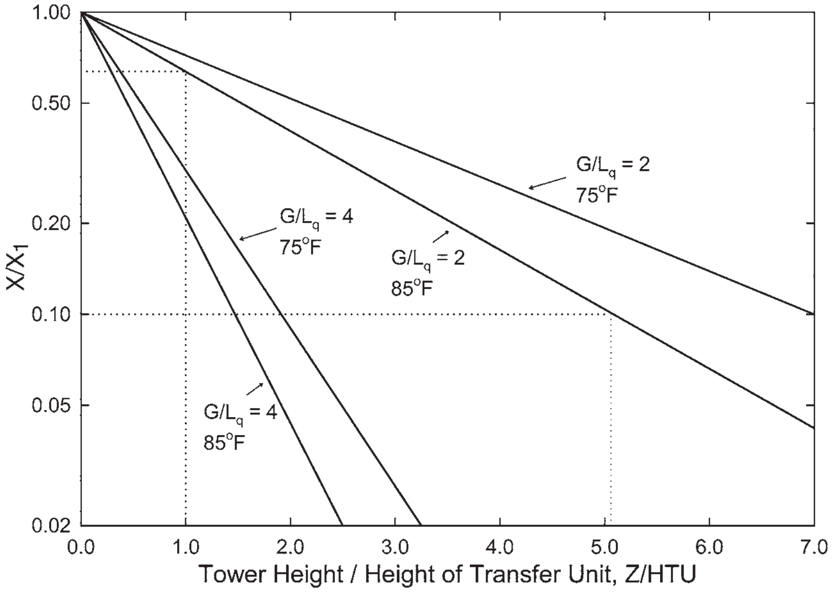

Fig. 9. Example of design relationship of Z/HTU vs X/X_1 for ammonia stripping tower (15).

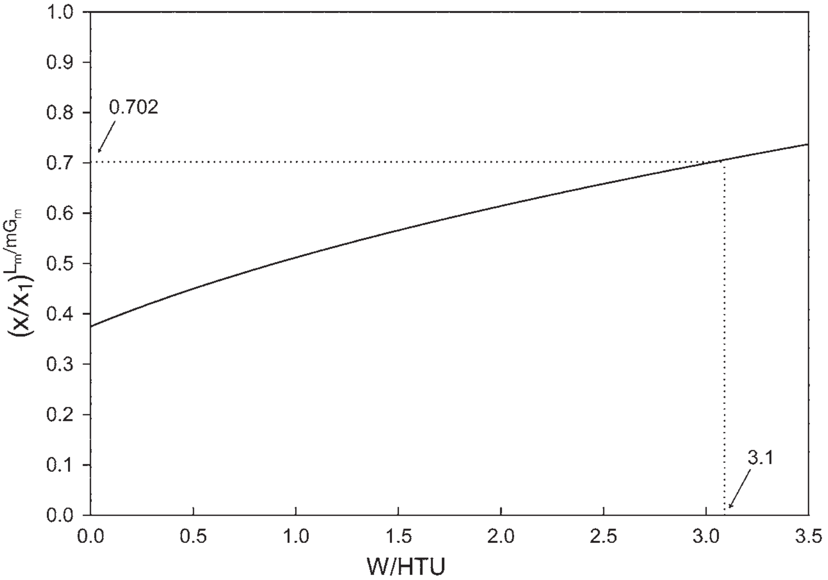

Fig. 10. Typical design relationship of W/HTU vs $(X/X_1)^{L_m/mG_m}$ at Z/HTU = 1.0 (15).

from the equipment manufacturer. In South Tahoe, a tower having a plan area of 900 ft^2 and a height of 24 ft with a nominal capacity of 3.75 MGD was installed at a cost of $310,000 based on the 1969 FWPCA STP Construction Cost Index of 127.1 (12). This is equivalent to about $8.00/MG if the investment is amortized at 5% interest over 25 yr. Costs for operation and maintenance are about $8.75/MG.

Table 1
Required Design Data for the Example Problem

1. Feed Stream Characteristics:
   a. average water flow, Q, 10 MGD
   b. peak water flow, 25 MGD
   c. water temperature, T, 85°F
   d. ammonia concentration in water, X_1, 20 mg/L as N
   e. pH of water, 11.0
   f. wet bulb air temperature, 75°F
2. Required Effluent Stream Characteristics:
   a. ammonia concentration, X_2, 2.0 mg/L as N
3. Design Decisions:
   a. liquid loading rate, L_q, 500 lb H_2O/h-ft^2
   b. gas loading rate, G, 1000 lb air/h-ft^2
   c. tower width, W, 60 ft
   d. excess capacity factor, 1.2
4. Packing Characteristics (from manufacturer):
   a. ammonia stripping height of a transfer unit (ft) vs gas/liquid ratio (see Fig. 8)
   b. height of a transfer unit (ft) for cooling vs gas and liquid loading rates
   c. pressure drop characteristics as function of gas loading

Some other representative cost relationships can also be found in this reference (12), but these cannot be used as a substitute for data from the supplier. In general, the equipment costs include the following components: fans, water pumps to deliver the water to the top of the tower, tower structure and packing, exterior covering, and electrical installation. The principal operating and maintenance costs are electrical power for pumping water and air, operating and maintenance labor, and chemicals to raise the pH.

C. *Example Design Problem for a Crosscurrent Tower*

The design data shown in Table 1 are to be used to design a crosscurrent ammonia-stripping tower. The wastewater to be treated is municipal sewage that has been treated by activated sludge followed by lime clarification. A 90% ammonia removal efficiency is desired. The packing is assumed to have the characteristics shown in Fig. 8.

1. Calculate the gas/liquid loading rate ratio:

$$\frac{G}{L_q} = \frac{1000\,\text{lb air/h-ft}^2}{500\,\text{lb H}_2\text{O/h-ft}^2} = 2.0$$

2. Calculate the plan area of the tower and its length:

$$\begin{aligned}\text{Plan area of each section} &= \frac{Q}{2L_q} \times \frac{8.34\times 10^6}{24}\\ &= \frac{10}{2\times 500} \times \frac{8.34\times 10^6}{24}\\ &= 3475\ \text{ft}^2\end{aligned}$$

Because the total tower width is 60 ft (in two sections), the width of each section is 30 ft. Thus, the length of the tower is 3475/30 = 116 ft. That is, the crosscurrent tower will consist of two sections, each 30 ft wide and 116 ft long.

3. Calculate tower height, Z:
   a. $G/L_q = 2.0$
   b. Calculate Henry's law constant, H_c, at 85°F and H_cG_m/L_m:

$$\begin{aligned} H_c &= 0.1117e^{0.02612\times 85} = 1.02866 \\ G_m &= 1{,}000/29 = 34.5 \\ L_m &= 500/18 = 27.8 \\ H_cG_m/L_m &= 1.029\times 34.5 \div 27.8 = 1.277 \end{aligned}$$

   c. Obtain the value of HTU from Fig. 8:
   $G/L_q = 2.0$; thus, from Fig. 8, HTU = 9.7 ft
   d. Calculate W/HTU:
   W/HTU = 30/9.7 = 3.1
   e. From Fig. 10 at W/HTU = 3.1, obtain:

$$\left(\frac{X}{X_1}\right)^{\frac{L_m}{H_cG_m}} = 0.702 \text{ at } Z/\text{HTU} = 1.0$$

   Thus, to obtain X/X_1 at Z/HTU = 1.0, the value of 0.702 must be raised to the H_cG_m/L_m power:

$$\frac{X}{X_1} = (0.702)^{1.277} = 0.636 \text{ at } Z/\text{HTU} = 1.0$$

   f. Correlate X/X_1 vs Z/HTU:
   At the top of the tower, Z/HTU = 0; $X/X_1 = 1.0$
   At Z/HTU = 1.0, $X/X_1 = 0.636$
   With these two points, plot a straight line as shown in Fig. 9 (for $G/L_q = 2.0$ and T = 85°F)
   g. Obtain the value of Z/HTU from Fig. 9:
   At $X/X_1 = 0.1$ (for 90% ammonia removal efficiency),
   Z/HTU = 5.1
   h. Calculate the tower height:
   Z = (HTU from Fig. 8) × (Z/HTU from Fig. 9)
   = 9.7 x 4.5 = 49.5 ft.

   The above calculation has assumed that the water temperature (85°F) has remained unchanged down the tower. In reality, the water temperature will tend to approach the wet bulb temperature of the air. Because the water temperature will never drop below the wet bulb temperature, the wet bulb temperature can thus be used as a limit of reduced performance.

   Therefore, the above computation procedure can be repeated with the water temperature of 75°F. Henry's law constant, H_c, will have a value of 0.793 and H_cG_m/L_m will have a value of 0.985. Raising 0.702 to this power gives 0.706. The upper line for a G/L_q ratio of 2 in Fig. 9 would represent the limit of reduced performance due to cooling of the water. With this temperature cooling effect, the maximum tower height required is:

$$Z = 9.7 \times 6.8 = 66 \text{ ft}$$

4. Optimization of tower height and the G/L_q ratio: Because these tower heights are large, it is necessary to examine the effect of increasing the G/L_q ratio to 4. From Fig. 8, read HTU as 23.5 ft. Thus, width/23.5 is 1.278. Enter Fig. 10 and read 0.545 for

$(X/X_1)^{L_m/H_cG_m}$. For 85°F, H_cG_m/L_m = 2.56 and the intercept is 0.21. At 75°F, H_cG_m/L_m = 1.97, and the intercept is 0.302. These two lines are also shown in Fig. 9.

Thus, for a value of G/L_q of 4.0, the values of Z/HTU for X/X_1 = 0.1 are 1.49 for 85°F and 1.95 for 75°F. The height of the tower at 85°F is 1.48 × 23.5 = 34.8 ft, whereas at 75°F it becomes 1.95 × 23.5 = 45.8 ft. This shows that setting the G/L_q ratio to 4.0 instead of 2.0 would result in a shorter tower. The amount of air required, however, is not doubled: 34.8 times 2 divided by 49.5 = 1.40. Thus, at this higher air loading rate, only 40% more air is required. To find the optimum G/L_q ratio, the entire design must be priced and the minimum cost tower selected. This requires repetitive calculations using a computer and incorporating reasonably accurate cost data as well as mass transfer, enthalpy transfer, and pressure drop characteristics on the detailed analysis. To complete the design, the pressure drop through the two sections must be computed from the manufacturer's data. The cost of the structure, packing, and pumps must be computed. The electrical power consumption can be computed from the air pressure drop and the height of the tower together with the volume flows of air and water.

D. *Example Design Problem for a Countercurrent Tower*

The same design conditions used for the crosscurrent tower will also apply to the countercurrent tower in this problem. Because we have no valid data for the height of a transfer unit for the packing used in the countercurrent configuration, we will use the same value of 9.7 ft for the purpose of illustration.

1. The values of G/L_q = 2.0, H_c = 1.02866 at 85°F and 0.793 at 75°F, and total plan area = 6950 ft^2 are calculated the same as for the crosscurrent tower. The term $A = H_cG_m/L_m$ has a value of 1.277 at 85°F and 0.985 at 75°F.
2. Using Eq. (18) for a removal of 90%, the value of Z/HTU at 85°F is 3.906; so the tower height is 3.906 × 9.7 = 37.9 ft. The corresponding crosscurrent tower height was calculated to be 49.5 ft. However, at 75°F, the value of Z/HTU is 9.82; so the tower height becomes 9.82 × 9.7 = 95.3 ft. This is larger than the value of 66 ft calculated for the crosscurrent tower.

This demonstrates how the countercurrent design may become prohibitive if performance above a certain level is required. Furthermore, in most instances the water within the tower will be cooled, and Henry's law constant will be lower. This would result in less efficient gas transfer near the bottom of the tower. This effect can be evaluated on the computer program, but not in hand calculations. This example simply delineates the maximum and minimum possible tower heights, and shows the necessity for consideration of the effect of cooling.

7. WATER QUALITY PROBLEMS

When the water entering an air stripper contains inorganic substances near the limits of their solubility, precipitation of these metals or minerals within the air stripper may occur. At the aeration nozzle, ferrous iron in solution oxidizes and precipitates as insoluble ferric oxides. Manganese may also be oxidized to an insoluble form within the air stripper. Carbonate or bicarbonate ions may form an insoluble scale. The result is that the nozzle and packing material in the air stripper may become encrusted, and the efficiency of mass transfer is reduced. In a case study at a hazardous waste site, poor removal of benzene, trichloroethylene, and other volatile organics were achieved by air stripping (16). Coating of the packing material by iron and manganese was cited as the culprit.

Where air stripping is used in conjunction with other water treatment processes such as flocculation, the positioning of the air stripper in the supply flow stream may be important. Positioning of the stripping tower downstream of the flocculation unit has been accomplished successfully where strict control over the quantities of floc particles released into the water stream has been maintained.

Two approaches are used to prevent precipitation of inorganics in the air stripper. A chelating system introduces an agent that binds with the inorganic material that would otherwise precipitate. Citric acid is often used to keep iron in solution as it passes through the air stripper. A second approach is the use of a sequestering agent that reduces surface tension within the system and thereby prevents encrustation.

The efficiency of an air stripper may also be impeded by biological fouling. Large populations of microorganisms are often found in water contaminated by volatile organic compounds, because these compounds serve as a nutrient source for certain species of bacteria. At installations in metropolitan areas or proximate to sewage treatment facilities, coliform bacteria are often present in large numbers. The organisms are not destroyed by the air-stripping process; rather, the air stripper may provide an environment conducive to their progeneration. Hand et al. (8) reported increases in coliform counts between air stripper influent and effluent on three sampling dates. Field inspections under these conditions often reveal accumulations of these organisms on the packing material, drastically reducing removal efficiency.

The most common method for reducing the numbers of these organisms is by chlorination of the influent water. Periodically, it may be necessary to clean and disinfect the air stripper by “shocking” the tower with acid or chlorine, or by surging the tower with peroxide. Routine inspections and cleaning of the air stripper must be considered normal maintenance and a part of the operational expense. In addition, corrosional effects and an increase in the formation potential of THMs (trihalomethanes: chloroform and bromoform) may result from chlorination.

8. OFF-GAS EMISSIONS

Air stripping removes VOCs (volatile organic compounds) from water by facilitating their transfer to the gaseous phase where presumably by dilution they become less hazardous. In some cases, however, the ambient air quality is sensitive enough to require discharge limitations on point sources as small as an air stripper. Although it is easier to control the air effluent from an air stripper than from a process such as mechanical aeration, the potential environmental impacts and costs for treatment of such emissions, if required, require consideration from the earliest design phases.

Dispersion modeling techniques have been developed over the past decade that allow accurate evaluation of the ground-level concentrations of a pollutant emanating from a single point source. One such method is PTPLU (from PoinT PLUme), an algorithm based on Gaussian plume modeling concepts, developed by the US EPA (17). The model has input parameters for the height of the discharge stack, the quantity and concentration of pollutant, the wind speed and meteorological stability, the height of the receptor, and other variables. This program permits the analysis of potential air quality effects that would originate as a result of an air stripper installation.

When it is determined that an air-stripper gas effluent will require treatment, a conventional method for the reduction of air emissions is the use of GAC (granular activated carbon). GAC will usually provide suitable adsorption of airborne VOCs (16).

In a report produced for the API (American Petroleum Institute) (10), the annual cost estimate presented for the treatment of off-gas using GAC was shown to approach 50% of the total annual cost for removal and treatment of phase-separated hydrocarbons and groundwater at a petroleum spill site. Although the cost of treating the air stripper off-gas in this fashion in some cases equals the cost of using GAC as the primary water treatment method, the two technologies are frequently used in conjunction when the influent levels of VOCs are high. Some states require that air-stripper gas effluent be treated, but do not specify a treatment level, posing a theoretical, but not substantial, cost obstacle to the use of air stripping as a viable treatment alternative.

A technology that has recently been applied to the abatement of off-gas emissions is catalytic incineration. At this time the unit cost is high (approaching $30,000) and yearly operational costs uncertain due to the necessity of supplying heat to promote complete combustion of the VOCs. This technology will nonetheless provide substantial cost savings over GAC, particularly for large systems where high concentrations of contaminants are encountered in the air effluent.

Even where off-gas treatment adds significant costs to the treatment process, air stripping may still be clearly indicated as a primary treatment technology. GAC and other treatment methods are not capable of sufficient removal of some species of volatile organic compounds, and are often used in conjunction with gas stripping.

9. CAPITAL AND OPERATIONAL COST ANALYSIS

9.1. Minimizing Power Costs

Methods to select the correct tower dimensions and operating parameters were discussed previously. Some latitude exists in the selection of the air-to-water ratio, gas-pressure drop, and tower height that will produce desired removal rates of a target compound. The goal of design, using these concepts, is to produce a system operating in a region favorable to each parameter, and therefore, not overly sensitive to small variations in each.

Increasing tower height or air-to-water ratio was shown by the design equations to effect greater removals of volatile contaminants. Hand et al. (8) showed that for trichloroethylene at three different gas-pressure drops, decreasing the air-to-water ratio below approx 30:1 necessitated exponential increases in the height of the air stripper to maintain removal efficiency. Figure 11 illustrates the typical relationship between tower height and the air-to-water ratio at various gas pressure drops. Hand et al. (8) shows that for air stripping of trichloroethylene at air-to-water ratios below approx 30:1, water pump brake power requirements increased sharply as did tower height, but that at higher air-to-water ratios, blower requirements increased. Typical relationships between pump and blower break power and the air-to-water ratio at various gas pressure drops are shown in Fig. 12. Roberts and Levy (4) performed a similar energy-cost analysis for removal of chloroform by air stripping. He achieved results similar to Hand et al., finding that energy requirements for removal of chloroform were minimized by maintaining an air-to-water ratio of approx 30:1.

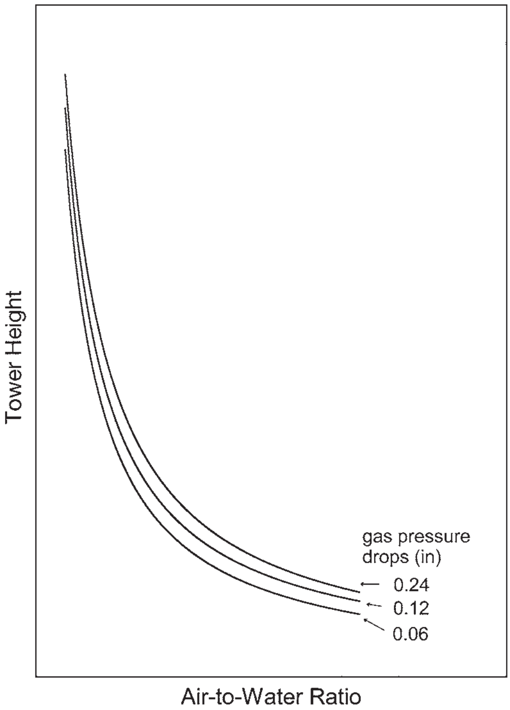

Fig. 11. Typical relationship between tower height and the air-to-water ratio at various gas pressure drops.

Selection of an appropriate packing material will have a direct effect on the capital cost of the air-stripper system and an indirect effect on the operational cost. Selecting a packing with a high packing factor such as Berl Saddles or Raschig Rings may provide the maximum available surface area for mass transfer and thereby minimize tower dimensions, but may also produce an unacceptable pressure drop and associated operational costs. More detailed information of the packing materials can be found in ref. 18 or obtained from the manufacturers. A packing factor with a high unit price may offer a large surface area combined with a reasonably low pressure drop, and thereby compensate for the initial price differential by offering increased removal efficiency and lower blower power requirements. Hand et al. (8) found that for a twofold increase in tower volume a gas-pressure drop from 0.49 to 0.06 in. H_2O/ft occurred, resulting in a 70% decrease in power requirements.

Design equations are combined with cost-modeling techniques described in the literature (19) to optimize system design and minimize energy requirements. The capital cost savings afforded by using readily available production air-stripper assemblies must be balanced against the operational cost savings represented by the most efficient design in order to assess the total system cost.

9.2. Comparisons of Capital and Operational Costs

The large surface area of the packing in an air stripper promotes the transfer of volatile organic compounds to the vapor phase without undergoing any reaction with

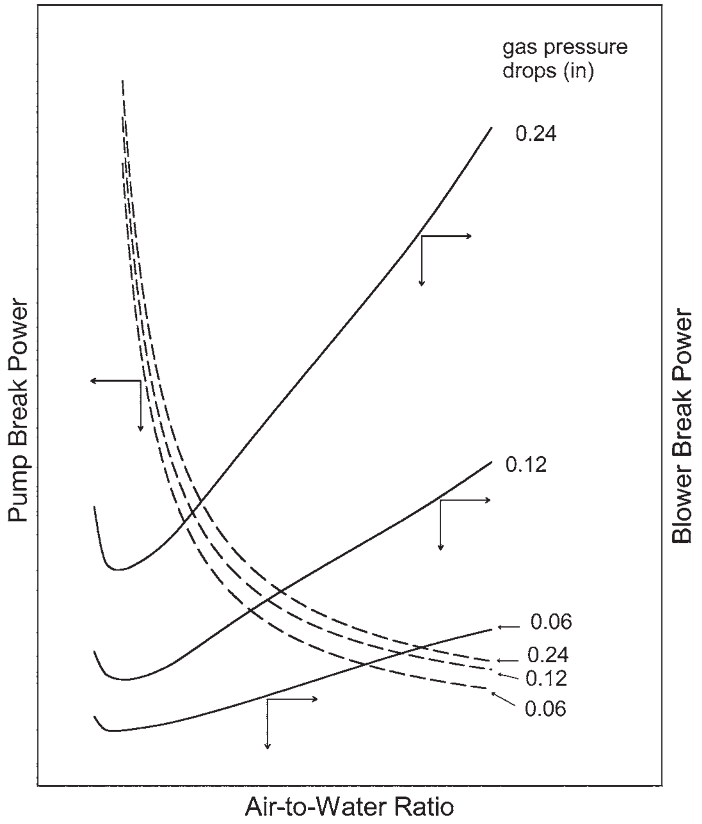

Fig. 12. Typical relationship between pump and blower break power and the air-to-water ratio at various gas pressure drops.

these compounds. An air stripper may be expected to remove contaminants from a water for years provided that maintenance to prevent and remove fouling of the packing is performed. Cost comparisons with treatment mechanisms that require regeneration, such as GAC, are favorable.

Influent water quality, effluent water quality requirements, and total system capacity are the major factors that determine the cost of a water treatment system. Capital and operational costs for air-stripper systems increase with the concentrations of the volatile organic compounds to be removed. Taller packed towers and higher air-to-water ratios required for greater removals increase the blower and pump power requirements. At low concentrations, however, operating costs appear to be equally affected by the mass-transfer coefficient of the target compound (18). The costs for removing low levels of TCE are nearly twice those for removing vinylidine chloride, a compound with a much higher Henry's constant.

Prior to installation of an air stripper (20) to remove TCE, DIPE, and MTBE from a municipal water supply, GAC had been used for this purpose. Carbon bed life had decreased to 4–6 wk shortly before the air stripper was put on-line, at a regeneration cost of $32,000 per replacement. The total capital cost for the GAC system was approx $200,000, while the installed cost of the air stripper was approx $375,000. The yearly operational cost savings provided by switching to air stripping exceeded $100,000. Following air stripper start-up, the GAC system was initially maintained to “polish” the air-stripper effluent, but the air stripper proved to be so effective that the carbon units were placed on stand-by. The production wells were capable of increased yield as a result of the elimination of the head loss imposed by the carbon units.

Analysis of influent water quality prompted the selection of air stripping over GAC for treatment of a contaminated surface water supply (7). Although the carbon units provided good adsorption of TCE, rapid breakthrough of 1,1-dichloroethane and 1,1,1-trichloroethane was noted.

An air-stripping system designed to minimize energy requirements (8) was installed to remove volatile organic compounds at levels between 200 and 250 μg/L from drinking water supplied by a municipal well field. The system was capable of treating 2.16 MGD (8,176 m^3/d) at effluent levels not exceeding 10 μg/L total VOCs. Total installed cost was approx $200,000, and operational costs were less than $20,000/yr.

Sites where petroleum losses to the subsurface have occurred are typified by high levels of dissolved hydrocarbons in the groundwater. Increasingly, the presence of gasoline additives, such as MTBE, is also found. When used to treat groundwater contaminated by these volatile organic compounds, rapid breakthrough of GAC systems occurs. Air stripping offers substantial capital cost savings and overwhelming operational cost savings when compared to GAC under these conditions (10). Capital and operational costs for air stripping are not as sensitive to influent water quality and flow rate as are costs for carbon.

Air stripping is not suited to the removal of non-volatile organic compounds. These compounds may be successfully removed by adsorption on carbon, however. The installation of an air stripper and GAC in a water treatment system is a frequent practice. The air stripper greatly extends the bed life of the carbon by removing the bulk of the volatile organic compounds, while the carbon unit removes the remaining compounds that are not amenable to air stripping. The resulting operational costs are higher than the costs for air stripping alone, but significantly lower than the costs for treatment with GAC alone (10,38).

10. RECENT ADVANCEMENTS

Air-stripping processes using crosscurrent and countercurrent packed towers have been well developed and practiced in the last decade. The processes have been extensively applied for ammonia stripping, groundwater remediation, and industrial wastewater (ammonia and VOCs) stripping (21–24,38). Crosscurrent stripping was found to be an advantage over the conventional countercurrent stripping because the mass-transfer coefficient in crosscurrent operation is insensitive to the gas flow rate, thereby allowing a high air-to-water ratio, G'/L', without chances of flooding (21). Crosscurrent stripping also offers a significant economic advantage over countercurrent stripping due to the savings in energy costs, when the target contaminants are considerably less volatile (23). However, the drawback of applying a high air-to-water ratio in crosscurrent stripping is the increased cost of off-gas treatment. Details can be found in Tables 4 and 5 in ref. 23.

With progressive development of the computer technology, substantial advancement has been made in the area of developing models to simplify the air-stripping tower design procedure so that the tower configuration associated with tower performance can be optimized and the overall cost (sum of capital and operating costs) associated with installation and operation can be minimized (22,23,25–29). The relationships of optimum design parameters to Henry's law constants and the sensitivity of tower overall cost to specific design parameters can be well demonstrated by computer simulation (23). By computer iteration, these programs provide a quick prediction of the tower performance with limited inputs of design parameters. However, these models may suffer from underestimation or overestimation of the actual costs (23), especially when the designing engineers are facing unfamiliar packing materials or contaminants. Under this circumstance, these models may only be used as a preliminary screening and evaluation tool. In most cases, further pilot-scale testing is needed.

One limitation of these proposed models comes from the uncertainty of the estimated mass-transfer coefficients. The Onda correlations (30) are most commonly used for estimating mass transfer of volatile chemicals from water during air stripping with random packings. However, the correlations are only valid for liquid loading rates between 1.1 and 63 gpm/ft^2 (0.8 and 43 kg/m^2-s), gas loading rates between 2.206 and 267.9 cfm/ft^2 (0.014 and 1.7 kg/m^2-s), and nominal packing sized up to 2 in. (0.0508 m). The Onda correlations were found to be fairly inaccurate to predict mass transfer with large random packings, especially at high gas flow rates and when the gas-side resistance is large (31). It has been reported that the Onda correlations underpredicted k_G for the saddles by about 40% on average and overpredicted k_G for the spheres by more than 50% (32). Advancement in estimating mass-transfer coefficients has been made. Little and Selleck (33) have proposed new mass-transfer correlations for two types of packing in a crossflow tower based on experimental data, while Piche et al. (34) applied artificial neural network (ANN) modeling to predict mass-transfer coefficients.

Thom and Byers (35) discussed the design and construction issues that can lead to the inaccurate model predictions compared to field observations in that liquid distribution, packing materials, fouling, chemical reaction, and end effects were of great importance.

Another limitation and restriction of these models are the data reliability of the Henry's law constants. It is very important that accurate Henry's law constants shall be available for modeling an air stripper as all design parameters and costs are strongly sensitive to the Henry's law constants (22). For many common VOCs, the constants are available in books as well as the literature. For uncommon contaminants, the constants may be looked up in an extensive database by Sander (36) or predicted by using quantitative structure-activity relationship (QSAR) model for Henry's law constant (37). However, if the data are absent or data reliability is of question, pilot testing or laboratory measurement of the Henry's law constant is recommended (38).

11. CONCLUSIONS

Volatile compounds exhibit high activity coefficients in water and are easily evaporated. The countercurrent air stripper provides a large wetted surface area for mass transfer in a compact unit. Although routine maintenance is required, the components of the air stripper should have long service lives. The air stripper is capable of removing large numbers of volatile compounds at relatively low cost.

The design of an air stripping tower is essentially similar to that of the conventional cooling tower (12). There are two basic types of tower configuration: crosscurrent and countercurrent, with the former being more common at the present time.

Although the ammonia-stripping operation is both reliable and flexible in its routine operation, it has some shortcomings which must be carefully considered by the design engineer. Some major problems are:

1. Problems associated with cold weather operation. Low temperature increases the ammonia solubility making the ammonia more difficult to release from the liquid to the gaseous phase. In severe winter conditions, fogging and icing may occur, which hamper the tower operation.
2. Problems associated with calcium carbonate scale formation. Because ammonia stripping is operated at a high pH (11 or above), calcium deposits on the packing materials can be expected. If these deposits are not periodically dislodged and broken up by the hydraulic force, excessive accumulation can restrict the flow of both the wastewater and the air, thereby reducing the effectiveness of the system.

There has also been concern over the potential air pollution problem that can be caused by the ammonia present in the off-gas. However, it has been reported (12) that the ammonia concentration in the off-gas from a stripping tower seldom exceeds 10 mg/m^3 even before its dispersion in the surrounding air. The threshold for odor is about 35 mg/m^3; therefore, there is little likelihood for the ammonia-stripping operation to cause an odor problem. However, small concentrations of ammonia in air may react with sulfur dioxide to form aerosols or fog. Under such a situation, ammonia can be removed from the off-gas by a scrubber of by bubbling it through a dilute sulfuric acid solution.

Operating costs can be minimized and operating efficiency maximized by applying the principles herein outlined in the design of an air-stripping system. For small systems designed to remove relatively common contaminants, existing engineering data may be sufficient to design a suitable air stripper. Production units are designed to remove a wide range of compounds over the normal range of ambient temperatures. Where the target compounds are difficult to remove or the mass-transfer coefficients are not well known, pilot studies are required to furnish data for final, full-scale design. Large systems require extensive design work and pilot study data to minimize potential excessive operating costs.

Accurate characterization of the influent water quality is required before air-stripper parameters can be specified. In addition, the presence of substances other than the target compounds may reduce the efficiency of removal of the target compounds. Modifications to and maintenance of the system will usually permit good removal efficiency under these conditions.

Treatment of the air effluent from a packed tower adds an additional cost factor to the process. Use of GAC to remove the volatilized compounds from the air effluent, although an apparent redundancy, may be less expensive than the use of GAC alone.

Non-volatile compounds are not removed from water by air stripping. Air stripping may be used in conjunction with another treatment method, such as GAC, flocculation, or chlorination, to achieve treatment levels at an operating cost below that possible by the use of a single technology. Consideration of the factors herein presented allows an accurate assessment of the effectiveness of air stripping for specific water treatment objectives.

NOMENCLATURE

a	specific interfacial area, m^2/m^3
C_o	molar density of water (55.6 kmol/m^3)
C_{inf}	concentration of the contaminant in the influent water
C_{eff}	concentration of the contaminant in the effluent water
C_f	packing factor
C_G	concentration of contaminant at equilibrium in the gaseous phase
C_L	concentration of contaminant at equilibrium in the liquid phase, kg/m^3
$C_L{}^*$	liquid concentration in equilibrium with the gas phase concentration, kg/m^3
D	molecular diffusion coefficient of the compound in water
G	air flow rate through the stripping tower, moles air/unit time
G'	optimum gas flow rate
G'/L'	volumetric air-to-water ratio
G_m	gas loading rate, lb moles/ft^2-h
H^o	enthalpy change resulting from the dissolution of the compound in water
H_c	Henry's law constant, atm m^3/mole
HTU	height of a transfer unit, ft or m
k	a compound-dependent constant, unitless
k_G	gas mass transfer coefficient, m/s
k_L	liquid mass transfer coefficient, m/s
K_L	overall liquid mass transfer coefficient, m/s
K_La	transfer rate constant, s^{-1}
L	molar flux rate of the contaminant in the liquid phase, kmol/m^2-s
L'	liquid loading rate, kg/m^2-s
L'/G'	volumetric water-to-air ratios
L_M	liquid mass flux rate, kg/m^2-h
L_m	liquid loading rate, lb moles/ft^2-h
L_q	liquid flow through the stripping tower, moles water/unit time
m	mass of the solute, kg
n	constants specific to the packing type
NTU	Number of transfer units
Q	average water flow, MGD
Q_L	design flow, m^3/s
Q_{max}	peak water flow, MGD
Q_w	liquid loading rate for the tower, lb/h
R	universal gas constant, 0.000082057 atm m^3/mole-K
R_G	resistance to the rate of mass-transfer by the gas-phase boundary layer, s
R_L	resistance to the rate of mass-transfer by the liquid-phase boundary layer, s
R_T	total resistance to the rate of mass-transfer, s
S	a concept known as the stripping factor
T	temperature, Kelvin (K)
U_L	liquid viscosity
V	liquid volume, m^3
W	tower width, ft
X	ammonia concentration at Z ft down the tower, mg-N/L

X_1	ammonia concentration in the inlet water, mg-N/L
x_1	inlet water ammonia concentration, moles ammonia/mole water
X_2	ammonia concentration in the outlet water, mg-N/L
x_2	outlet water ammonia concentration, moles ammonia/mole water
Y_1	ammonia concentration in the outlet air, mg-N/L
y_1	outlet air ammonia concentration, moles ammonia/mole air
Y_2	ammonia concentration in the inlet air, mg-N/L
y_2	inlet air ammonia concentration, moles ammonia/mole air
Z	height of the packed column, m or ft
α	constants specific to the packing type
ρ_G	air density, 1.205 kg/m^3
ρ_L	liquid density, 998 kg/m^3
ϕ	tower diameter, m

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3

Adsorptive Bubble Separation and Dispersed Air Flotation

Lawrence K. Wang

CONTENTS

1. INTRODUCTION

1.1. General Description

Adsorptive bubble separation process is a very effective technology for solid–liquid separation that has been in use outside the environmental engineering field for more than 60 years. Originally applied in the field of mining engineering, the process now provides the means for separation and/or concentration of 95% of the world's base metals and other mineral compounds (1,2). Recently, the adsorptive bubble separation process has become increasingly important in such diverse applications as (a) the separation of algae, seeds, or bacteria from biological reactors, (b) removal of ink from re-pulped

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Table 1
Impurities to be Removed by Adsorptive Bubble Separation

Suspended Solids
Wood fiber
Cotton fiber
Activated sludge
Free oil
Chemical flocs
Fats
Colloidal Solids
Algae
Bacteria
Titanium dioxide
Turbidity
Soluble Organics
Lignin and tannin
Humic acid
Protein
Soluble oil
BOD, COD
Color
Soluble Inorganics
Heavy metals (lead, copper, chromium, zinc, etc.) phosphate, sulfate iron, manganese, hardness, etc.
Surface-Active Substances
Soap
Detergent
Industrial surfactants
Dye
Volatile Solids
Xylene
Toluene
Ethylbenzene
Butylbenzylphthalate
Trihalomethanes (chloroform, etc.)
Trichloroethylene

paper stock, (c) recovery of protein and fat from food processing streams, peas from pea pods, coal from slate, gluten from starch, and oils from industrial effluents, and (d) more recently, treatment of drinking water, cooling water, wastewater, and sludge (3–120). This chapter briefly introduces all adsorptive bubble separation processes, but introduces dispersed air flotation in detail.

1.2. *Adsorptive Bubble Separation*

Adsorptive bubble separation process may be defined as the mass transfer process of a solid from the body of a liquid to the liquid surface by means of bubble attachment (42,75,84). The solids can be in dissolved, suspended, and/or colloidal form. The three basic mechanisms involved are bubble formation, bubble attachment, and solids separation (43,75).

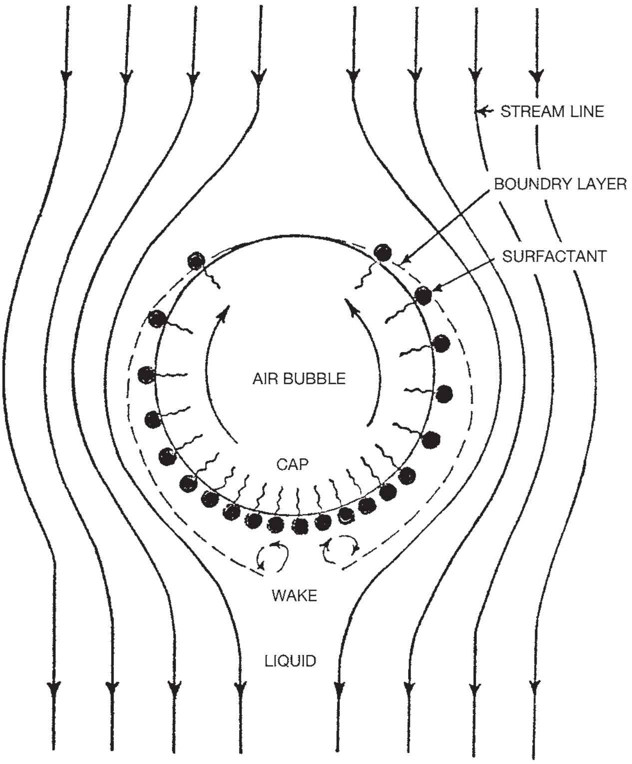


Fig. 1. A rising bubble in bubble separation column containing surface-active agent.

Table 1 indicates the solids or substances that can be effectively separated by the adsorptive bubble separation process. In general, the light-weight suspended solids, such as fibers, activated sludge, free oil, chemical flocs, and fats, can be readily separated by the process in accordance with the physical–chemical bubble attachment mechanism shown in Fig. 1. The colloidal solids, soluble organics, soluble inorganics, and surface-active substances can be separated from the bulk liquid by the bubble separation process after they are converted from colloidal or soluble form into insoluble form (i.e., suspended solids), which can then be floated by gas bubbles.

Alternatively, an adsorptive bubble separation process in accordance with its surface-adsorption phenomena, shown in Fig. 1, can separate the soluble surface-active substances easily. Non-surface-active suspended solids, colloidal solids, soluble organics, and soluble inorganics can all be converted into surface-active substances. All surface-active substances (in either soluble form or insoluble form) can be effectively floated by gas bubbles (75).

The volatile solids shown in Table 1 are simply stripped out from the water phase into the gas phase (i.e., air) by bubbles according to Henry's law.

In summation, the adsorptive bubble separation process, in theory, can remove or separate almost any kind of light-weight and/or surface-active substances from water. Because there are various types of adsorptive bubble separation processes, selection of an appropriate type for a specific application is an important skill (43,84).

Table 2
Types of Flotation Processes

1.	Plain gravity flotation	
	Example:	API Oil–water separator
		Wax water separator
2.	Dissolved air flotation (DAF)	
	Example:	Full flow pressurization system
		Partial flow pressurization system
		Recycle flow pressurization system
	Flow pattern:	Laminar flow, Fine air bubbles
	Air Addition:	1% of liquid influent flow
3.	Dispersed air flotation (or induced air flotation)	
	Example:	Deinking flotation
		Foam separation
		Gas stripping
		Aeration/oxidation
		Ore flotation
	Flow pattern:	Turbulent flow, large air bubbles
	Air addition:	400% of liquid influent flow
4.	Vaccum flotation	
	Example:	Scum vacuum flotation
5.	Electrolytic flotation (or electroflotation)	
	Example:	Sacrificing electrode system
		Non-sacrificing electrode system
	Flow pattern:	Laminar flow, fine bubbles
	Gas production:	
		Anode: $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$
		Cathode: $4e^- + 4H_2O \longrightarrow 2H_2 + 4OH^-$
		$2H_2O \longrightarrow 2H_2 + O_2$
6.	Biological flotation	
	Example:	Activated sludge thickening under denitrification condition
	Flow pattern:	Laminar flow and fine bubbles
	Gas production:	
		$6NO_3^- + 2CH_3OH \longrightarrow 6NO_2^- + 2CO_2 + 4H_2O$
		$6NO_2^- + 3CH_3OH \longrightarrow 3N_2 + 3CO_2 + 3H_2O + 6OH^-$
		$6NO_3^- + 5CH_3OH \longrightarrow 5CO_2 + 3N_2 + 7H_2O + 6OH^-$

Although many gases, such as carbon dioxide, nitrogen, hydrogen, oxygen, and ozone, are suitable, air is the cheapest and most readily available for bubble generation. Based on the technique and the type of gas used for bubble generation, the adsorptive bubble separation process can be classified mainly as dissolved air flotation, dispersed air flotation, vacuum flotation, electrolytic flotation (i.e., electroflotation) and biological flotation, as indicated in Table 2. If no gas is involved or used at all, the substances (such as oil or wax) are separated from liquid by the density difference between the target substance and the liquid, and the process is termed plain gravity flotation. The most common plain gravity flotation is the oil–water separation process. The following section briefly defines various adsorptive bubble separation processes.

2. BUBBLE SEPARATION PROCESS DESCRIPTIONS AND DEFINITIONS BASED ON THE TECHNIQUES USED FOR BUBBLE GENERATION

2.1. *Dissolved Air Flotation*

Dissolved air flotation (DAF) is a process involving pressurization of air at 25–95 psig for dissolving air into water, and subsequent release of pressure (to 1 atm) under laminar flow conditions for generating extremely fine air bubbles (normally 20–80 microns), which become attached to the impurities to be removed. The air flow rate is about 1% of influent liquid flow rate. The attachment of air bubbles to the impurities can be a result of physical entrapment, electrochemical attraction, surface adsorption, and/or gas stripping. The specific gravity of the bubble–impurity agglomerates is less than 1, resulting in buoyancy or non-selective flotation (i.e., a save-all process) (1,75). Another chapter of this handbook series presents the theory, principles, operation, maintenance, design criteria, costs, chemical additives, process control, applications, tests, and design examples of dissolved air flotation in detail (2). In the past 40 years, dissolved air flotation has been used mainly for sludge thickening and fiber recovery (3,4,117,118). Now dissolved air flotation becomes a high technology for potable water purification (2,5–9,18,119) and wastewater treatment (2,10–17,22). Table 3 summarizes the US Environmental Protection Agency (US EPA) data on separation of pollutants by dissolved air flotation.

2.2. *Dispersed Air Flotation*

Dispersed air flotation (or induced air flotation) is a process involving introduction of air directly into the water through a revolving impeller, a diffuser, or an ejector at low pressure (slightly higher than 1 atm) for generating large air bubbles (normally 80 microns to over 1 mm) in large volumes under turbulent conditions. The air flow rate is about 400% of influent liquid flow rate. Physical entrapment and electrochemical attraction play minor roles in a dispersed air flotation system. The attachment of air bubbles to the impurities is mainly a result of surface adsorption, gas stripping, and oxidation. Surface-active substances (inks, detergents, and so on) are selectively separated in a foam phase (1). Volatile substances are removed by gas stripping. Reducing agents, such as ferrous ions, can be oxidized to ferric ions by air for subsequent separation in ferric hydroxide form. Dispersed air flotation can be used in ore separation (67–70,87, 88,92–96,101–107,110–116), coal purification (114), fiber de-inking (17,21,89), wastewater treatment (2,19,20,22,30,41,116), water purification (23), surfactant separation (24), lignin separation (43,44,53,54), and so on. Because of its significance, this chapter introduces this process in detail.

2.3. *Vacuum Flotation*

In vacuum flotation, the influent process liquid to be treated is saturated with air at atmospheric pressure. There is an air-tight enclosure on the top of the flotation chamber in which a partial vacuum is maintained (75). The fine air bubbles (20–80 microns) are generated under laminar flow conditions by applying such a vacuum to the flotation chamber. The theory is that the lower the pressure, the lower the air solubility in water. The soluble air originally in water is partially released out of solution as extremely fine bubbles due to a reduction in air solubility caused by negative vacuum pressure. The

Table 3
Control Technology Summary for Flotation

	Effluent concentration		Removal efficiency (%)
Pollutant	Range	Median	Median
Classical pollutants (mg/L)			
BOD (5-d)	140–1000	250	68
COD	18–3200	1200	66
TSS (fiber, sludge, floc)	18–740	82	88
Total phosphorus	<0.05–12	0.66	98
Total phenols	>0.001–23	0.66	12
Oil & grease	16–220	84	79
Toxic pollutants (μg/L)			
Antimony	ND–2300	20	76
Arsenic	ND–18	<10	45
Xylene	ND–1000	200	97
Cadmium	BDL–<72	3	98
Chromium	2–620	200	52
Copper	5–960	180	75
Cyanide	<10–2300	54	10
Lead	ND–1000	70	98
Mercury	BDL–2		75
Nickel	ND–270	41	73
Silver	BDL–66	19	45
Zinc	ND–53000	200	89
Bis(2-ehtylhexyl) phthalate	30–1100	100	72
Butylbenzylphthalate	ND–42		>99
Carbon tetrachloride	BDL–210	36	75
Chloroform	ND–24	9	58
Dichlorobromomethane	NA		>99
Di-*n*-butyl phthalate	ND–300	20	97
Diethyl phthalate	NA		>99
Di-*n*-octyl phthalate	ND–33	11	78
N-nitrosodiphenylamine	NA	620	66
2,4-Dimethylphenol	ND–28	14	>99
Pentachlorophenol	5–30	13	19
Phenol	9–2400	71	57
Dichlorobenzene	18–260	140	76
Ethylbenzene	ND–970	44	65
Toluene	ND–2100	580	39
Naphthalene	ND–840	96	77
Anthracene/phenanthrene	0.2–600	10	81

NA = not available; BDL = below detection line; ND = not detected.
Source: US EPA.

bubbles and the attached solid particles rise to the surface to form a scum blanket, which can be removed by a continuous scooping or skimming mechanism. Grit and other heavy solids that settle to the bottom are raked to a central sludge sump for removal. Auxiliary equipment include an aeration tank for saturating the wastewater with air, vacuum pumps, and sludge pumps (1,2). In theory, vacuum flotation is similar to dissolved air flotation because both processes rely on pressure reduction for generation of fine bubbles. The reactor designs of two processes, however, are significantly different. Vacuum flotation has been gradually replaced by dissolved air flotation in various practical applications.

2.4. Electrolytic Flotation

Electrolytic flotation is also called electroflotation, which is a process involving the generation of hydrogen and oxygen bubbles in a dilute aqueous solution by passing a direct current between two electrodes (75). The anode reaction generates oxygen bubbles and hydrogen ions, while the cathode reaction generates hydrogen bubbles and hydroxide ions. Either aluminum or steel sacrificial electrodes can be employed for generating the gas bubbles as well as coagulants. Non-sacrificial electrodes are employed for generating the gas bubbles only, and can be made of titanium (as the carrier material) and lead dioxide (as the coating material). Electrical power is supplied to the electrodes at a low voltage potential of 8–20 V DC by means of a transformer rectifier. Small bubbles in the range of 20–50 microns are produced under laminar flow conditions feasible for separation of fragile flocs in a small system. There can be unexpected advantages and disadvantages when electrolytic flotation is employed (1). Electroflotation process has been employed for treatment of septic tank effluent (25,26), groundwater (26), and industrial wastes (27,120–122). The following are the author's electroflotation reactions (1) occurring at an anode and a cathode assuming the process water contains sufficient but not excessive amounts of electrolytes:

$$\begin{array}{lr} \text{Anode:} & 2H_2O \longrightarrow 4H^+ + O_2 + 4e^- \\ \text{Cathode:} & 4e^- + 4H_2O \longrightarrow 2H_2 + 4OH^- \\ \hline & 2H_2O \longrightarrow 2H_2 + O_2 \end{array}$$

It can be seen that normally water produces fine hydrogen bubbles at a cathode and fine oxygen bubbles at an anode. In the presence of excessive electrolytes, other types of gaseous bubbles may also be produced from the electroflotation system depending upon the types and concentrations of electrolytes in the water. This is the reason why electroflotation may give either unexpected good results or unexpected bad results (120,121).

2.5. Biological Flotation

In a biological flotation system, fermentations take place in the presence of anaerobic bacteria, nitrates, and substrates under anaerobic environment. Anaerobic bacteria in waste sludge convert nitrate and the substrate with carbon source (such as methanol) to nitrite, water, and carbon dioxide fine bubbles. Nitrite further reacts with a substrate (such as methanol) in the same waste sludge, producing fine nitrogen bubbles, more fine carbon dioxide bubbles, water, and hydroxide ions. The biological waste sludge, such as activated sludge can then be floated to the surface by the fine nitrogen and carbon dioxide bubbles. While the energy consumption of this process is low, its detention time is as long as 1–2 d (1,3). The following are the author's chemical reactions in a biological flotation reactor for thickening of secondary activated sludge under denitrification conditions assuming nitrate (NO_3^-) is present in the sludge and methanol (CH_3OH) is a substrate added to the sludge:

$$\begin{array}{l} 6NO_3^- + 2CH_3OH \longrightarrow 6NO_2^- + 2CO_2 + 4H_2O \\ 6NO_2^- + 3CH_3OH \longrightarrow 3N_2 + 3CO_2 + 3H_2O + 6OH^- \\ \hline 6NO_3^- + 5CH_3OH \longrightarrow 5CO_2 + 3N_2 + 7H_2O + 6OH^- \end{array}$$

It should be noted that the secondary activated sludge usually contains residual soluble BOD, COD, or TOC, which may avoid the necessity of adding a substrate CH_3OH. In addition, biological flotation may also occur under common anaerobic conditions (instead of denitrification conditions).

2.6. Deep-Shaft Flotation

In deep-shaft flotation the entire volume of water to be treated is subjected to the increased pressure by passing the water down and up a shaft approx 10 m deep (4). At the bottom of the shaft, on the down-comer side, air is injected by one air blower under low pressure (20 psig). Undissolved air rises up the shaft against the flow, thus increasing the saturation of the water. As the water rises in the up-flow section, the hydrostatic pressure decreases. Some of the soluble air is then released out of solution in the form of fine air bubbles due to a reduction in air solubility caused by pressure reduction. Floc agglomeration and bubble generation occur simultaneously and gently; providing good attachment of the air bubbles to the flocs. The amount of air that can be dissolved is limited by the depth of shaft (e.g., hydrostatic pressure provided). The saturation of the water with air at that depth is dependent on the way the air is introduced to the system (e.g., size of air bubbles produced at point of injection) (1). Deep-shaft flotation, in principle, is similar to dissolved air flotation although the two process reactors are totally different (3,4,28).

3. BUBBLE SEPARATION PROCESS DESCRIPTIONS AND DEFINITIONS ACCORDING TO THE TECHNIQUES USED FOR SOLIDS SEPARATION

According to the collection procedure for the enriched gas–liquid and/or gas–solid interfaces, adsorptive bubble separation processes or techniques can also be divided into two large categories: (a) foam separation, which involves the production of foam in the process, and (b) nonfoaming adsorptive bubble separation, which involves no production of foam. Foam separation can be further subdivide into foam fractionation and flotation. Nonfoaming adsorptive bubble separation, however, can be further subdivided into bubble fractionation, solvent sublation, and nonfoaming flotation. Lemlich (84) and Wang (1,75) provided the definitions of these technical terms in their books.

3.1. Foam Separation

Foam Separation is classified as follows:

(a) Foam fractionation
(b) Froth flotation
    (b-1) Precipitate flotation
    (b-2) Ion flotation
    (b-3) Molecular flotation
    (b-4) Microflotation and colloid flotation

(b-5) Macroflotation and ore flotation
(b-6) Adsorption flotation

3.1.1. Foam Fractionation

Foam fractionation is one of the two foam separation processes. A foam fractionation system is always homogeneous. In a foam fractionation process reactor, the surface-active agent tends to adsorb at the bubble interface generated by a gas producer (i.e., a gas diffuser, a dissolved-air pressure chamber, or equivalent) and are removed in the foam phase. Wace et al. (29) and Grieves (30) have discussed the parameters and procedures for the design of foam fractionation and other foam separation processes. The foam fractionation technique was initially used by medical scientists and researchers. In 1952, London et al. (31) fractionated an enzyme by foaming off inactive protein. The separation and purification of enzymes through foaming was further conducted by Charm (32) in 1966. Schnepf and Gaden (33) and Wallace and Wilson (34) successfully separated proteins from water by foam fractionation. Other good work has been done to fractionate alcohol (35), anionic surfactants (36), and cationic surfactants (38). Treatment of either kraft black liquor (39,40) or dyeing bath waste (41) by foam fractionation, however, was found to be only partially successful.

3.1.2. Froth Flotation

Flotation is the term used to describe a process in which the species being separated from the bulk liquid media are insoluble particulates. Froth flotation is another one of the two foam separation processes. It also involves the production of foam in a heterogeneous aqueous system, and has a great deal of potential for the water and wastewater treatment. Froth flotation can be subdivided into at least seven categories (42,43,84), including precipitate flotation, ion flotation, molecular flotation, microflotation, adsorption flotation, ore flotation, macroflotation, and adsorbing colloid flotation. They are described separately below.

3.1.2.1. PRECIPITATE FLOTATION

Both precipitate flotation and ion flotation involve heterogeneous systems, in which a hydrophilic (solvent-loving) surface is made hydrophobic (solvent-hating) by reaction with a surfactant. Precipitate flotation involves the flotation of precipitates; in this process a non-surface-active agent (i.e., precipitating agent) is first added to the system to precipitate the ion to be removed and then a surfactant is added to float this precipitate, which then becomes attached to the bubble interfaces and is then removed in the foam phase. Under research supported by the US Department of Interior (44), a precipitate flotation process was conducted for the removal of Kraft lignin from water, and higher than 95% of lignin removal was achieved by an optimized system, in which alum and quaternary ammonium compound were used as precipitator and collector, respectively. In addition to the organic lignin removal, precipitate flotation technique has also been used by many researchers for removing radioactive contaminants (45–47), metal ions (48–50), and cyanide (51,52).

3.1.2.2. ION FLOTATION

The term ion flotation is applied to the process in which there is an initially homogeneous solution that becomes heterogeneous after the addition of an oppositely charged surfactant due to the reaction between the surfactant and specific ion(s); thus, insoluble complexes are formed. These insoluble complexes will then attach themselves to the bubbles passing through the solution and thus leave the bulk solution in the foam phase. Researches conducted by Rutgers University (43,53,54) have demonstrated that the Kraft lignin in the Kraft pulp-mill effluents, and the lignin sulfonate in the sulfite pulp-mill effluents, can be efficiently removed by ion flotation using quaternary ammonium compounds as the flotation agents. Karger et al. (55,56) has used ion flotation technique to separate the ionic dyes effectively by using an ionic flotation agent of the opposite charge. The researchers investigated the feasibility of treating dyeing bath waste stream by ion flotation and concluded that a removal of 52.1% of the COD, 89.2% of the color, and 75.3% of the turbidity was effected by using 50 mg/L of a quaternary ammonium compound as the flotation agent. Besides, ion flotation has also successfully been used by Grieves et al. (57,58) for floating inorganic ions from aqueous solution.

3.1.2.3. Molecular Flotation

Molecular flotation is very similar to ion flotation, except that the surfactant forms an insoluble complex with a nonsurface-active molecule (i.e., not an ion) and the product is floated out. Because the formation of dipolar complexes molecular flotation is much weaker than that of ion-pair complexes in ion flotation, to date, almost all the work has involved flotation of ions using an oppositely charged surfactant (59).

3.1.2.4. Microflotation and Colloid Flotation

Microflotation involves the removal of microscopic particles such as microorganisms (60–64) and colloids (65) (i.e., colloid flotation) by foaming. The term colloid flotation is specifically used when colloidal materials, other than microorganisms, are removed by a flotation process. Rubin et al. have successfully floated *Escherichia coli* and several species of algae using low gas-flow-rate foam separation technique (61) and removed *Aerobacter aerogenes* using both anionic and cationic collectors (62). The work conducted by Cassell and Rubin (65) has shown that microflotation is a rapid, efficient, nonselective technique. The separation of microscopic particles (including both microorganisms and colloidal color-causing materials) from water has, in some cases, advantages over gravity sedimentation. Combined with the high-rate filtration, microflotation may lead to an extremely efficient and compact treatment process for both water and wastewater treatment. In 1966, Dolzhenkova (66) improved the microflotation by replacing the single-capillary air-feeding device with a porous-glass/diaphragm, by giving a pear-shaped form to the air inlet chamber, by using a microcompressor (instead of a compressed-air cylinder) as a source of compressed air, and by modifying the air-supply rate controlling device.

Adsorbing colloid flotation involves the flotation of colloidal particulate upon which dissolved material is adsorbed. The major objective of this adsorbing, colloid flotation process is the removal of the dissolved material rather than the colloidal particles. Wang (72) has used a colloidal surface-active agent, dimethyl dihydrogenated-tallow ammonium chloride, as a flotation agent to treat tannery waste, and found that the adsorbing colloid flotation is efficient for the removal of suspended solids (i.e., more than 0.9 fractional reduction), but is inefficient for the removal of dissolved organics (i.e., less than 0.6 fractional reduction) from a tannery effluent. Kim and Zeitlin (74) has separated zinc and copper from sea water by adsorbing colloid flotation, which utilizes a negatively charged ferric hydroxide collector, a cationic surfactant, dodecylamine, and air.

3.1.2.5. MACROFLOTATION AND ORE FLOTATION

Contrary to the microflotation (and colloid flotation), the terms of macroflotation and ore flotation represent the removal of macroscopic particles by foaming. Both macroflotation and ore flotation are practically the same, but it was felt necessary to take special note of the mineral dressing process, and thus the foam separation of minerals is termed ore flotation (59), which is a well-established process in the mining industry (67–70). In the field of environmental engineering, separation of biological sludge or other macroscopic pollutants from wastewater can be accomplished efficiently by macroflotation if a surface-active agent is added to the system as a collector of particulate species, drawing and attaching the species to the generated gas bubbles, and as a frother to produce a stable foam in which the macroscopic pollutants are concentrated and removed. In other cases, a surface-active agent already present in the wastewater can be utilized as a flotation agent (i.e., collector or frother) for the foam separation of macroscopic particles.

3.1.2.6. ADSORPTION FLOTATION

Adsorption flotation involves the removal of dissolved pollutants by activated carbon in a bubble reactor, and subsequent removal of activated carbon as well as other suspended particles by flotation technique (71). This process was found efficient for removing both dissolved organics and suspended solids from an industrial effluent (72), and for removing the emulsified oil from water (73). The mechanism of removal has been proposed by Wang (72,73).

All the aforementioned process terms can simply be called foam separation. It is important to note that although any type of technique can be used for bubble generation in a foam separation system, the most common bubble generation technique for a foam separation system is dispersed air flotation, which is also known as induced air flotation.

3.2. Nonfoaming Adsorptive Bubble Separation

The following are the classifications of nonfoaming adsorptive bubble separation:

(a) Bubble fractionation
(b) Solvent sublation
(c) Nonfoaming flotation
    (c-1) Nonfoaming precipitate flotation
    (c-2) Nonfoaming adsorption flotation
    (c-3) Nonfoaming flotation thickening

Again, any type of technique can be used for generating gas bubbles in a nonfoaming adsorptive bubble separation system. The most effective bubble generation techniques for a nonfoaming system are dissolved air flotation and electrolytic flotation. The following are the process descriptions of selected nonfoaming processes.

3.2.1. Bubble Fractionation

Bubble fractionation is similar to foam fractionation except that there is no foam produced in the system; thus, it is applied to dilute surface-active solutions that do not foam; while foam fractionation is applied to surface-active solutes at high concentration (76,77). Technically speaking, bubble fractionation represents an operation in which gas is bubbled up through a vertical bubble reactor containing the surface-active solute(s) to provide adsorbing interfaces of air/water in the aqueous medium. The solute is adsorbed on the surfaces of the rising bubbles and is carried upward to the top of the column where the bubbles break, releasing part of the solute back to the solution. This transport of the solute establishes a vertical concentration gradient along the bubble reactor. The solution is rich in the solute at the top and lean at the bottom. Subsequent removal of the concentrated liquid layer from the top then allows effective removal of the solute.

Separation of dilute dye stuffs, lignins, and detergents by continuous bubble fractionation has been performed by Wang and his co-workers at Rutgers University (77–79). The separability of the three kinds of surface-active substances was found to be in a decreasing order of detergents, dye stuffs, and lignins. Under an optimum operational condition, the LAS (i.e., linear alkylate sulfonate) and ABS (i.e., alkyl benzyl sulfonate) detergents with strengths of 5.85 mg/L can be reduced to about 0.1 mg/L.

Continuous bubble fractionation can be a potential pretreatment process for the reduction of dilute, refractory surfactants present in the water or wastewater. Besides, effective solution separation should result in some valuable by-product recovery.

3.2.2. *Solvent Sublation*

Solvent sublation involves the collection of the enriched material on the bubble surface in an immiscible liquid above the bulk liquid media. More specifically, it is a technique in which the material raised to the surface of a solution by flotation is collected and prevented from redispersing into the bulk phase. This is achieved by spreading a thin layer of an immiscible organic solvent on the surface of the solution which causes the floated material to dissolve or to become suspended.

Karger et al. (80) have studied the effects of gas-flow rate and surfactant concentration on the rates of extraction of two dyes by solvent sublation. Because in solvent sublation there is no longer the necessity for producing a foam, they concluded that the technique should be possible to selectively remove ionic solutes or impurities from an aqueous phase at trace concentrations.

Sheiham and Pinfold (81) have attempted to remove a cationic surfactant, hexadecyltrimethylammonium chloride, by both solvent sublation and foam fractionation. A comparison (81) between the rates of surfactant removal by the two separation techniques shows that the separation of the cationic surfactant from 10^{-5} M solutions by solvent sublation into 2-octanol is slower but preferable if the foams are unstable.

Solvent sublation would appear to have a potential for large-scale water quality control processes and a definite role in trace analytical separation (82).

3.2.3. *Nonfoaming Flotation*

One of the most important adsorptive bubble separation processes is nonfoaming flotation. The process is termed flotation because the species being separated from the bulk media are mainly or partially insoluble particulates, such as sludges or agglomerates. It is a nonfoaming process system in which no production of foam is involved.

3.2.3.1. NONFOAMING PRECIPITATE FLOTATION

Potable water clarification and tertiary wastewater treatment (4–9) by dissolved air flotation cells are typical examples of nonfoaming precipitate flotation in which the soluble/colloidal impurities are precipitated by flocculants and the flocs as well as other suspended solids are floated.

3.2.3.2. NONFOAMING ADSORPTION FLOTATION

If powdered activated carbons (or other adsorbents) are added to water or wastewater for removing soluble pollutants, the spent carbons are then flocculated and floated by a dissolved air flotation cell (or by an electroflotation cell), in which no foam is produced, the process system is termed nonfoaming adsorption flotation (83).

3.2.3.3. NONFOAMING FLOTATION THICKENING

Sludge thickening and fiber separation by dissolved air flotation cells (2,3) are typical examples of nonfoaming flotation thickening in which the target sludges or fibers are originally in insoluble forms and ready to be floated.

There are too many terminologies used for classification of "adsorptive bubble separation processes." In order to avoid the confusion which exists regarding the interrelationship of various adsorptive bubble separation methods, four important terms should always be remembered: (a) flotation (either a foaming or a nonfoaming system): the liquid to be processed is heterogeneous such as industrial effluents which contain both insoluble particles (or complexes) and dissolved organics; (b) fractionation (either a foaming or a nonfoaming system): the liquid to be processed is homogeneous, such as a detergent solution; (c) foam separation (either homogeneous or heterogeneous): the system involves the production of foam; and (d) nonfoaming bubble separation (either homogeneous or heterogeneous): the system involves no production of foam.

4. BUBBLE SEPARATION PROCESS DESCRIPTIONS AND DEFINITIONS ACCORDING TO THE OPERATIONAL MODES

4.1. Continuous Adsorptive Bubble Separation

An adsorptive bubble separation process is assumed to be a continuous process in which the influent is continuously fed into the process system, while the effluent is continuously withdrawn from the process system.

4.2. Sequencing Batch Reactor Adsorptive Bubble Separation

One of many sequencing batch reactor (SBR) processes developed by Wang, Kurylko, and Wang in 1994 (125) is a physicochemical sequencing batch reactor adsorptive bubble separation (SBR-ABS) process, which can be used for potable water purification, industrial water treatment, wastewater effluent treatment, and groundwater decontamination (126). There are various types of SBR-ABS systems: (a) physicochemical SBR flotation, (b) physicochemical SBR fractionation, (c) biological SBR flotation (2,3,4). The physicochemical SBR flotation has been used successfully in full-scale operation in Europe (123).

5. SURFACE ADSORPTION

Solids, liquids, and solutions exhibit many properties that can only be explained in terms of the action of their surfaces. A surface is actually a boundary, where the mass of one body ends and the mass of another begins. Consider a rising air bubble immersed in a liquid pool. The surface of the air faces a corresponding surface of the liquid; the region enclosed by these two surfaces is known as an interface, and it is within this interfacial region that adsorption occurs. There are five types of possible interfaces (43):

- Gas–Liquid
- Liquid–Liquid
- Liquid–Solid
- Solid–Gas
- Solid–Solid

The action at these interfaces includes: interfacial tensions, adsorption, the spreading of liquids on surfaces, insoluble surface films, and the catalytic activity of various solid surfaces for many types of chemical reactions.

Of the five types of interfaces mentioned above, adsorption at gas–liquid (e.g., air–water) interfaces is of interest in all adsorptive bubble separation methods. In the liquid pool, a molecule is acted upon by molecular attractions, which are distributed more or less symmetrically about the molecule. However, at the air–water interface, a water molecule is only partially surrounded by other like molecules; as a consequence, an attraction tends to draw the surface molecules inward, and in doing so makes the water behave as if it were surrounded by an invisible membrane. This behavior of the surface is called surface tension. Surface-active substances possess the ability to lower the surface tension of water even at low concentrations.

A phenomenon of concentration of a substance on the interface is called adsorption. Surface activity is due to the unequal distribution of a solute between the surface and the bulk solution. Quantitative description of the adsorption of a solute at gas–liquid interfaces, under an equilibrium condition, is expressed by the Gibbs adsorption equation as

$$dr = -RT \sum E_{xi} d\left(\ln a_i\right) \tag{1}$$

where r represents the surface tension of the solution, dyne/cm, R is the universal gas constant, dyne-cm/(g-mole K), T is the absolute temperature, K, E_{xi} is the surface excess, g-mole/cm^2, which is essentially the concentration the component i at the interface; and a_i is the activity of the its component.

For an ideal two-component solution consisting of a solvent and a single surface-active solute at equilibrium condition, and with concentration assumed to be equivalent to activity (i.e., dilute solution), Eq. (1) may be written as

$$E_x = (-L/RT)\ (dr/dL) \tag{2}$$

where dr/dL is the rate of variation of the surface tension of the solution with bulk concentration. L is the bulk solute concentration, g-mole/cm^3. When the surface tension of a solution decreases with concentration, dr/dL is negative, E_x is positive, and the surface contains a higher concentration of solute than the bulk solution. Equation (2) is the form in which the Gibbs adsorption equation is usually quoted. In the adsorption of ionic surfactants into the surface phase, with or without the presence of inorganic electrolyte, equal numbers of cations and anions must enter the surface and different modifications must be made before the equation is formally applied. Theoretically, for the adsorption of a dilute univalent ionic surfactant, the following modified adsorption equation should be applied:

$$E_x = (-L/2RT)\ (dr/dL) \tag{3}$$

A detailed derivation of Eq. (3) may be found elsewhere. In the presence of excess inorganic electrolyte in the univalent ionic surfactant system, the factor 2 in Eq. (3) can be reduced to 1 by thermodynamic modification.

Adsorption from the liquid solution and adsorption of gases generally follow the same principles and are subject to the same factors. When adsorptive bubble separation processes are applied to the treatment of industrial effluents containing high suspended solids or applied to the purification of raw water containing high turbidity, some other mechanisms are responsible for liquid–solid as well as liquid–gas adsorption phenomena. The process of liquid–solid adsorption can be of three types—physical adsorption, chemical adsorption, and electrostatic adsorption. Physical adsorption results from molecular condensation (of adsorbate) in the micropores of the adsorbent by so-called inner van der Walls or dispersion forces. Chemical adsorption (or chemisorption) results in the formation of a chemically bound monomolecular layer of the adsorbate on the adsorbent surface through forces of residual valence of the solid surface molecules. Electrostatic adsorption is an attractive force responsible for adsorbing ionic solute on an oppositely charged adsorbent. Electrostatic adsorption forces can also result from ion exchange phenomena between adsorbate and adsorbent. It can be altered because of the affinity of hydrogen and hydroxide ions for the adsorbent surface.

There are several other physical and chemical variables that affect the adsorption rate and the adsorption equilibrium of an adsorption system involving the separation of a solute from aqueous onto an adsorbent. These include the total surface area of an adsorbent, concentration of adsorbent, concentration of adsorbate, nature of adsorbent, nature of adsorbate, nature of the mixture of solutes (such as dissolved solids content), hydrogen ion concentrations of the system, and the temperature of the system. In a multicomponent bubble separation system, several adsorption mechanisms are involved. True adsorption phenomena cannot be clear until laboratory experiments are conducted.

In water solution containing small particles (i.e., suspended solids or turbidity) and non-surface-active solutes, when air is bubbled through it, little or no particles will be removed by any adsorptive bubble separation process. This is because the particles have virtually no natural affinity for air bubbles and hence there is no adhesion when contact is made. This particular phenomena may be explained by the contact angle between a particle and an air bubble. Consider the case of the three-phase line of contact between a smooth, rigid, solid phase, a liquid phase and a gas phase. The equilibrium contact angle A_e can be expressed in terms of the average surface tensions (i.e., interfacial tensions, dyne/cm) of the liquid-gas (r_{LG}), solid-liquid (r_{SL}), and solid-gas (r_{SG}) interfaces, by the well-known Young's equation:

$$r_{\mathrm{SG}} = r_{\mathrm{SL}} + r_{\mathrm{LG}} \cos (A_e) \tag{4}$$

The definition of contact angle is illustrated in Fig. 2. For a system containing no surface-active agents, the contact angle between a particle and an air bubble is said to be zero because of complete wetting. If some appropriate surface-active agents were added to this system, they would be adsorbed on the surface of the particle and the particle surface would become hydrophobic, thus it would attach itself to an air bubble which came in contact with it. In general, high contact angles are produced by interaction between the adsorbed layers of collector molecules at the solid–liquid interfaces

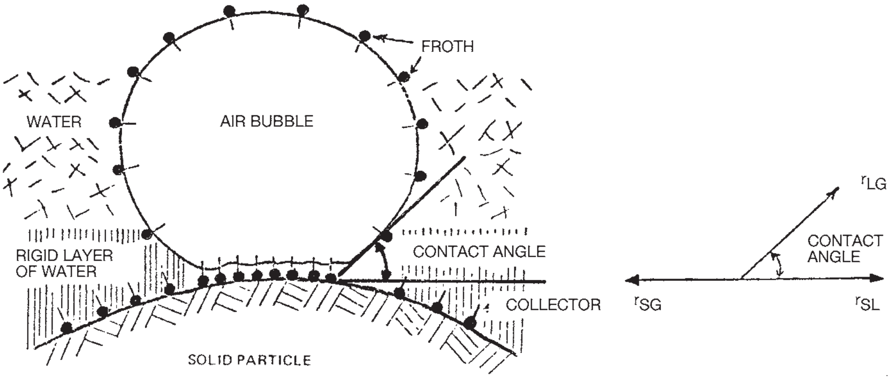


Fig. 2. Attachment of air bubble to sold particle at flotation.

in solution and frother molecules at the gas–liquid interfaces. The association produced a mixed monolayer at the solid–gas interfaces. Collectors are surface-active agents that normally attach themselves to nonfloating particles endowing them with hydrocarbon-like surfaces, thereby making them capable of adhering to air bubbles. Frothers are organic compounds such as pine oil and cresols slightly soluble in water. When frothers are added in small amounts to a solution that has air bubbling through it, the bubbles become smaller and a frothy layer several inches thick forms. This layer containing the solid pollutants can be skimmed off. Figure 2 shows how an air bubble is attached to a solid particle at flotation. The solid surface, which is wetted by water, is surrounded by more or less rigid layers of water. The properties of these layers differ from those of ordinary fluid water—the vapor pressure is higher, for example.

6. BUBBLE PHENOMENA

Figure 1 shows the structure of a bubble ascending in a surfactant solution under the influence of drag force and buoyant force. In the Stokes' law range, the fluid will flow smoothly over the bubble surface, leaving no wake. Only skin friction (viscosity shear stresses) contributes to the total drag on the bubble. Beyond the Stokes' law range, increasing Reynolds number (N_R) gradually separates the boundary layer from the bubble surface, produces wakes in the rear, and contributes more and more form drag to the total drag force. Form drag results from pressure differences caused by the acceleration of the fluid flowing around the bubble and from the high velocities of the turbulent eddies in the wake (77).

The interference of surface-active agents upon the bubble movement can also be understood by the same figure. During the bubble rise the surfactant film adsorbed on the bubble wall will be driven to the tail end of the gas bubble where it condenses, forming a solid cap. As a result a surface force will be set in the direction of the front end of the air bubble, opposing the liquid drag forces, which may cause a retardation in the bubble rising velocity and opposing the hydrodynamic stress responsible for interfacial renewal. Other interferences caused by the adsorption of a surfactant monomolecular film at the air–water interface (such as bubble wall) are a reduction in the gas transfer rate and gas adsorption rate.

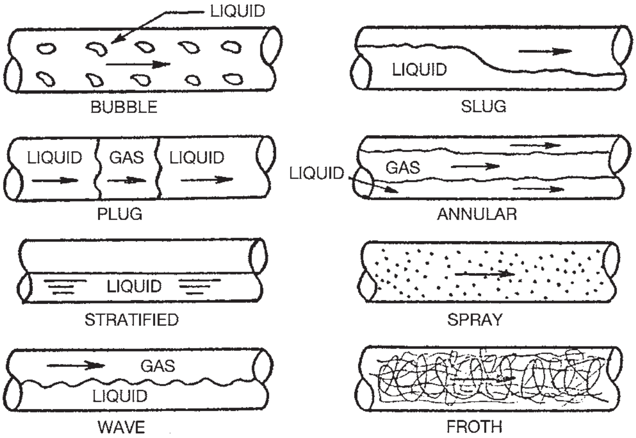


Fig. 3. Various flow regimes encountered in two-phase flow.

Increasing surfactant concentrations in the aeration cell has been found to decrease bubble diameter, bubble velocity, axial diffusion coefficient, but increase bubble's surface-to-volume ratio, and total bubble surface area in the system. The effect of a surface-active agent on the total surface area of the bubbles is also a function of its operating conditions. The surfactant's effect is pronounced in the case of a coarse gas diffuser where the chances of coalescence are great; and the effectiveness of a surface-active solute in preventing coalescence increases with the length of its carbon chain.

7. MULTIPHASE FLOW

The mechanics and applications of multiphase flow has been an area of continuing interest to chemical, environmental, and civil engineers (23,77). The multiphase flow patterns may be classified as bubble flow, plug flow, stratified flow, wave flow, slug flow, annular flow, spray flow, and froth flow. Typical sketches of these various flow patterns are shown in Fig. 3. They are self-explanatory. In the field of absorptive bubble separation processes, only multiphase bubble flow and froth flow are of interest to the process engineer.

Type of flow pattern(s) involved in an adsorptive bubble separation system depends on the type of process used. For example, bubble fractionation involves two-phase (gas-phase and liquid-phase) bubble flow, while solvent sublation involves multiphase bubble flow in their vertical bubble cells. Foam fractionation involves a two-phase bubble flow in the bottom bubble cell, and a two-phase froth flow in the top foam cell. However, all froth flotation processes (i.e., precipitate flotation, ion flotation, molecular flotation, ore flotation, microflotation, adsorption flotation, macroflotation, and adsorbing colloid flotation) involve multiphase bubble flow and multiphase froth flow.

All batch adsorptive bubble separation processes involve no net movement of liquid, but steady bubbling of gas through the stagnant liquid. The relative bubble velocity in the bubble cell is the function of buoyancy component and the superficial gas velocity.

In the bubble cell of any continuous adsorptive bubble separation process, the relative bubble velocity is the function of buoyancy component, the superficial gas velocity, and the superficial liquid velocity. The superficial velocity of gas and liquid are caused by the continuous entry of the gas and liquid phases into the bubble cell. Figures 4 (A) and 4 (B) show the relative bubble velocity in various two-phase bubble flow systems (43).

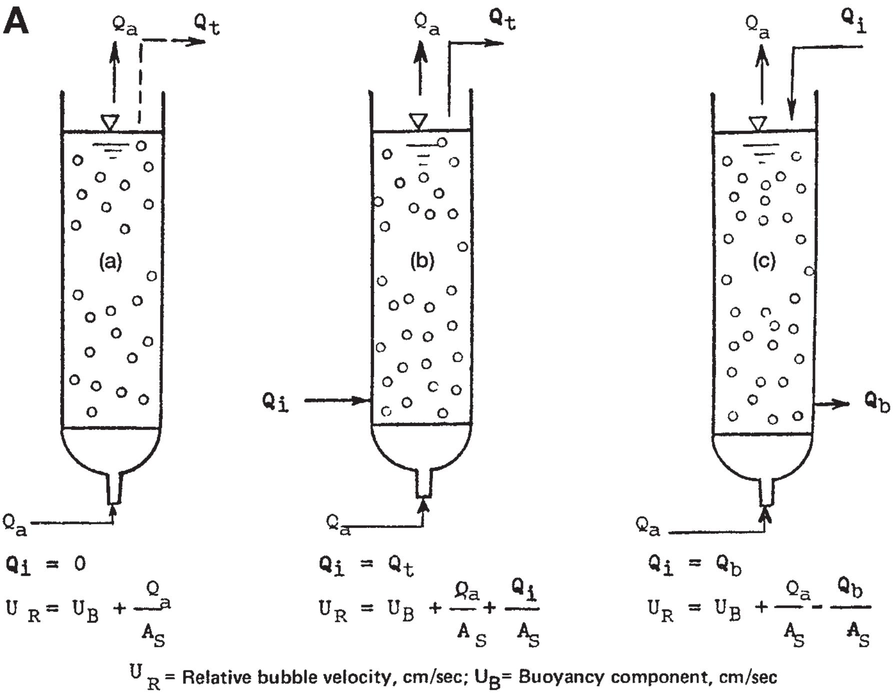


Fig. 4. **(A)** Relative bubble velocity in a two-phase bubble flow—systems (a), (b), and (c).

The bubble size distribution in a bubble flow is primarily dependent on the rate of air supply to the gas diffuser. The size of the largest bubbles may change somewhat with the rate of air discharge and orifice size. When the liquid moves relative to the orifices, the maximum bubble diameter is equal to 2.4 times the square root of the gas-flow rate per jet divided by the liquid velocity. However, the size distribution of bubbles below the largest can be obtained only from experiment.

8. MATERIAL BALANCES

In the batch adsorptive bubble separation processes, a feed solution was introduced to a bubble separation column (or chamber) containing an aqueous solution of surface-active materials. Surface-active solutes or complexes that are hydrophobic and readily attachable to the air bubbles are carried up to the surface of the water by the bubbles. The enriched material at the top (whether collapsed foam from a foam separation column or overflow liquid from a nonfoaming bubble separation column) and the clarified drain solution at the bottom are withdrawn from the system. The overall material balance for the process is as follows:

$$V_i = V_t + V_b \tag{5}$$

in which V_i is the initial volume, V_t is the collapsed foam (as liquid) volume from the batch process, and V_b is the residual liquid volume in separation column. For the substance other than collectors (i.e., target solute or solid), which may be separated by the foaming process, the following material balance may be used:

$$V_i L_i = V_t L_t + V_b L_b \tag{6}$$

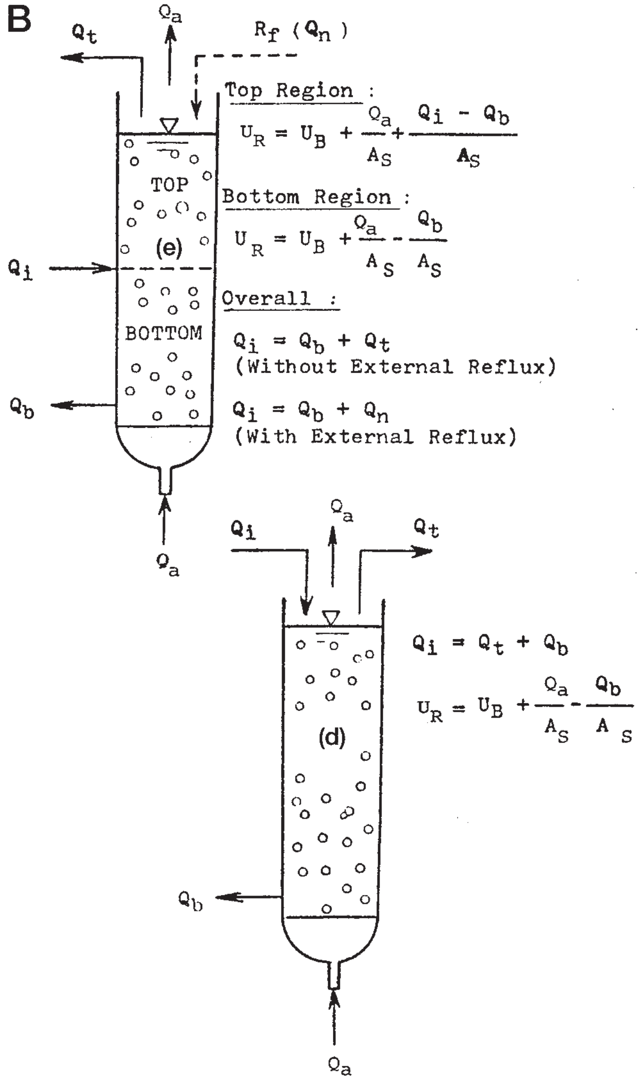


Fig. 4. **(B)** Relative bubble velocity in a two-phase bubble flow—systems (d) and (e).

in which L_i is the surface-active solute or solid concentration in the feed, L_t is the surface-active solute or solid concentration in the collapsed foam phase, and L_b is the residual surface-active solute or solid concentration in the drain. Considering the additional collector necessary for foaming, the material balance may be written as:

$$V_i S_i = V_t S_t + V_b S_b \tag{7}$$

where S_i is the collector concentration in the feed, S_t is the collector concentration in the foam phase, and S_b is the residual collector concentration in the drain.

In case of continuous adsorptive bubble separation processes, the following set of material balance equations at the steady state will be obtained.

$$Q_i = Q_t + Q_b \tag{8}$$

$$Q_i L_i = Q_t L_t + Q_b L_b \tag{9}$$

$$Q_i S_i = Q_t S_t + Q_b S_b \tag{10}$$

in which Q_i, Q_t, and Q_b are volumetric liquid flow rates of feed, overhead, and drain, respectively. For a single-solute fractionation system, Eqs. (7) and (10) are dropped because no collector is used. Another basic solute balance for the continuous bubble separation system is

$$E_x Q_a f' = Q_t (L_t - L) \tag{11}$$

where E_x is the surface excess, L is the bulk solute concentration, Q_a is the volumetric gas rate, and f' is the surface to volume ratio of the bubble. Generally, the size of the bubbles are not uniform and an effective average radius is used:

$$r_e = \Sigma(N_i r_i^3)/\Sigma(N_i r_i^2) \tag{12}$$

where N_i is the number of bubbles of radius r_i, and r_e is the effective average bubble radius. r_e is also defined as the bubble radius averaged by the ratio of the third moment (volume) to the second moment (surface area). For spherical bubbles,

$$f' = 6/d = 3/r_e \tag{13}$$

where d is the effective average bubble diameter. Equation (11) can then be written as:

$$E_x = d\, Q_t (L_t - L)/6Q_a \tag{14}$$

9. FOAM SEPARATION BY DISPERSED AIR FLOTATION CELL

Many contaminants in wastewater today, such as dissolved dyestuffs, lignins, detergents, proteins, fatty acids, tannins, and so on, possess surface-active properties that decrease surface tension and oxygen transfer rate, but increase the demand for dissolved oxygen. Particularly, the sharp reduction in surface tension of water by these pollutants seems to be a basic cause of increasing the susceptibility of aquatic life to the surfactant poison.

Foam separation process involves the selective adsorption of the surface-active pollutants at the gas–liquid interfaces of fine air bubbles in a foam separation column. The surface-active pollutants, which are adsorbed on the surfaces of the rising bubbles, can be carried upward to the top of the foam separation column and thus removed from the aqueous system as condensed foam. Foam separation can be used for both waste treatment and water purification. This section presents the data on the feasibility of removing various organics and inorganics by the foam separation processes. A general survey of foam separation process and its fundamental principles are also presented.

The basic principle for solid/liquid and solute/liquid separation by the adsorptive bubble separation processes has been introduced previously. This section further presents fundamental principles on foam phenomena and foam separation cell's operation.

For foam separation processes, adsorption takes place in solution, the essential basis exists for solute separation by foaming. Foam consists of gas bubbles separated by thin liquid films. The liquid films are often formed by the mutual approach of two already existing liquid surfaces (e.g., two bubbles below the surface). Foam structures may vary between two extreme situations. The first is wet foam, which consists of nearly spherical bubbles separated by rather thick liquid films. The second is dry foam, which may develop from the first type as a result of drainage (i.e., foam drainage).

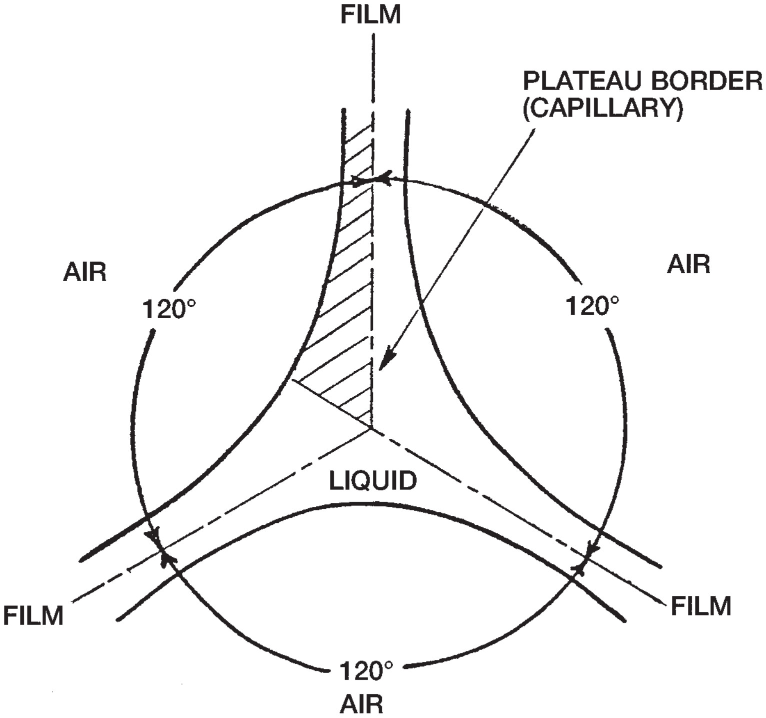
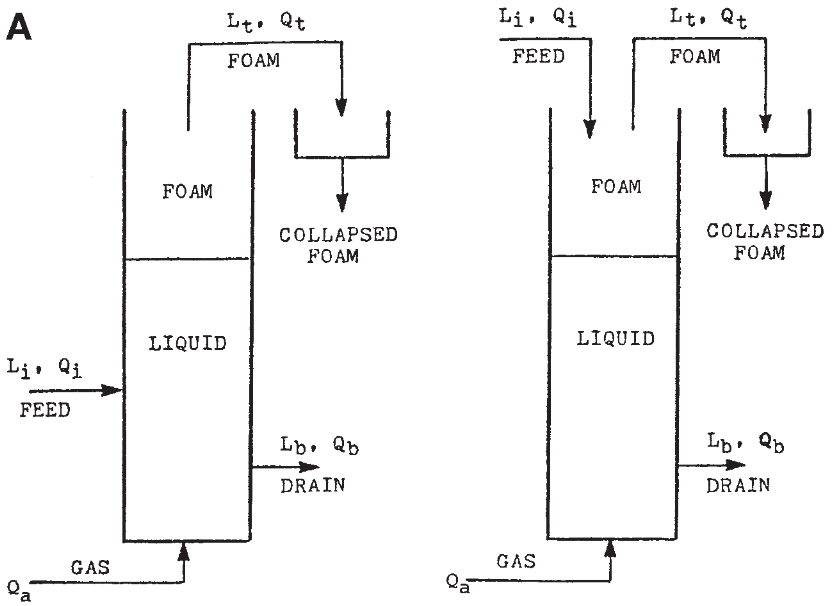


Fig. 5. Cross section of plateau border and films in foam.

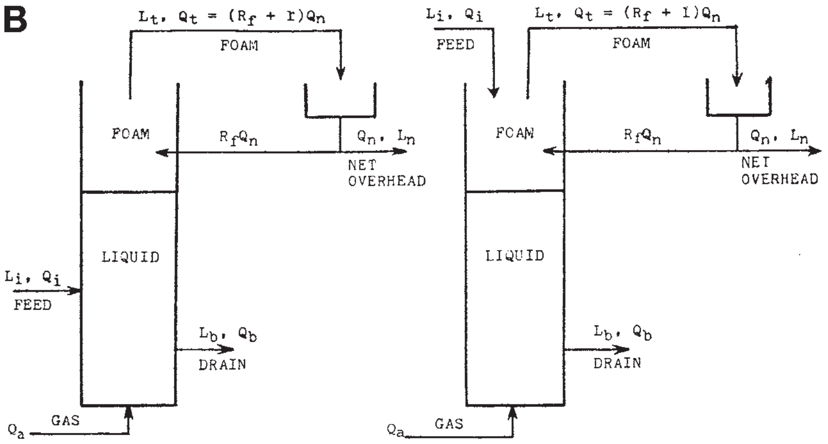
The bubbles in the froth flow (i.e., foam) press against each other, more or less flattening the faces or films in between, particularly for dryer foams. These films intersect three at a time to form capillaries or channels, which are often called plateau borders (Fig. 5). The uniform foam bubbles are nearly regular dodecahedra, which implies that there is a dihedral angle of 120° between intersecting films. Foam drainage occurs primarily through the interconnecting network of capillaries rather that from film to film. The flow through the capillaries is incompressible and laminar.

In froth flow of foam separation column, bubble coalescence within the rising foam is important. Coalescence in foam is of two types. The first is gas diffusion or bubble growth, which arises from the difference in pressure between adjacent air bubbles of differing size. As a result of the surface tension, the smaller air bubble has a higher pressure than the larger. This causes air to diffuse from the smaller bubble, across the film, to the larger bubble. Accordingly, the larger bubble grows larger while the smaller continues to shrink. The smaller bubble will completely disappear if sufficient time is given. The overall affect is a decrease in film surface area.

The second cause of coalescence is the film rupture between bubbles. This can easily be very significant. Physically, the film rupture stems from a depletion of surfactant at the film surface when the surface is stretched. The film stability is commonly ascribed in large measure to the so-called Marangoni effect and Gibbs effect. The Marangoni effect involves the inability of surfactant molecules to diffuse instantaneously to any locally stretched area in the film surface. The resulting lag permits the stretched surface to be momentarily depleted of surfactant. The Gibbs effect involves



(a) SIMPLE MODE (b) STRIPPING MODE



(c) ENRICHING MODE (d) COMBINED MODE

Fig. 6. **(A)** Foam separation modes (without external reflux). **(B)** Foam separation modes (with external reflux) (43).

the possible insufficiency of molecules within the film liquid to recoat the stretched surface completely regardless of diffusion rate. Another mechanism is the electrostatic repulsion between the charged surfaces that opposes film thinning and foam rupture. This can be important with some ionic surfactants in thin films.

Whatever the cause, coalescence within the rising foam furnishes internal reflux that enriches the foam and, therefore, increases the solute concentration in the overflow foam stream. Foam coalescence due to external reflux will be discussed later.

There are four modes for the continuous foam separation process: the simple mode, the stripping mode, the enriching mode, and the combined mode. Only the first two modes (simple and stripping), which involve no external reflux, are of interest to the feasibility studies. This is because the simple and the stripping modes (Fig. 6A) are easy to operate in a small laboratory. Besides, once a particular type of foam separation process has been proved to be feasible by its simple mode or stripping mode operations, the enriching mode or the combined mode (Fig. 6B), which both involve external reflux, can readily be operated in a larger pilot-plant scale or full scale successfully.

External reflux can be accomplished simply by a mechanical or any other suitable means, and then returning a portion of the collapsed foam to the top of the cell, as shown in Fig. 6B (enriching mode and combined mode). In the external reflux operation, some collapsed foam serves as reflux and drains back down through the rising foam. The resulting countercurrent contact enriches the rising interstitial liquid and thus enriches the overflow. For external reflux, either "dephlegmation" or total external coalescence is required. Dephlegmation is the deliberate partial collapse of the foam at the top of the foam cell. By whatever means accomplished, the partial reflux so created drains back down through the rising foam thus enriching it. The uncollapsed portion of the foam simply flows off overhead, and can be broken separately. Total external coalescence is accomplished simply by breaking (collapsing) all the overhead foam in some suitable manner, and then returning a portion of the collapsed foam to the top of the cell, as shown in Fig. 6B. Enriching the foam is also expected.

For the cells of simple mode (Fig. 6A), feed is introduced into the liquid pool under the following three assumptions: there is no appreciable bubble coalescence in the rising foam with the column; foam leaving the liquid surface is in equilibrium with the completely mixed bulk solution; and the bulk solute concentration is equal to the drain solute concentration. For a sufficiently long column, the separation ratio L_t/L_b and the stripping ratio L_b/L_i are given by Eqs. (15) and (16):

$$L_t/L_b = 1 + f'\,Q_a\,E_b/L_b\,Q_t \tag{15}$$

$$L_b/L_i = 1 - f'\,Q_a\,E_b/L_i\,Q_i \tag{16}$$

Equation (15) is derived from Eq. (14) by replacing L with L_b; while Eq. (16) is derived from Eqs. (8), (9), and (15). The surface to volume ratio of bubble (f') for the simple mode (Fig. 6A) is equal to $6/d$. The surface excess value (E_b) is in equilibrium with drain concentration L_b. d is the effective average bubble diameter.

For the cells of stripping mode (Fig. 6A), feed is introduced into the system some distance above the liquid pool. It tends to replace the rising interstitial liquid of pool concentration with downcoming liquid of feed concentration. Therefore, the foam leaving the liquid surface is in equilibrium with the feed solution. L, in Eq. (14), should be replaced with L_i. The results of the countercurrent stripping action are

$$L_t = L_i + f'\,Q_a\,E_i/Q_t \tag{17}$$

$$L_b = L_i - f'\,Q_a\,E_i/Q_b \tag{18}$$

$$f' = 6.59/d \tag{19}$$

in which the surface to volume ratio of air bubble (f') for stripping mode has been changed to $6.59/d$. The surface excess value is in equilibrium with the feed concentration L_i. d is the effective average bubble diameter.

Table 4
Foam Separation Modes

1. Simple mode	
$L_t = L_b + f'Q_aE_b/Q_t$	(15)
$L_b = L_i - f'Q_aE_b/Q_i$	(16)
$f' = 6/d$	(13)
2. Stripping mode	
$L_t = L_i + f'Q_aE_i/Q_t$	(17)
$L_b = L_i - f'Q_aE_i/Q_b$	(18)
$f' = 6.59/d$	(19)
3. Enriching mode	
$L_n = L_b + f'Q_aE_b/Q_n$	(20)
$L_b = L_i - f'Q_aE_b/Q_t$	(21)
$f' = 6.59 - 0.59/(R_f + 1)$	(22)
4. Combined mode	
$L_n = L_i + f'Q_aE_i/Q_n$	(23)
$L_b = L_i - f'Q_aE_i/Q_b$	(24)
$f' = 6.59/d$	(19)

Similarly the cell performance equations for the enriching mode and combined mode can be derived. Table 4 summarizes the cell performance Eqs. (13)–(24) of foam separation.

It should be noted that the assumption of no appreciable bubble coalescence in the rising foam is difficult to be measured to any extent and magnitude because the rising foam is not sufficiently stable. Although bubble coalescence within the foam is quite often the case, it frequently goes unrecognized because of nonuniformity in bubble size, which makes changes difficult to detect by eyes, the effect of such internal coalescence is to destroy some bubble surface, thus releasing adsorbed material that trickles back down through the rising foam, enriching the foam, and, therefore, increasing the solute concentration in the overflow foam stream. Using a different surface to volume ratio *(f')* for a different mode of operation resulted from the consideration of bubble coalescence in the rising foam.

An empirical model can be developed, relating some operational variables of continuous foam separation (simple mode and stripping mode)

$$Q_b = a_1 - a_2L_i + a_3T_c - a_4\,Q_a \tag{25}$$

and

$$L_b = -\,b_1 + b_2\,L_i + b_3T_c - b_4\,Q_a \tag{26}$$

in which a_1, a_2, a_3, a_4, b_1, b_2, b_3, and b_4 are constants, and T_c is temperature in °C.

In general, surface excess E varies with its equilibrium concentration L in a foam separation reactor. For trace concentration of surfactants, this variation can often be represented by a linear isotherm (77,78)

$$E = KL \tag{27}$$

where K is an equilibrium constant for surface adsorption, cm; L is the concentration of surface active solute, g-mole/cm^3; and E is the solute surface excess in equilibrium with L, g-mole/cm^2.

For a surfactant that is present in a foam separation reactor at a concentration near or above its critical micelle concentration, the surface excess may be approximately a constant representing a completely saturated air–water interface:

$$E = K' \tag{28}$$

where K' is another equilibrium constant for surface adsorption, g-mole/cm^2.

For a better foam separation than that obtainable with the simple mode, the process operation can be cascaded by employing one of the countercurrent modes as shown in Figs. 6A and 6B. For the countercurrent modes of process operation, the number of transfer units (NTU) can be calculated in terms of an upflowing stream of interstitial liquid plus bubble surface, and a downflowing stream of just interstitial liquid. If the surfactant concentration in the upflowing interstitial liquid is L, and the solute surface excess at the bubble surface is E (which is taken to be equilibrium with L), then the effective concentration in the upflowing stream on a gas-free basis is generalized as

$$y = L + f' Q_a E/Q \tag{29}$$

where y = effective concentration of solute in the upflow within a foam separation reactor on a gas-free basis, g-mole/cm^3 of liquid; L = concentration of surface active solute, g-mole/cm^3; Q = volumetric rate of liquid upflow in a foam separation reactor, cm^3/s; and f' = ratio of bubble surface area to bubble volume, cm^{-1}. The number of transfer units (NTU) in the foam based on the upflow stream can be calculated by Eq. (30).

$$\text{NTU} = \int_{y^*}^{L_t} \frac{dy}{y^* - y} \tag{30}$$

where y^* is the effective concentration of solute, in equilibrium with L_t, in the upflow within a foam separation reactor on a gas-free basis, g-mole/cm^3.

10. CHEMICAL REAGENTS FOR ADSORPTIVE BUBBLE SEPARATION

Promoters or collectors provide the substances to be separated with a water-repellent air-avid coating that will adhere to air bubbles. Typical collectors for flotation of metallic sulfides and native metals are dithiophosphates and xanthates. Fatty acids and their soaps, petroleum sulfonates, and sulfonated fatty acids are widely used as collectors in flotation of fluorspar, iron ore, phosphate rock, and others. Fuel oil and kerosene are used as collectors for coal, graphite, sulfur, and molybdenite. Cationic collectors such as fatty amines and amine salts are widely used for separation of quartz, potash, and silicate minerals.

Pine oil, cresylic acid, aliphatic alcohols, and polypropylene glycol ether are commonly used as the "frothers."

Bubble separation "modifiers" include several classes of chemicals described below: activators, alkalinity regulators, depressants, deflocculants, and defoaming agents.

"Activators" are used to make a mineral surface amenable to collector coating. Sodium sulfide is used to coat oxidized copper and lead minerals so that they can be floated by a sulfide mineral collector. Copper ion is used to activate sphalerite (ZnS), rendering the sphalerite surface capable of adsorbing a xanthate or dithiophosphate collector.

"Alkalinity regulators" such as caustic soda, lime, soda ash, and sulfuric acid are used to control or adjust pH, a very critical factor in many adsorptive bubble separations.

"Depressants" assist in selectivity (sharpness of separation) or stop unwanted minerals from floating. Typical depressants are sodium or calcium cyanide to depress pyrite (FeS_2), while floating galena (PbS), sphalerite (ZnS), or copper sulfides; zinc sulfate to depress ZnS while floating Pbs; sodium ferrocyanide to depress copper sulfides while floating molybdenite (MoS_2); lime to depress pyrite; sodium silicate to depress quartz; quebracho to depress calcite ($CaCO_3$) during fluorite (CaF_2) separation; lignin sulfonates and dextrins to depress graphite and talc during sulfide separation.

"Dispersants or deflocculants" are important for control of slimes, which sometimes interfere with selectivity and increase reagent consumption. Soda ash, sodium silicate, lime, and lignin sulfonates are used for this purpose.

A "defoaming agent" is a formulation of surface-active materials used at low concentrations to prevent the formation of unwanted foam or to destroy foam which has formed.

Any chemicals or substances which can be dosed to increase the efficiency of a flotation cell is termed the "flotation aid."

11. LABORATORY FOAM SEPARATION TESTS

11.1. Sequencing Batch Reactor Foam Separation

A bench-scale foam separation unit, Foamer Tester, has been developed by Krofta Engineering Corporation and Lenox Institute of Water Technology, both in Lenox, MA, USA. It is for use in these types of SBR-foam separation experiments. Figures 7 and 8 show the tester dimensions and piping arrangements, respectively.

To start the SBR foam separation (or dispersed air flotation, or induced air flotation) experiments, sufficient volume of raw water is adjusted to the desired pH with 1.0 *N* sodium hydroxide or 1.0 *N* sulfuric acid, an appropriate amount of surfactant is added to the raw water, and the mixture is poured into the Foamer Tester (Fig. 7). Compressed air is then diffused through the liquid mixture by means of a plastic cloth grid (Fig. 8). Foam is withdrawn from the top and collected in a container. The run is allowed to proceed until no additional foam is formed. A sample of the bulk liquid near the reactor bottom is analyzed for pH, color, turbidity, and other water quality parameters. The foam is collapsed in a beaker and its volume is measured.

From batch foam separation experiments, one may be able to determine the feasibility of the process and the approximate optimum chemical dosages.

11.2. Continuous Foam Separation

Figure 9 shows an experimental set-up for continuous foam separation experiment. Continuous pilot plant operations allow the engineers to determine not only the optimum chemical dosages but also the optimum operational conditions in terms of flows, feed locations, chemical dosages, and so on.

For the continuous foam separation study, sample solution is prepared, mixed well, and placed in the large feed tank. Four liters of initial sample are taken with the desired amount of collector added, the initial color, turbidity, optical density, surfactant concentration, streaming current reading, conductivity, and pH are determined. The collector is also uniformly prepared and placed in a smaller feed tank. The solutions of influent feed

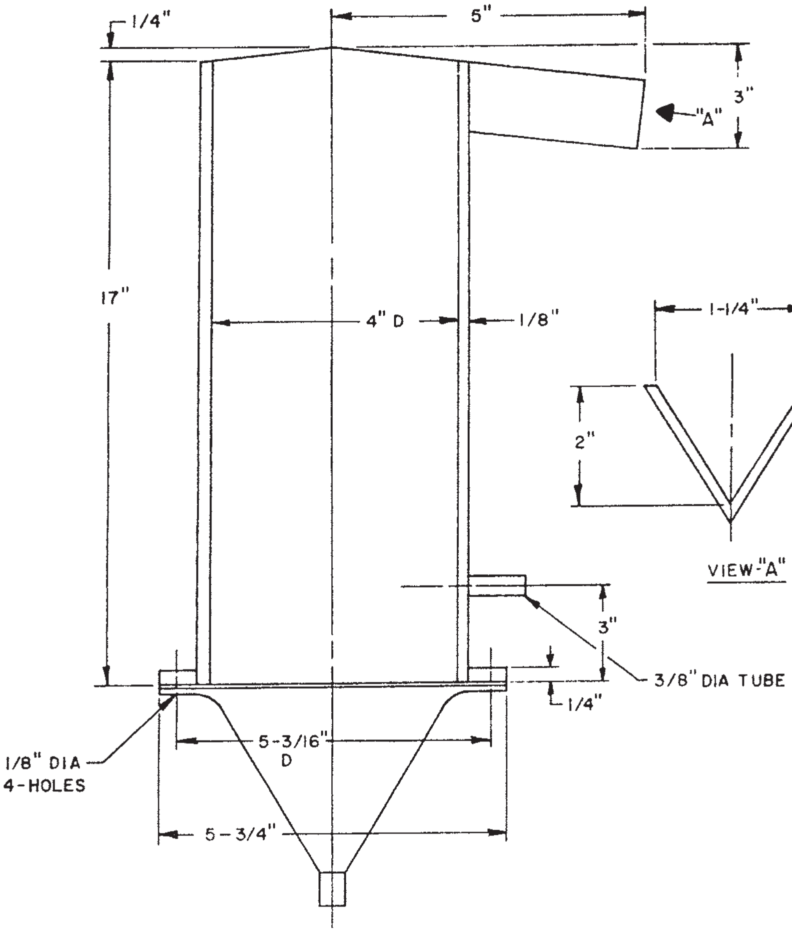


Fig. 7. Dimensions of a bench-scale batch dispersed air flotation unit.

and collector are pumped into the foam separation cell at specified rates for each run. The concentrations in the feed tanks are adjusted to provide the desired concentrations of target solute and of collector. Compressed air is diffused through the solution by means of the coarse gas diffuser. After start-up, the bulk liquid is pumped through the system, and the optical density is continuously recorded. The run is continued until a steady state is reached (i.e., there is no change in the optical density). During the steady state, the bubble velocity and bubble size are measured, Samples of bottom effluent and collapsed foam are taken throughout the entire experiment. Samples are analyzed for color, optical density, residual solute concentration, residual surfactant concentration, turbidity, streaming current reading, conductivity, and pH.

12. ENGINEERING APPLICATIONS

12.1. De-inking Process for Waste Paper Purification and Recycle

Many books on the market are now printed on recycled paper containing almost 80% recycled fibers produced in a de-inking plant equipped with a dispersed flotation clarifier.

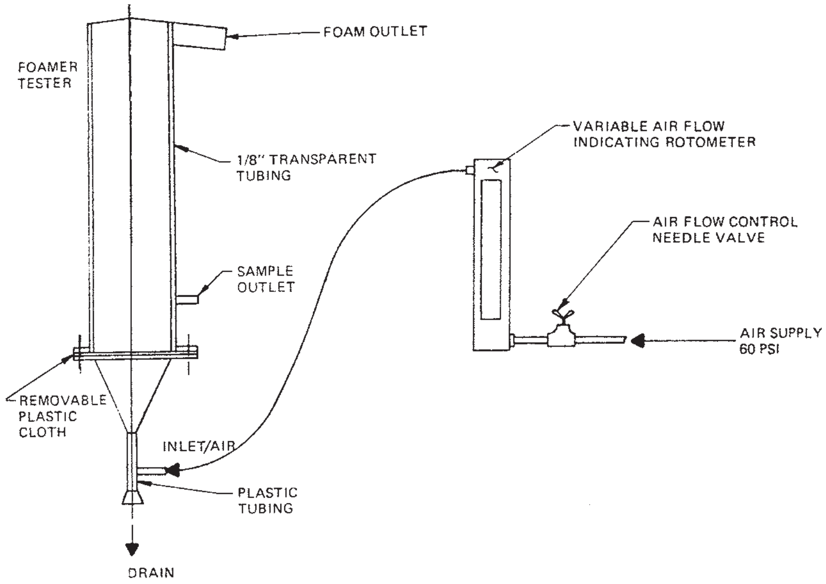


Fig. 8. Piping arrangement of a bench-scale batch dispersed air flotation system.

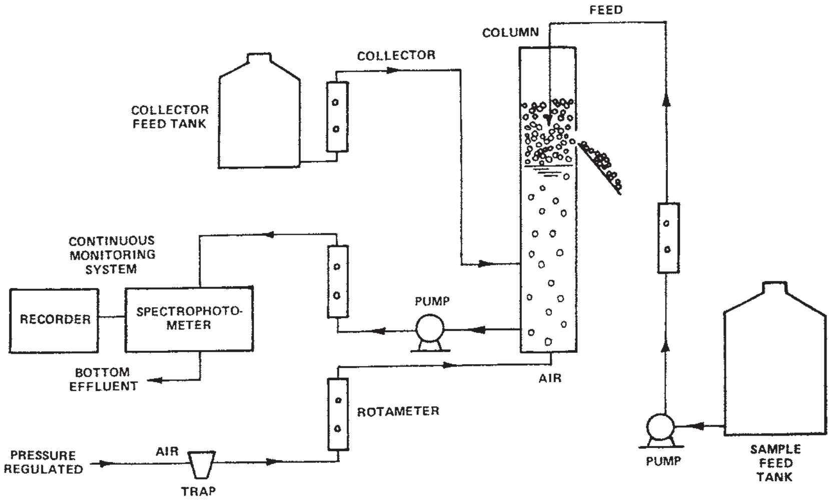


Fig. 9. Apparatus for continuous foam separation experiments.

This section introduces a real case history in the United Kingdom. St Regis Paper Co. Ltd. is owned by David S. Smith (Holdings). In addition to eight paper mills, the holdings company includes Severnside Waste Ltd., which supplies large quantities of waste paper for recycling. The recycling plant's process includes a two-stage de-inking treatment, shown in Fig. 10, that allows a wider range of available waste papers to be converted to high quality printing paper (123).

Water is drawn from a stream passing through the plant. During the production process, the water is recycled and reused, and eventually passes to the effluent control plant. This plant treats the water by screening, settlement, and controlled microbic action. The discharges meet the strict requirements of the regulatory authority, the UK National Rivers Authority.

12.1.1. Pulping Operation

The initial pulping is intended to breakdown and detach the ink from the fibers of the base paper. This process requires the use of some chemicals but the most significant factors are temperature, consistency, and an efficient mechanical action. The conditions achieved disintegrate the waste paper and aid the detachment of the ink from the paper surface. This pulping stage is achieved at relatively low temperature with a low energy output. Considerable attention is given to the liming of the pulping cycle which contributes to the agglomeration of sticky contaminants and aids their removal at a later stage.

To ensure that the ink has been detached and dispersed, a sample sheet of paper is prepared and checked before the stock is diluted and discharged though a coarse dumping screen, to remove large foreign objects, to a holding tank at 5 % concentration. Following further stages of progressively high density screening, the stock is diluted to 1.5 % concentration prior to de-inking.

12.1.2. First-Stage Dispersed Air Flotation for Primary De-inking

De-inking is carried out using a dispersed air flotation cell (i.e., foam separation cell), which provides good de-inking efficiency and high fiber yield with minimal water and energy consumption. Flotation de-inking places a minimal load on the effluent system, with both flow rate and chemical oxygen demand being kept relatively low. The process requires the generation of a foam by the injection of air in the presence of a chemical mix containing caustic soda for pH control, a proprietary soap as a foaming agent, with sodium silicate and hydrogen peroxide to brighten and clean. Chemical usage is low and being progressively reduced as further technical developments allow. No chlorine bleaching is used (123).

Overall de-inking efficiency of the dispersed air flotation is aided by recirculating the liquids by pumping from the top of the cell to the bottom. The foam is removed at the top of the cell by suction heads and sent to a centrifuge where the ink-loaded sludge waste is concentrated to around 50% solids for landfill disposal. The landfill site is managed by the company and is subject to strict environmental control covering the emission of landfill gases and groundwater seepage. Special attention is given to any possible heavy metal contamination. Liquid waste is directed from the centrifuge to the industrial effluent treatment plant for further treatment when necessary.

On leaving the dispersed air flotation cell, the de-inked stock is further diluted before passing through another fine screening process to remove small solids. The materials are then pumped to a drum thickener prior to he dispersion stage.

12.1.3. Second-Stage Dispersed Air Flotation for Dispersion and Secondary De-inking

Dispersion is carried out at the lowest acceptable temperature to minimize energy requirements, and is designed to complement the preliminary dispersion action in the pulper. Thickened stock is progressively dewatered to around 40% concentration in preparation for the kneader disperser stage, which breaks down the ink/fiber bonding of more difficult printed materials (123).

Dewatering ahead of kneading is an essential requirement, but throughout the entire process emphasis is placed on water recovery and re-use.

The intermediate dispersion stage contributes substantially to the reduction in dirt particles in the finished paper and allows the processing of a wider range of waste papers. The kneading action grinds down contaminants and produces an unavoidable "graying" of the stock; however, the "whiteness" is more than regained through the second stage of flotation de-inking which follows.

Although operation of the second dispersed air flotation cell is similar to that of the first, no further chemicals are added, as the inevitable carry-over from the first stage is sufficient.

Following de-inking, the stock is pumped to a second drum thickener from which, at around 6% concentration, it is available to be blended with other constituents, if required, ahead of the papermaking process.

12.1.4. *Advantages*

The dispersed air flotation (or induced air flotation) de-inking process allows the use of a wider range of printed waste paper. The amount of dirt in the finished paper is reduced, thereby improving quality and reducing the amount of reject paper. The brightness of the finished paper is improved without the use of chlorine bleaching.

The energy requirements are low. The demands on effluent and waste disposal are minimal. The plant is safe to operate giving minimum risk to personnel and the environment.

12.2. *Flotation Process for Calcium Carbonate Recovery from Water Treatment Sludges*

12.2.1. *Process Description*

Froth flotation is an important and common process in the present mineral industry for separating various types of minerals or compounds present as discrete particles in an aqueous slurry. The process depends on being able to coat selectively the surface of the particles so as to give them an affinity for air. Then, with the addition of a frothing agent and fine air bubbles introduced into the mixed slurry, the coated particles are collected on the air bubbles and are carried off with the froth. The uncoated wetted particles remain in the slurry. In the field of environmental engineering, froth flotation can be economically and effectively used to produce a relatively high grade calcium carbonate, with a good recovery from the sludges obtained, when using magnesium carbonate with lime for flocculation in water treatment (124).

The calcium carbonate recovered can be calcined to give lime for recycle to the treatment process as well as by-product lime for marketing. In addition, removal of the calcium carbonate, the major ingredient in sludge from water softening treatment plants, reduces the disposal problem to a fraction of that previously required.

In order for the flotation to be effective, the sludge must be recycled to increase the particle size of the calcium carbonate. This recycle also gives heavier flow in the settling basins, which results in faster settling rates. For the flotation to be effective, the magnesium hydroxide in the sludge must also be completely dissolved by the carbon dioxide and washed out. In the froth flotation process (used to separate the calcium carbonate from the clay, silt, or other water contaminants), an aqueous slurry of the sludge is first conditioned (mixed) with soda ash and sodium silicate to disperse the clay and

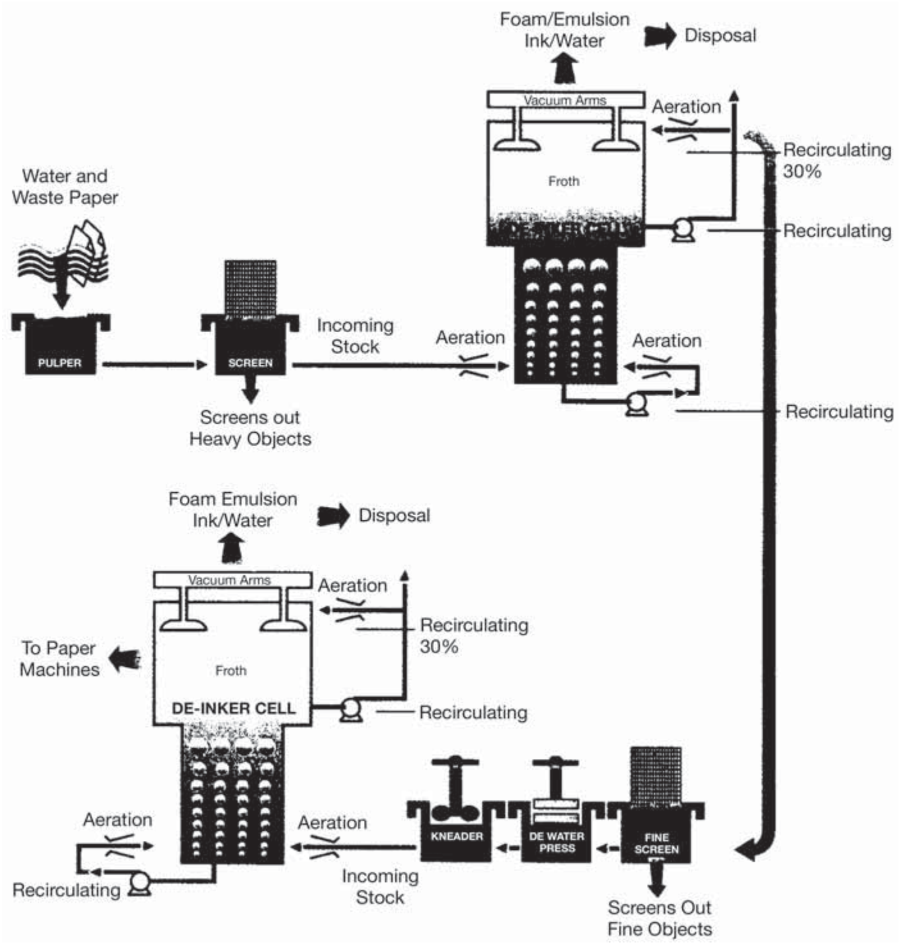


Fig. 10. De-inking flotation process system for waste paper purification and recycle (123).

adjust the pH. Then the slurry is conditioned with a fatty acid soap, which selectively coats the calcium carbonate particles with an insoluble soap making them hydrophobic and collectable. In the flotation machine, which mixes as well as disperses fine air bubbles into the slurry, the coated particles attach to the bubbles so that they can float to the surface and be removed from the machine. The clay and silt, which are still water-wetted, remain in the slurry (124).

12.2.2. Mechanism of Froth Flotation

Many theories have been advanced concerning the mechanisms involved in surfacing the mineral particles so as to create a hydrophobic hydrocarbon film on the mineral surface, and many investigations have been carried out to define these mechanisms. When froth flotation is used in an aqueous medium that carries the solids to be separated (together with dispersed air bubbles and possibly an organic liquid) a three- or possibly a four-phase system must be considered. In most froth flotation processes, the solid particles are initially completely water-wetted, and the solid–liquid interface must be replaced by a solid–gas interface by using suitable reagents. Studies of the changes in thermodynamic properties such as free energy and chemical potentials have done much to advance the understanding of flotation (124).

Whether the adsorption of the reagent at the surface of the solid is by physical adsorption, chemisorption, or chemical reaction, there is a definite correlation between the flotability of most minerals and the solubility of the compound formed by the collector agent and the compound to be floated. Theory postulates the formation of an insoluble metal organic compound at the particle surface. For example, in the use of xanthates for the collection of sulfides, it has been shown that the insoluble metal xanthate formed with lead and copper results in a floatable particle. With the more soluble zinc xanthate, zinc sulfide is not floatable unless it is activated by the addition of copper sulfate. Although the actual reactions may be more complex, the following simplified reactions of an organic compound with a polar–nonpolar configuration such as a xanthate are indicative:

$$2\ \mathrm{RCOSSNa} + \mathrm{PbS} \longrightarrow \mathrm{Pb(RCOSS)_2} + \mathrm{Na_2S} \tag{31}$$

$$\mathrm{ZnS} + \mathrm{CuSO_4} \longrightarrow \mathrm{CuS} + \mathrm{ZnSO_4} \tag{32}$$

$$2\ \mathrm{RCOSSNa} + \mathrm{CuS} \longrightarrow \mathrm{Cu(RCOSS)_2} + \mathrm{Na_2S} \tag{33}$$

The organic portion, R, in the xanthate is generally obtained from alcohols ranging from ethyl to amyl (C_2H_5OH to $C_5H_{11}OH$).

The mechanism for surfacing (collecting) the carbonate and oxide compounds by the use of fatty acid or fatty acid soaps can also be described by the formation of insoluble organic metallic compounds at the surface of the particles. The use of an oleic acid soap ($NaO_2H_{33}C_{18}$) for the flotation of limestone ($CaCO_3$) demonstrates the basic chemistry:

$$2\ \mathrm{NaO_2H_{33}C_{18}} + \mathrm{CaCO_3} \longrightarrow \mathrm{Ca(O_2H_{33}C_{18})_2} + \mathrm{Na_2CO_3} \tag{34}$$

13. ANALYTICAL METHODS AVAILABLE FOR PROCESS MONITORING

Influent concentrations and residual concentrations of cationic surfactants, anionic surfactants, cationic polyelectrolyte, anionic polyelectrolyte, proteins, colloids, oxygen, ozone, detergents, suspended solids, and so on, in the adsorptive bubble separation systems can be determined by the analytical methods reported in the literature (82,127–149).

14. GLOSSARY

Important flotation process terminologies are briefly introduced in this section (1,75,124).

Activators: Activators selectively react with particles to cause the collector to surface. The classic example, as mentioned above, is the use of copper sulfate for the activation of zinc sulfide so that it can be collected by standard sulfide mineral collectors. Another example is the surfacing of lead carbonate, copper carbonate, and copper oxide with the use of sodium sulfide so that collection is also possible by the sulfide collectors.

Air Dissolving Tube or Retention Tank: A metal tank in which the water flow and compressed air are held under high pressure for several minutes to allow time for the air to dissolve into water.

Air to Solid (A/S) Ratio: A/S is the ratio of the pounds (or kilograms) of air available for flotation and the pounds (or kilograms) of suspended solids to be floated. The A/S ratio is independent of flotation surface area.

Clarified Effluent: The liquid being discharged from the flotation unit.

Collectors: Collector reagents are used to provide a water-repellent surface on the particles to be floated in order to obtain adherence to the air bubbles. The collectors are classified according to their cationic or anionic reaction and type of minerals to be floated. The anionic types of collectors react with the metal portion (cation) in the compound to be floated, whereas the cationic types react with anion portions.

Degree of Treatment: The desired or required degree of treatment depends on objectives. It may meet the effluent discharge standards, or the requirements for water reuse, or the quantity/quality of recovered material.

Depressants: Depressants act to prevent the surfacing of the collector on a particle. An example is the use of zinc sulfate in preventing zinc sulfide from floating while allowing lead sulfide to be collected. Sodium silicate not only aids in the dispersion of slimes or colloidal material, but depresses silica and silicates. The cyanide ion aids in selectively assisting in the activation of lead sulfide but depressing pyrite (iron sulfide) and zinc sulfide. Lime concentrations at a relatively high pH 10–12 depress pyrite, allowing the copper or zinc sulfide mineral to float. Organic colloids such as starch, glue, and tannins act as dispersants, and an excess can prevent any collection. In controlled amounts, they are used to depress carbonaceous material, clays, talc, and calcium carbonate.

Design Flow: Feed or influent to be applied to the flotation unit for design purpose. It can be obtained by examining existing or expected flow data.

Float or Floated Sludge: The concentrated material scooped or skimmed from the top of the flotation unit. The concentration is measured in percent solids, or mg/L.

Flocculating Agent or Flocculant or Coagulant: Any chemical that can convert soluble or colloidal substances to insoluble flocs.

Flotation Aid: Any chemical that produces coagulation, breaks an emulsion, and/or aids in the adsorption of air bubbles by the liquid or particles to be removed.

Flotation Chamber or Flotation Tank: A tank where the water enters and the air comes out of solution in minute bubbles throughout the entire volume of liquid for flotation of impurities.

Froths: A frothing agent is used to form a stable yet brittle froth at the surface of the flotation machine so that the froth can be removed from the slurry along with the attached particles, thus accomplishing a separation of the hydrophobic and wetted particles. The froth generated should be able to support the particles, but should also readily break down when removed from the flotation machine so as not to interfere with subsequent processing. Frothing agents function by reducing the surface tension of the water. Compounds used are generally heteropolar. They contain an organic nonpolar radical that repels water and a polar portion that attracts water. Used in limited quantities, the heteropolar molecules are aligned at the gas–liquid interface with the polar end toward the water and the nonpolar end toward the air. This monomolecular film tends to retain the size of the bubble formed by the flotation machine and prevents the bubbles from breaking as they burst through the top of the water layer. A wide variety of organic compounds could function to a greater or lesser degree as frothing compounds, but the number that are low in cost, readily available, effective in low concentrations, and essentially free of collector properties is limited. Initially, most frothers contained a hydroxyl (OH) polar group and had limited water solubility. Compounds included in this group are amyl alcohol ($C_5H_{11}OH$), cresol ($CH_3C_6H_4OH$) in cresylic acid, and terpineol ($C_{10}H_{17}OH$) in fine oil.

Hydraulic Loading: The hydraulic loading rate of the flotation unit is expressed in GPM/ft^2 of flotation area. The influent loading rate is the influent flow divided by the surface area. The total hydraulic loading rate is the influent flow plus the recycle flow divided by the surface area.

Influent or Feed: The wastewater, process water, or sludge being delivered to the flotation unit. The concentration of impurities is generally measured in mg/L, and flow in GPM or MGD, or m^3/d.

Influent Characteristics: The nature and solids concentration of the influent stream and information relating to its source. They are necessary to determine what design parameters should be used.

Modifiers: Modifying agents may act as selective depressants, selective activators, pH regulators, or they may reduce the harmful effects of colloidal material or soluble salts. Often one compound may perform several functions. Depending on the particle separation desired and the character of the slurry, the pH required may be from 1.0 to 12.5 or higher. Lime, soda ash, caustic, or acids are used for pH adjustment. The pH adjustment may act as an activator to aid in collector surfacing or as a selective depressant by preventing collector surfacing. As an example, soda ash (Na_2CO_3) may be an activator for some sulfides, a depressant if present in excess in calcite flotation, or a pH regulator.

Operating Cycle: The operational time of the flotation unit in hours/day. In most cases for industrial waste the operating cycle is determined by the production schedule.

Recycle Percentage: This applies to a flotation unit operating with effluent recycle. The recycle percentage is the percentage of the influent flow that is recycled.

Solids Loading: Loading of the flotation unit in pounds (dry solids) per ft^2 of effective flotation surface area per hour of operation (lb/ft^2/h), or in kilograms per m^2 of effective flotation surface area per hour of operation (kg/m^2/h).

NOMENCLATURE

a_1, a_2, a_3, a_4	constants
A_e	the equilibrium contact angle, degree
A_s	cross-sectional area of bubble separation reactor, cm^2
a_i	the activity of the *i*th component
b_1, b_2, b_3, b_4	constants
d	the effective average bubble diameter, cm
dr/dL	the rate of variation of the surface tension of the solution with bulk concentration
E	the solute surface excess (g-mole/cm^2) in equilibrium with L
E_b	the surface excess value (g-mole/cm^2) in equilibrium with drain concentration L_b

E_i	the surface excess value (g-mole/cm^2) in equilibrium with the influent feed concentration L_i
E_x	the surface excess of the solute, g-mole/cm^2, or mg/cm^2
E_{xi}	the surface excess, which is essentially the concentration the component i at the interface, g-mole/cm^2
f'	the surface to volume ratio of gas bubbles (cm^{-1}); for the simple mode = $6/d$; for stripping mode = $6.59/d$
K	an equilibrium constant for surface adsorption, cm
K'	an equilibrium constant for surface adsorption, g-mole/cm^2
L	the bulk surface active solute concentration, g-mole/cm^3, or mg/cm^3
L_b	the surface active solute or solid concentration in the drain, g-mole/cm^3, or mg/cm^3
L_i	the surface active solute or solid concentration in the feed, g-mole/cm^3, or mg/cm^3
L_n	the surface active solute or solid concentration in the net overhead, g-mole/cm^3, or mg/cm^3
L_t	the surface active solute or solid concentration in the collapsed foam phase, g-mole/cm^3, or mg/cm^3
N_i	the number of bubbles of radius r_i
NTU	the number of transfer units in the foam based on the upflow stream
Q	the volumetric rate of liquid upflow in a foam separation reactor, cm^3/s.
Q_a	the volumetric rate of air, cm^3/s
Q_b	the volumetric liquid flow rate of bottom drain, cm^3/s
Q_i	the volumetric liquid flow rate of influent feed, cm^3/s
Q_n	the volumetric liquid flow rate of net overhead, cm^3/s
Q_t	the volumetric liquid flow rate of top overhead, cm^3/s
r	the surface tension of the solution, dyne/cm
r_e	the effective average bubble radius, cm = the bubble radius averaged by the ratio of the third moment (volume) to the second moment (surface area)
r_i	the radius of the ith bubble, cm
R_f	external reflux factor
r_{LG}	the average surface tensions (i.e., interfacial tensions) of the liquid–gas interface, dyne/cm
r_{SG}	the average surface tensions (i.e., interfacial tensions) of the solid–gas interface, dyne/cm
r_{SL}	the average surface tensions (i.e., interfacial tensions) of the solid–liquid interface, dyne/cm
R	the universal gas constant, dyne-cm/(g-mole K)
S_b	the residual collector concentration in the drain, mg/cm^3
S_i	the collector concentration in the feed, mg/cm^3
S_t	the collector concentration in the foam phase, mg/cm^3
T	the absolute temperature, K
T_c	temperature in °C
U_B	buoyancy component, cm/s
U_R	relative bubble velocity, cm/s

V_b	the residual liquid volume in the separation column, cm^3
V_i	the initial volume, cm^3
V_t	the collapsed foam (as liquid) volume from the batch process, cm^3
y	effective concentration of solute in the upflow within a foam separation reactor on a gas-free basis of liquid, g-mole/cm^3
y^*	the effective concentration of solute, in equilibrium with L_t, in the upflow within a foam separation reactor on a gas-free basis, g-mole/cm^3

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4

Powdered Activated Carbon Adsorption

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CONTENTS

1. INTRODUCTION

Historically, the use of activated carbon has been limited to treatment applications for drinking water. In the past two decades, more attention has been given to the potential use of activated carbons for wastewater treatment. The interest in such a process has stemmed from the growing concern over the quality of rain water from which we get our potable water. Concern exists for the protection of both surface and groundwater supplies throughout the nation. In 1974, the United States Environmental Protection Agency (US EPA) identified a total of 154 organic compounds in drinking waters (1). The identification of these organic pollutants, along with an unknown number of inorganic pollutants in receiving waters, has placed an emphasis on effluent water quality. In the past decade, effluent water qualities from all sources have been placed under increasingly stringent effluent quality guidelines by the US EPA. Specific reference must be made to the Safe Drinking Water Act of 1974 (2).

Finding an appropriate yet cost effective treatment solution for reducing organic contaminants in receiving waters represents an interesting challenge in treatment technology. As stated previously, the use of activated carbons for additional treatment has continued

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to rise since its introduction into the treatment scheme. Adsorption of a wide range of pollutants using granular activated carbons (GAC) has been found to be successful; however, the use of GAC technology is often accompanied by increased capital and operating costs. An available alternative to GAC adsorption exists without sacrificing any of the latest technology at a much reduced price tag; that is, the addition of powdered activated carbon (PAC) to existing treatment schemes. This chapter focuses on the use of PAC for treatment of both water and wastewater.

Before undertaking further discussion, it is imperative to first address the physical characteristics and the method by which activated carbon removes pollutants. All activated carbons act on a principle called adsorption, which is an adherence of a substance to the surface of the activated carbon. The attraction of a substance in a solution (adsorbate) to an activated carbon particle (adsorbent) occurs in three distinct steps:

1. The adsorbed molecule must be transferred from the bulk phase of the solution to the surface of the adsorbent particle. In so doing, it must pass through a film of solvent that surrounds the adsorbent particle. This is called film diffusion.
2. The adsorbate molecule must be transferred to an adsorption site on the inside of the pore. This process is referred to as pore diffusion.
3. The adsorbate must become attached to the surface of the adsorbent. This is the actual adsorption step.

Adsorption may be characterized as either physical or chemical. Physical adsorption consists mainly of van der Walls forces and is reversible. This occurs when the molecular forces of attraction between the adsorbent and the solute are greater than the forces of attraction between the solvent and the solute. Chemical adsorption, as the name implies, involves a chemical reaction between the adsorbent and the adsorbate. Physical adsorption is generally a much stronger type of adsorption and is often times irreversible.

Recently developed applications of activated carbon to wastewater treatment involve the addition of PAC to conventional activated sludge aeration tanks. The combination of PAC with biological process is often times referred to as the PACT or PAC-activated sludge process (3). The PACT process has attracted a great deal of interest because it is a method by which the performance of a waste treatment facility may be improved in various areas. Technical advantages that can potentially be achieved by adding PAC to biological reactors include:

1. Provides system stability against shock loading, temperature changes, etc.
2. Improves removal of nonbiodegradable organics.
3. Removes color.
4. Improves the removal of compounds on the EPA priority pollutant list.
5. Resists biologically toxic substances in the wastewater.
6. Improves the hydraulic capacity of existing plants.
7. Improves nitrification.
8. Suppresses foaming in aerators.
9. Improves settling, thickening, dewatering of sludge.
10. Reduces sludge bulking.

The PAC-activated sludge process is shown in Fig. 1. The activated sludge process is used extensively to degrade municipal as well as industrial wastes. Because activated

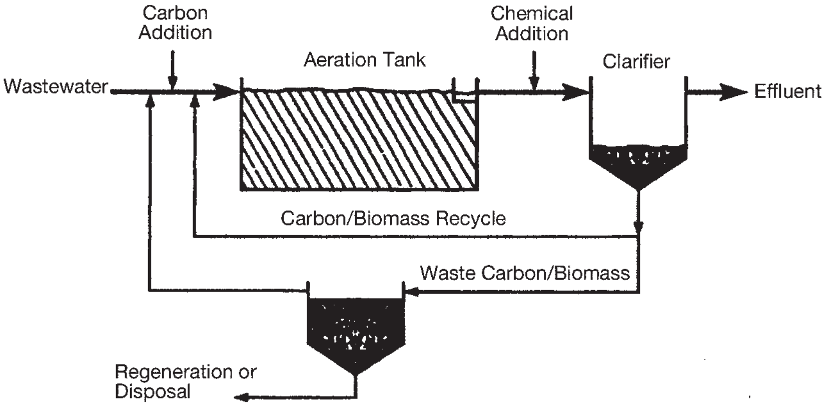

Fig. 1. Powdered activated carbon sludge process.

sludge is a biologically oriented process, it would seem to reason that optimization of the biological controllable bears great importance. It is generally assumed that bacteria favor attached or supported growth over suspended growth. The mechanism of PAC enhancement of the activated sludge process is not totally defined, and the possibility of biological activity and carbon adsorption acting independently within the same reactor is highly improbable. It has been speculated that a synergistic effect exists through PAC stimulation of biological activity, sometimes referred to as biological activated carbon (BAC).

An example of this would be the bioregeneration of activated carbon, which occurs when microorganisms degrade adsorbed particles, creating "new" adsorption sites (4).

2. PROPERTIES OF ACTIVATED CARBON

Activated carbons are produced from materials including wood, coconut shell, peat, lignin, bituminous coal, lignite, and petroleum residues. Granular carbon, produced from medium volatile bituminous coal or lignite, has been commonly applied to wastewater treatment, since it is relatively inexpensive and readily available. The activation of carbon is essentially a two-phase process that includes burning off the amorphous decomposition products and enlarging the pores in the carbonized material. The carbonization phase involves drying the carbon at approx 170°C, heating the material to 270–280°C with the evolution of carbon monoxide, carbon dioxide, and acetic acid, and, finally, completing the carbonization process at a temperature of 400–600°C. Carbonization results in a yield of about 80%. The intermediate product is then activated by using carbon dioxide or steam at a temperature of 750–950°C to burn off decomposition products, to expose and widen the pores in the development of macroporous structure. The selected parameters for describing activated carbons are given in Table 1 (5).

The effectiveness of activated carbon for the removal of organic pollutants from water by carbon adsorption is enhanced by its large surface area, an important factor in the adsorption process. The surface area of activated carbon typically can range from 500 to 1400 m^2/g. Table 2 presents the surface areas of several commercially available activated carbons (6). Some have large surface areas as high as 2500 m^2/g.

Table 1
Selected Properties of Activated Carbon

Property	Importance
Particle size	Rate of adsorption increases as particle size decreases. Head loss through packed column increases as particle size decreases.
Surface area	A measure of the area available for adsorption. The larger the surface area, the greater the adsorptive capacity. Measured by determining the amount of nitrogen adsorbed by the carbon and reported as m^2/g.
Pore volume	Measure of total macropore and micropore volume within the carbon particles. Measured in cm^3/g.
Iodine number	Refers to milligrams of iodine adsorbed during standard test. Measures the volume present in pores from 10 to 28 Å in diameter. Carbons with a high percentage of pore sizes in this range would be suitable for adsorbing low-molecular-weight substances.
Molasses number	Refers to milligrams of molasses adsorbed during standard test and measures the volume in pores greater than 28 Å in diameter. Carbons with a high percentage of these size pores would be suitable for adsorbing high-molecular-weight substances.
Abrasion number	Measures ability of carbon to withstand handling and slurry transfer. This property is of limited value because measuring techniques are not reproducible.
Bulk density	Useful in determining the volume occupied by a given weight of carbon.

After US EPA, 1973.

Table 2
Surface Areas of Some Commercially Available Activated Carbons

Commercial name	Origin	Surface area (m^2/g)
PCC SGL	Bituminous coal	1000–1200
PCC BPL	Bituminous coal	1000–1200
PCC RB	Bituminous coal	1200–1400
PCC GW	Bituminous coal	800–1000
Columbia CXA/SXA	Coconut shell	1100–1300
Columbia AC	Coconut shell	1200–1400
Columbia G	Coconut shell	1100–1150
Darco S 51	Lignite	500–550
Darco G 60	Lignite	750–800
Darco KB	Wood	950–1000
Hydro Darco	Lignite	550–600
Nuchar Aqua	Pulp mill residue	550–650
Nuchar C	Pulp mill residue	1050–1100
Nuchar (various)	Pulp mill residue	500–1400
Norit (various)	Wood	700–1400

Of less significance than the surface area with respect to the adsorption process is the chemical nature of the carbon's surface. This chemical nature or polarity varies with the carbon type and influences attractive forces between molecules. Alkaline surfaces are

Table 3
Properties of Several DARCO Powdered Carbons

		DARCO Powdered Carbons		
Property		S-51	G-60	KB
Bulk Density, 1b/ft^3, 30 min temp test		32	25	28
Storage space, ft^3/ton		80	100	75
Particle size				
Through 100 mesh		98	95	99
Through 325 mesh		70	70	70
Moisture		8%	8%	25%
Decolorizing efficiency[*]		100	125	190
pH of water extract		5	5	5
Water-soluble ash (four boiling leaches)		1%	0.2%	1.3%
Rate of filtration[**]		25	45	20
Total surface area, m^2/g, dry basis (d.b.)		650	600	1450
Total pore volume, mg/g, dry basis		1	1	1.5
Pore volume distribution	<20 Å	0.25	0.1	0.3
Volume in pores of given radii	20–50	0.15	0.1	0.4
mL/g dry basis	50–100	0.1	0.3	0.2
	100–500	0.2	0.35	0.45
	>500	0.3	0.15	0.15
Mean Pore Radius, Å (1×10^{-8} cm)		30	25	23

[*] Based on decolorization of standard blackscrap molasses relative to a reference with decoloring efficiency of 100.

[**] Gallons of water per h/ft^2 filter area/in. of carbon filter cake (40 psig).

characteristic of carbons of vegetable origins; this type of surface polarity affects adsorption of dyes, colors, and unsaturated organic compounds. Activated carbon surfaces are mostly nonpolar, making the adsorption of inorganic electrolytes difficult but the adsorption of organics easy.

Activated carbon may be found in two forms: powdered and granular carbon. PACs are particles that are less than US Sieve Series No. 50 (0.3 mm), while the GACs are larger (5). Table 3 lists the typical properties of some Darco powdered activated carbons (7).

Carbon particle size influences the adsorption rate, but not the adsorptive capacity, which is related to the total surface area. Reducing the particle size does not affect the surface area of a given weight. Particle size affects mainly the system's hydraulics, filterability, and handling characteristics.

Total surface area of activated carbon can be measured by the Brunauer–Emmett–Teller (BET) method, which measures the activated carbon's adsorption and desorption of nitrogen under varying pressures (8,9). However, it is recommended that the adsorption capacity of a particular carbon be determined experimentally with the water or wastewater of concern.

3. ADSORPTION ISOTHERM MODELS

Numerous mathematical models attempt to characterize the adsorption process. The three most widely accepted isotherm models are the Freundlich, the Langmuir, and the

BET models. The Freundlich isotherm is an empirical relationship, while the Langmuir and BET isotherms are based on theoretical developments. The Langmuir isotherm is based on the concept of monolayer adsorption, while the BET isotherm assumes multilayer adsorption.

The BET model (8) assumes that layers of molecules are adsorbed on top of previously adsorbed molecules. Each layer adsorbs according to the Langmuir adsorption model. The four basic assumptions for the BET multilayer adsorption model are (a) adsorbed molecules do not migrate on the surface; (b) the enthalpy of adsorption is constant for all molecules in a given layer; (c) all molecules in layers beyond the first have equal energies of adsorption; and (d) layers need not be completed for adsorption before the next one starts. The BET equation has the following formula for adsorption from a liquid solution:

$$\frac{x}{m}=\frac{b\,K\,C}{\left(C_s-C\right)\left[1+\left(K-1\right)\left(C/C_s\right)\right]} \tag{1}$$

where b = value of x/m when monolayer has been completed (mg/mg); C_s = concentration of adsorbate at saturation of all layers; and K = constant related to energy of interaction between adsorbent and adsorbate. The BET equation can be linearized as follows:

$$\frac{C}{\left(C_s-C\right)\left(\frac{x}{m}\right)}=\frac{\left(K-1\right)}{K\,b}\left(\frac{C}{C_s}\right)+\frac{1}{K\,b} \tag{2}$$

If the

$$\frac{C}{\left(C_s-C\right)\left(\frac{x}{m}\right)}$$

term is plotted against the C/C_s term, the result is a straight line with a slope of $(K-1)/Kb$ and an intercept of $1/Kb$ as shown in Fig. 2.

A plot of x/m vs C results in a curve of the form shown in Fig. 3. Theoretically, when C approaches the saturation value C_s, the moles of adsorbate adsorbed become very large because the BET model does not constrain the number of layers adsorbed. In practice, because the saturation concentration of C_s can only be estimated, an iterative process should be used in solving BET equation.

The Langmuir isotherm (10) assumes adsorption is reversible and occurs only for the monolayer on the adsorbent surface. The equation is shown below:

$$\frac{x}{m}=\frac{a\,b\,C}{1+a\,C} \tag{3}$$

where x = mass of adsorbate (mg), m = mass of dry adsorbent (mg), C = equilibrium concentration of adsorbate (mg/L), a = constant [L/(mg/L)], and b = maximum capacity, assumed to be monolayer coverage of adsorbent surface, or value of x/m when monolayer has been completed (mg/mg).

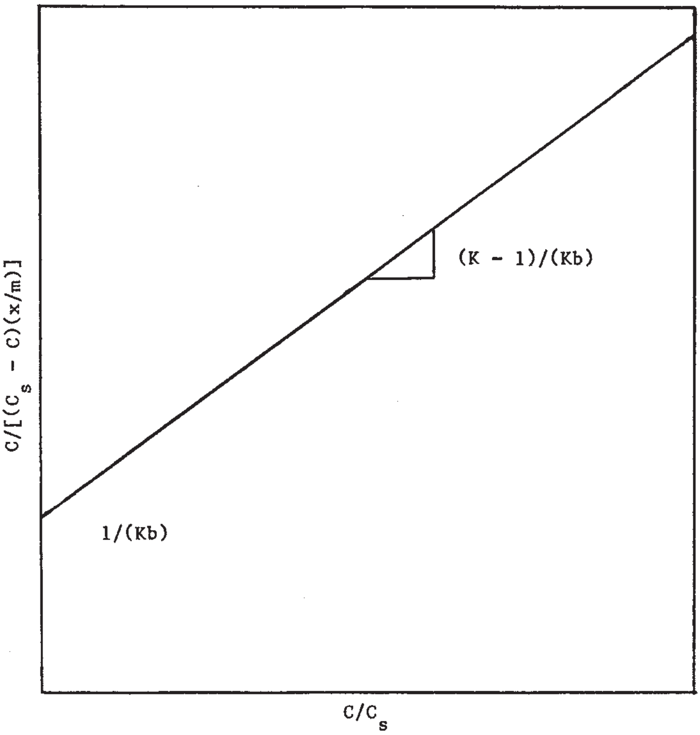

Fig. 2. Linear form of BET adsorption isotherm.

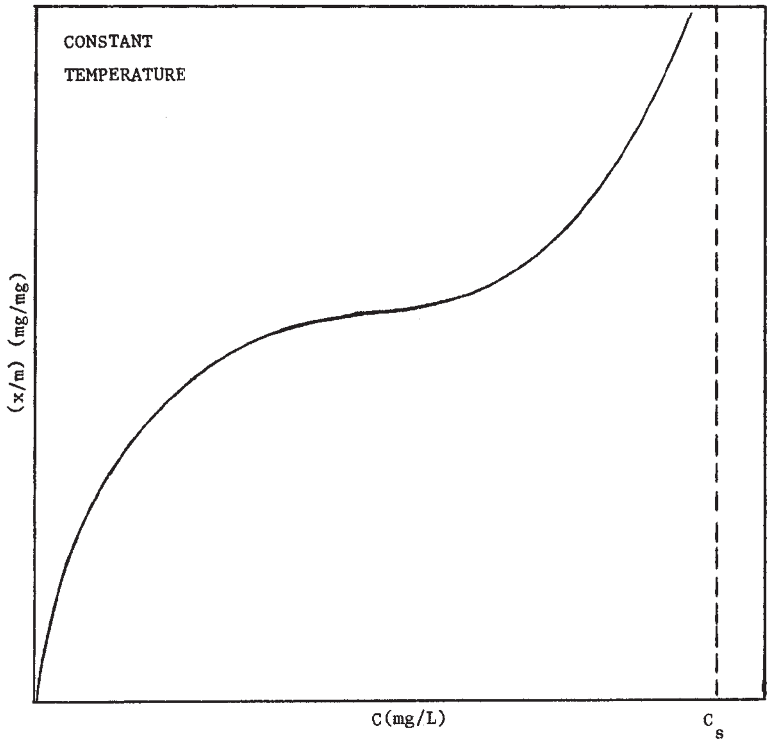

Fig. 3. Form of the BET adsorption isotherm.

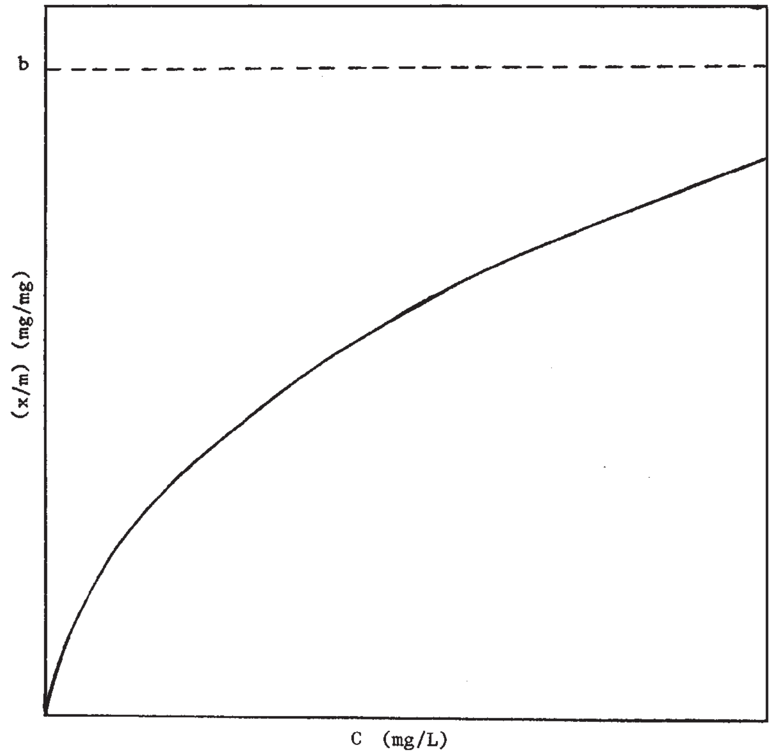

Fig. 4. Langmuir adsorption isotherm.

Figure 4 shows the form of Langmuir adsorption isotherm. The equation can be rearranged to yield a linearized form of $y = mx + b$:

$$\frac{1}{\frac{x}{m}} = \frac{1}{a\,b}\frac{1}{C} + \frac{1}{b} \tag{4}$$

When the reciprocal of the adsorption capacity $1/(x/m)$ is plotted against the reciprocal of the concentration $1/C$, the result is a straight line with a slope of $1/ab$ and an intercept of $1/b$ as shown in Fig. 5.

The second linear form in Fig. 5 gives extra weight to higher values of C and is useful because quite often these are far more reliable due to poor analytical sensitivity at low adsorbate concentrations.

Approximation of the linear form is not necessary for the Langmuir isotherm, and the first plot of the adsorption data will determine whether or not the model is applicable, and also will allow calculation of the adsorption coefficients. Usually a single model will not be satisfactory for a wide range of adsorbate concentrations but will only serve in narrow range of concentration. At low concentrations, $C/C_s << 1$, the BET model reduces to a Langmuir model.

The Freundlich equation written below is an empirical equation for the adsorption isotherm (11):

$$\frac{x}{m} = KC^{1/n} \tag{5}$$

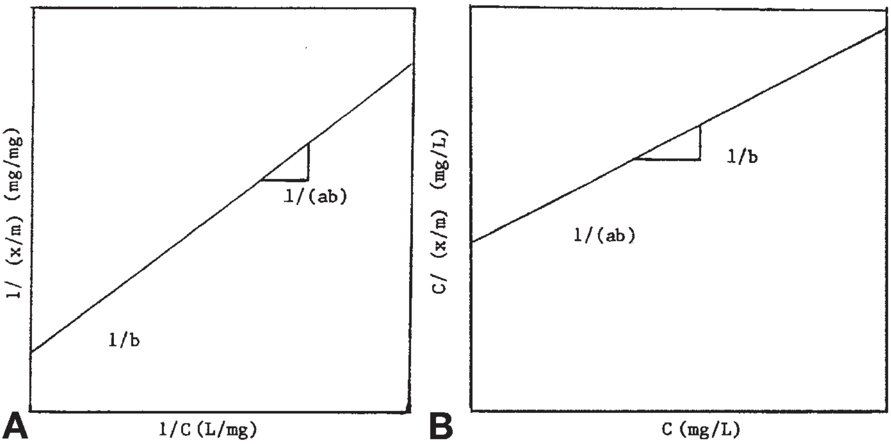

Fig. 5. (A) Conventional linear form of Langmuir isotherm. **(B)** Modified linear form of Langmuir isotherm for high concentration data.

where x/m = mass solute adsorbed/mass adsorbent (mg/mg), K = constant, C = concentration of solute in solution, mass/volume (mg/L), and n = constant, $n > 1$. By taking the logarithm of both sides of Eq. (5), the following linearized equation is obtained:

$$\log\frac{x}{m} = \frac{1}{n}\log C + \log K \tag{6}$$

As shown in Figure 6, when the log of the adsorption capacity (x/m) is plotted against the log of the concentration (C), a straight line often results with a slope of $1/n$ and an intercept of log K.

The Freundlich equation can be derived from the Langmuir equation by assuming that the adsorbent surface has a distribution of adsorption potentials. The Freundlich equation yields an erroneous result because the amount adsorbed predicted approaches a nonzero value as the concentration approaches zero. These two equations are very useful empirical equations. The constants derived from the linearized plots are useful parameters for comparing different systems but have no readily identifiable physical significance for adsorption from solution. The choice of equation used for plotting depends on which one gives the best-fit straight line. The Freundlich equation has been used more often than the Langmuir equation.

4. DESIGN CONSIDERATION OF PAC SYSTEMS

4.1. Design Considerations

Effluent quality is the first major consideration to be reviewed prior to implementation of activated carbon enhancement. If effluent quality standards are being met at the present time, there is no reason to use carbon addition. If the effluent quality standards are not being met, then it may be wise to investigate some form of activated carbon treatment.

The choice between PAC and GAC for an application depends on the following factors:

- Type of existing equipment.
- Projected carbon usage rate.
- Variability of flow rate, impurity concentration and composition.

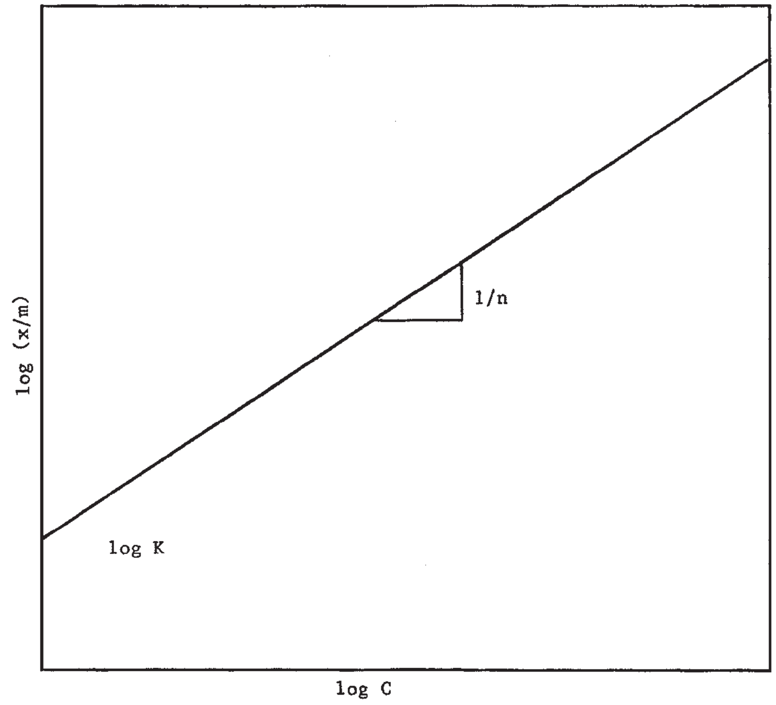

Fig. 6. Determinations of constants for Freundlich isotherm.

- Nature of the application.
- Cleanliness.
- Disposal.

The type of existing equipment may be easily adaptable to carbon addition. If it is not, considerable capital expenditure may be necessary. Carbon usage rate is an important factor for potentially determining the feasibility of regeneration or direct disposal. High variability in flow concentrations would lend itself to the use of GAC while more consistent flow concentrations would indicate the use of PAC. The type of removal desired (i.e., specific adsorption) would determine dosage rates. Cleanliness and disposal are two variables that do not need much explanation.

The required design considerations for PAC-activated sludge wastewater treatment systems are:

- Daily flow.
- Concentration of specific impurities (COD, BOD, color, and so on).
- Desired or regulated effluent quality.
- Required carbon dosage.
- Optimum contact time.

For steady-state operations, the required dosage and aerator carbon concentration can be related by the following equation:

$$\mathrm{PAC}_\mathrm{I} = \frac{\theta\ \mathrm{PAC}_\mathrm{R}}{\theta_\mathrm{C}} \tag{7}$$

where PAC_I = influent PAC concentration, mg/L; PAC_R = mixed-liquor PAC concentration in the reactor, mg/L; θ = HRT = hydraulic retention time, day; θ_C = SRT = design solids retention time, day.

Tests must be performed throughout implementation in order to optimize performance of the system. For example, indications are that PAC-activated sludge operates more efficiently on longer residence times and the same solids retention time. Temperature also has a major effect on reactor performance.

The major design parameters for a PAC system are described in this section. For a PAC mixing tank followed by a filter, the design parameters should include the influent flow rate, the contact time, the filtration rate, and the filtration time in the filter. For a PAC mixing tank followed by a settling tank, the design parameters should include the influent flow rate, the contact time, the overflow rate of settling tank, and a desirable effluent solids concentration. The design parameters of contact time, carbon usage, and the number of adsorption stages for PAC system are to be determined by laboratory analysis of adsorption isotherm.

4.2. Laboratory Procedures for Batch Adsorption Study (12)

Batch adsorption may be achieved using the following laboratory procedure:

1. Select one or several carbons for use in the study.
2. Grind 20 g of the carbon until all of the carbon passes a 325-mesh screen.
3. Set up at least five flasks and add a selected carbon dosage to each flask.
4. Analyze the wastewater to be treated for the initial concentration of the contaminant to be removed. Add a given amount (100–500 mL) of wastewater to each flask and place the flasks on a gyratory shaker table.
5. Shake the flasks for a period of 1–2 h.
6. After shaking, filter the samples to remove the carbon and analyze the filtrate for the contaminant remaining in solution. The amount of contaminant adsorbed by the carbon can then be determined.
7. If carbon dosages do not provide the desired range of results, repeat the test with different dosages.

It should be noted that the water temperature should be held constant during the test at the value for the wastewater to be treated. The pH of the sample should be held close to the actual wastewater. If the addition of carbon affects the pH of the samples by preferentially adsorbing acids or bases or supplying inorganics to solution (12), it will necessary to adjust the treated samples to the original pH before analyzing for residual contaminants.

Data collected during the batch adsorption study will be used in the determination of coefficients for the adsorption isotherms. The procedures are shown in the design examples in the following section.

5. REGENERATION

PAC is widely used in industry to remove undesired organic constituents, and has been used by many water purification plants. The residue is a wet, organic-loaded, carbon waste. In the past, these wastes were disposed into streams, incinerated, or buried. Recently, new developments seem to have overcome the problem of large quantity of carbon dust. Several systems show promise in reusing the powdered carbon and will be briefly discussed.

The Zimpro wet air oxidation process (13) can effectively restore the adsorptive properties of PAC without dewatering of the spent carbon slurry. Estimated carbon loss is about 5% per regeneration cycle. Zimpro, Inc. has used the wet air oxidation process to regenerate PAC used in wastewater treatment. A pilot plant was set up in Rothschild, WI, USA. The carbon was used through 23 cycles, and the average loss of the activated carbon per cycle was 4.7%.

The fluidized-bed-furnace (FBF) process is a regeneration system developed by the Battelle Institute (13). The results from several months of pilot plant operation were: (a) PAC can be successfully regenerated in a fluidized bed furnace at a temperature of 1250°F; (b) after six regenerations, the regenerated carbon is as effective as virgin carbon in removing organic matter from raw sewage; (c) average carbon losses per regeneration cycle were 9.7%; and (d) stack gases from the regeneration furnaces present no significant air pollution problems.

Westvaco Corp. (14) patented a method for powdered carbon regeneration called reactor process. Major steps in the process are drying, volatilization of organics, burning of volatiles, and steam activation of residual carbon. These steps occur almost simultaneously in the reactor. The overall reactor temperature for these steps is 1750–1850°F, depending on spent carbon loading. Suspended particles at 1800°F exit the reactor to a evaporative cooler in which the gas stream is cooled to 450°F with a water spray. Regenerated carbon is then collected in glass cloth bag filter. Carbon losses of 5–25% have been reported.

6. FACTORS AFFECTING PERFORMANCE

6.1. Variables for the Combined Activated Carbon–Activated Sludge Process

6.1.1. Carbon Type and Dosage

Carbon type and dosage are crucial variables that affect the performance of the PAC-activated sludge process. Both variables are significant in predicting effluent dissolved organic carbon (DOC) as shown in Fig. 7 (15). While the shape of these curves is generally similar for different wastes and carbon types, the coordinates vary with each wastewater and should be determined in the laboratory.

6.1.2. Solids Retention Time and Aeration Time

Lawrence and McCarty (16) have derived expressions for use of the solids retention time (SRT) concept. In fact, many designers now use SRT as a design parameter for submerged culture biological processes. The use of food/microorganism ratio, F/M, is not recommended for evaluation of combined activated carbon–biological processes because of the difficulty in assigning values to the microorganisms in terms of MLSS or MLVSS.

In general, aeration time is handled in the solids retention time studies as suggested by Lawrence and McCarty. There are some indications that a combined activated carbon–biological process performs better on some wastewaters at a longer residence time.

6.1.3. Temperature

Perhaps the most important variable in the design of biological system is temperature, particularly in cold climates. Results of low-temperature studies on treatment of chemical plant wastewater are listed in Table 4 (3). It is noted, for example, that at 10°C, an activated sludge process with carbon added can operate better at 2.6 h of aeration time

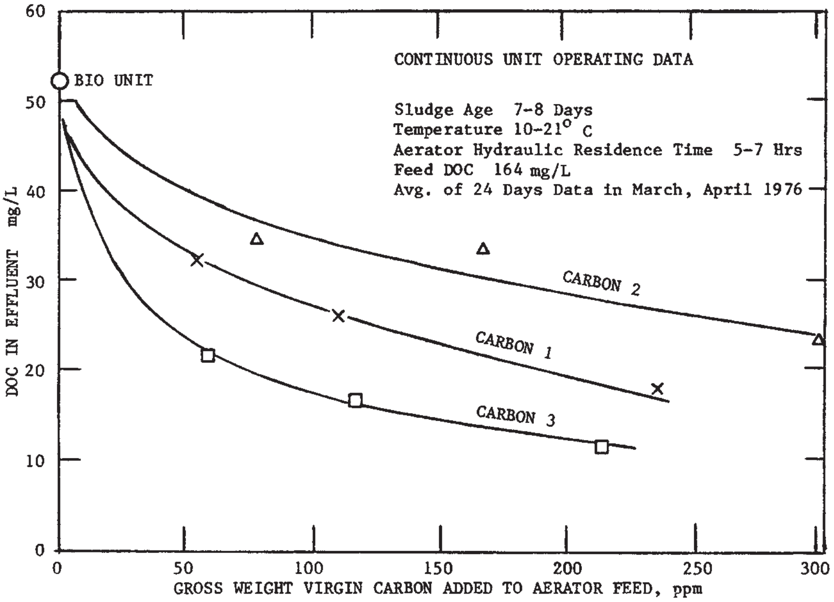

Fig. 7. Effects of carbon dose on effluent quality.

Table 4
Low-Temperature Studies on Treatment of Chemical Plant Wastewater

	Carbon–biological process	Activated sludge process
Aerator temperature, °C	10	10
Average mold time, hr	2.6	6.7
Average carbon dosage, mg/L	103	0
Average feed BOD, mg/L	52.1	55.3
Average BOD loading, g/d/g	0.12	0.67
Average effluent BOD, mg/L	17.9	21.3
Average BOD removal, %	66.4	63.1
Average feed TOC, mg/L	74.0	69.1
Average TOC loading, g/d/g	0.199	0.454
Average effluent TOC, mg/L	41.7	43.6
Average TOC removal, %	43.8	42.2
Average sludge volume index, cm^3/g	15.9	130.2

than an activated sludge process without carbon at 6.7 h of aeration time. The best example of the low-temperature advantage of carbon addition is the reported application of the combined activated carbon–biological system to treatment plants along the Alaskan Pipeline.

6.2. *Factors Affecting Adsorption*

6.2.1. *Molecular Structure*

The molecular structure of an adsorbate is important in determining the degree of adsorption that actually occurs. In general, branched-chain compounds are more sorbable than straight-chain compounds, and molecules that are low in polarity and solubility tend to be preferentially adsorbed. If the screening action of the carbon pore is effective, large molecules are more sorbab1e than small molecules of similar chemical nature.

Inorganic compounds show a wide range of adsorbability. Disassociated salts such as KCl and Na_2SO_4, are essentially nonsorbab1e; HgCl and $FeCl_3$ are relative sorbable; and iodine is one of the most adsorbable substances known. Generally, a significant reduction in inorganic materials is not expected in carbon systems. Organic compound sorbability varies to some extent. Primary alcohols and sugars, for example, are resistant to adsorption, while ethers and certain organic acids are highly sorbable.

6.2.2. *Solubility*

An increase in solubility tends to oppose the attraction of the adsorbate to carbon. Therefore, polar groups having a high affinity for water usually diminish adsorption from aqueous solutions; the greater adsorption of the higher aliphatic acids and alcohols is attributed in part to their relatively lower solubility in an aqueous solution.

6.2.3. *Ionization*

A change in ionization can greatly affect adsorption. A low pH, for example, promotes the adsorption of organic acids, whereas a high pH would favor the adsorption of organic bases. Phenol adsorption is lower at a neutral or low pH, while the adsorption of the phenolate salt is higher at a high pH. Ionization is generally adverse to adsorption by carbon as strongly ionized materials are poorly adsorbed. Hydrogen ions are an exception, because they are highly adsorbed under certain conditions. Some anions are more sorbable when associated with hydrogen ions. For this reason, mineral acids such as sulfuric acid are sorbable at higher concentrations.

6.2.4. *Temperature*

Adsorption reactions are generally exothermic. High temperatures usually slow the adsorption process, while lower temperatures favor adsorption, although rates and efficiency are affected in different ways. Little information is available on the temperature range of 65–90°F (typical of most wastewaters). Lower temperatures increase adsorption, but the effect in aqueous solutions is negligible.

6.2.5. *Adsorption of Mixed Solutes*

Most wastewater contain compounds that may mutually enhance, interfere, or act independently in the adsorption process. Factors affecting overall adsorption of multiple adsorbates include the relative molecular size and configuration, the relative adsorptive affinities, and the relative concentration of the solutes.

7. PERFORMANCE AND CASE STUDIES

Battelle Northwest and the Eimco Division of the Envirotech Corporation each conducted major investigations in the use of powdered carbon for the treatment of municipal wastewaters. One study was conducted by Battelle Northwest and the other was conducted by the Eimco Division of the Envirotech Corporation.

In the Battelle Northwest study (15,17), raw sewage was contacted with PAC to effectively remove the dissolved organic matter. An inorganic coagulant (alum) was then used to aid in subsequent clarification. Polyelectrolytes were added, followed by a short flocculation period. Solids were separated from the liquid stream by gravity settling, and the effluent was then discharged. A fluidized bed process was used to thermally regenerate carbon sludge. Alum was then recovered by acidifying the carbon–aluminum oxide mixture with sulfuric acid.

Based on the favorable results of the Battelle Northwest laboratory study, a 100,000 gpd pilot plant was constructed in Albany, NY, USA. The pilot plant comprised two major systems: a liquid treatment system and a carbon regeneration facility. During the 1972 operations, the average effluent turbidity, suspended solids, COD, and BOD concentrations were 0.67 JTU, 3.1 mg/L, 39 mg/L, and 17 mg/L, respectively. This represented average removals of 98.1% suspended solids, 82.6% COD, and 81.3% BOD. These results were achieved at total plant detention times averaged slightly less than 90 min. Recovery of 91% of powdered carbon was achieved.

In the Eimco study (18,19), a 100 gpm pilot plant in Salt Lake City, UT, USA, was constructed for the evaluation of PAC treatment of raw sewage. The pilot plant was operated for 16 mo to evaluate lime, alum, and ferric iron coagulation as well as single- and two-stage countercurrent carbon treatment processes. The chemically treated effluent then flowed to the carbon contactors, which could be operated either as a single-stage (parallel) treatment process or a two-stage countercurrent (series) treatment process. PAC was fed and maintained as concentrated slurry.

It was found for treating raw sewage that a single-stage carbon contact in a slurry contactor actually provided the equivalent of two to four contacts due to the biological action occurring in the slurry contactor. Hydrogen sulfide problems could be controlled. Based on these results, single-stage carbon contact appeared to be adequate for treating raw sewage. The influent soluble COD of 80–100 mg/L was reduced to 15 mg/L with 300 mg/L of powdered carbon and to 30 mg/L with 75 mg/L of carbon.

Another study examined the PAC–activated sludge process (14). The addition of powdered carbon directly into mixed liquor in an activated sludge plant aeration basin is referred to as the PACT process. The benefits attributed to this system are numerous, such as improved BOD and COD removal by adsorption, adsorption of color and toxic agents, reduction of aerator and effluent foam, and so on. The goal of the PACT process is to improve organic removal or to improve sludge settling characteristics.

DuPont evaluated the PACT process for several months in a 75 gpm pilot facility and installed a 30 MGD PACT system to treat industrial wastewaters at its Deepwater, NJ, USA, plant. The carbon was regenerated in a multiple hearth furnace. Zimpro, Inc. has also evaluated the PACT process at the Rothschild, WI, USA, sewage treatment plant, using wet air oxidation to regenerate the carbon.

The Jet Propulsion Laboratory (JPL) Process (20) has also been the subject of study. This process is a two-stage countercurrent adsorption system using PAC. Fresh activated carbon is mixed with wastewater in the secondary mixing basin and settled, and then the entire mixture of settled sewage solids and activated carbon is transferred to the primary mixing basin. Settled solids and carbon are removed from the primary settling basin, dewatered, and transferred to a pyrolysis reactor. The reactor produces activated carbon, which is then recycled to the secondary mixing basin.

Activated carbon is intended to serve two functions: (a) as an adsorbent of organics and other pollutants and (b) as a settling aid in both the primary and secondary basins.

It is also believed that the carbon acts as a filtration aid and prevents compression of sewage solids during dewatering. Pilot plants were constructed by JPL in Pasadena and in Fountain Valley, CA, USA, the latter also known as Orange County Sanitation District Plant No.1.

8. ECONOMICS OF POWDERED ACTIVATED CARBON SYSTEM

The economics of powdered carbon addition are difficult to assess. While the use of carbon might appear to increase material cost, reduction in total expense may, in some cases, be realized through savings on coagulants, sludge handling chemicals, and so on. In other cases, the cost of carbon can be justified if it provides treatment protection from hydraulic or toxic overloads.

Most industrial wastes require higher carbon dosage (20–300 ppm) than municipal wastes (10–40 ppm). In 1977, the delivered cost of powdered carbon was 55–66 ¢/kg (25–30 ¢/lb); the cost of carbon addition would be about 0.53–0.66 ¢/m^3 (2.0–2.5 ¢/1000 gal) of water treated for every 10 ppm of carbon dosage without carbon regeneration.

Depending on the type and mode of carbon application, capital and operating costs for the system will vary. Figures 8–10 (5) present capital costs of a carbon adsorber system based on various parameters. Figure 9 displays absorber costs based on its size, with and without carbon. Figure 9 is based on a 30-min wastewater-to-carbon contact time and considers the costs of a system necessary to treat design flow conditions. Figure 10 presents the costs of a carbon regeneration system considering the area of a single hearth furnace. Investments necessary for the basic furnace system are shown.

Estimates obtained from the above graphs must be adjusted to include engineering, administrative, land, interest, and legal expenses. Further operating and maintenance costs are not included. Typical operating costs for adsorption and regeneration are shown in Tables 5 and 6 (5).

9. DESIGN EXAMPLES

9.1. *Example 1 (Langmuir and Freundlich Isotherms Constants)*

The secondary effluent from a biological treatment plant is treated with the activated carbon adsorption process and allowed to arrive at equilibrium. The equilibrium data in terms of phenol are given below. Determine the constants for the Langmuir and Freundlich isotherms.

Phenol in solution (mg/L)	Phenol on carbon (mg/mg)
1.8	0.011
4.2	0.029
7.4	0.046
11.7	0.062
15.9	0.085
20.3	0.097

Solution

The Langmuir isotherm is

$$\frac{x}{m} = \frac{a\,b\,C}{1 + a\,C}$$

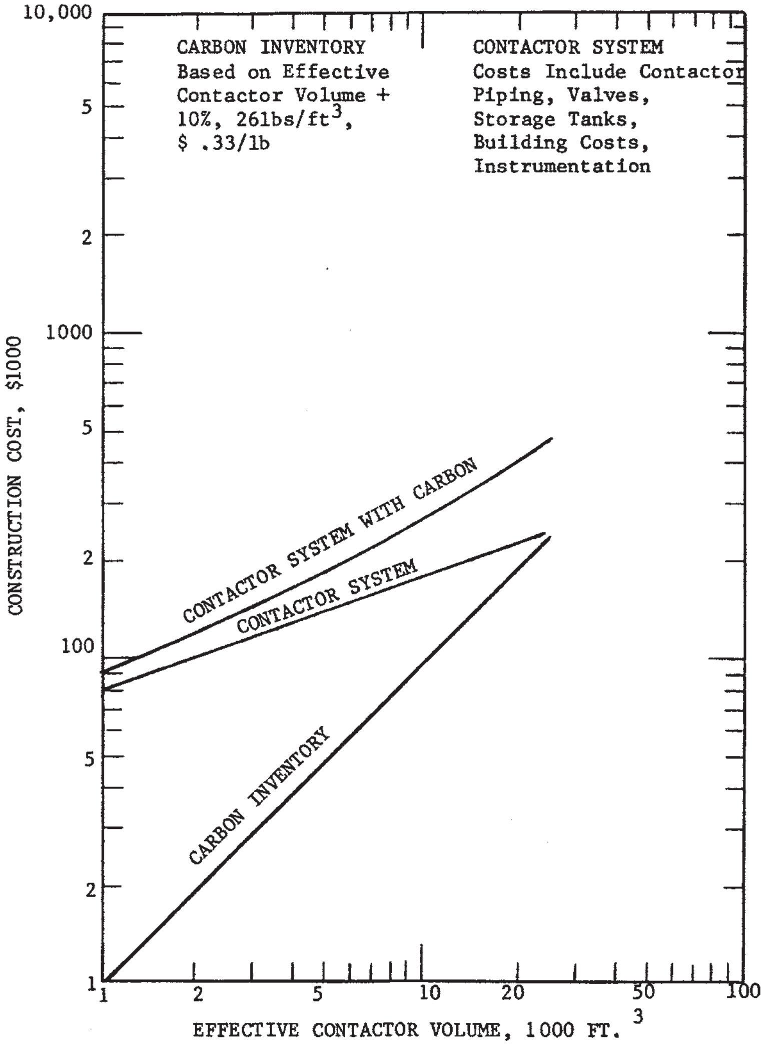

Fig. 8. Capital cost of a carbon contractor system with respect to size.

$$\frac{C}{\frac{x}{m}} = \frac{1}{b} C + \frac{1}{a\,b}$$

Plot

$$\frac{1}{\frac{x}{m}} \text{ vs } C:$$

$$\text{Slope} = \frac{1}{b}$$

$$\text{Intercept} = \frac{1}{a\,b}$$

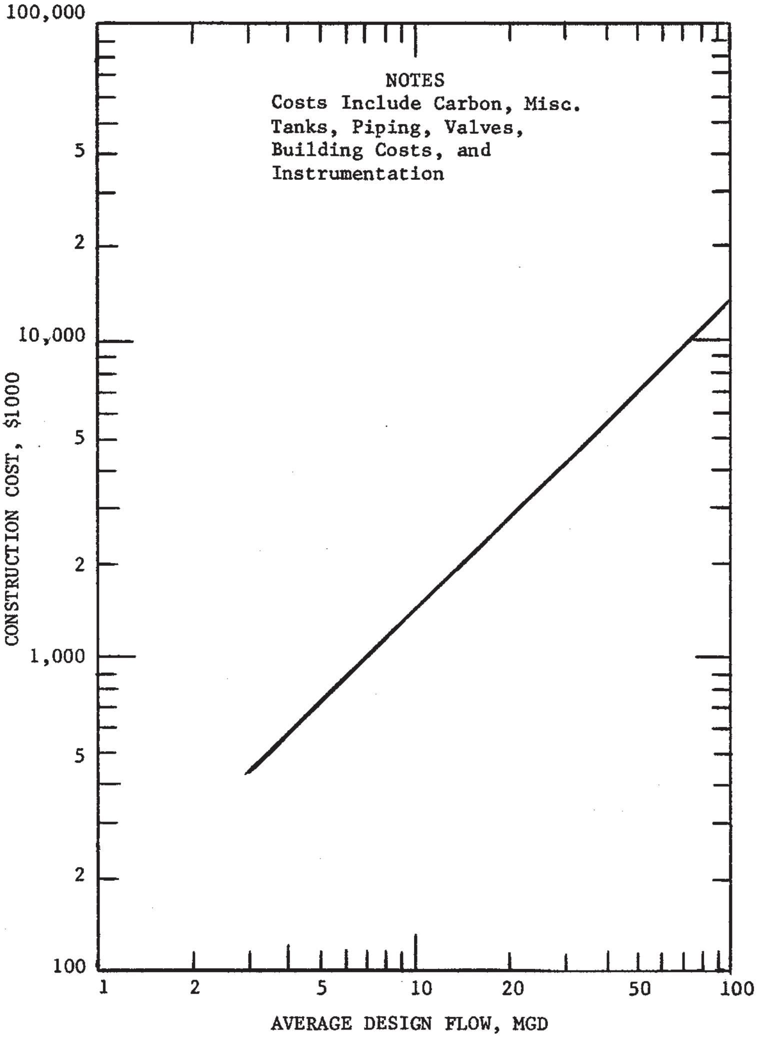

Fig. 9. Capital cost of a carbon contractor system with respect to plant capacity assuming a 30-min contact time.

From Fig. 11,

$$\text{Slope} = \frac{1}{b} = 2.9$$

therefore, $b = 0.34$ mg phenol/mg C.

$$\text{Intercept} = \frac{1}{a\,b} = 146$$

therefore, $a = 0.020$ L/mg phenol.

Freundlich isotherm:

$$\frac{x}{m} = K\,C^{\frac{1}{n}}$$

$$\log\frac{x}{m} = \frac{1}{n}\log C + \log K$$

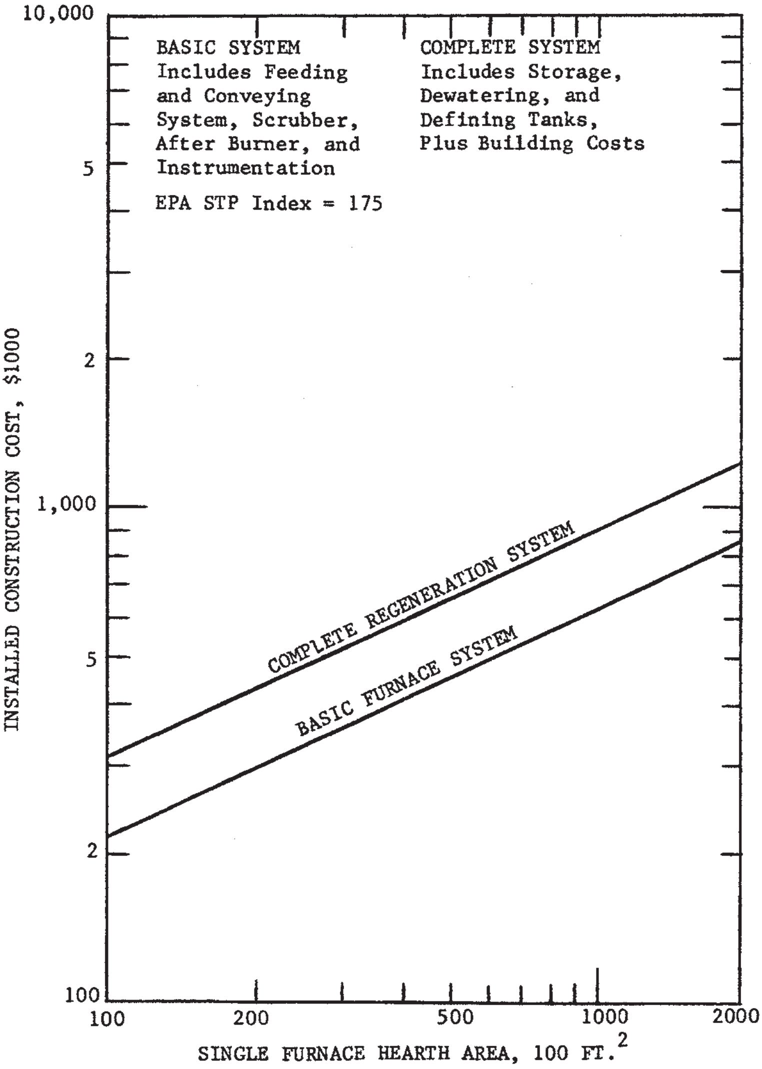

Fig. 10. Capital cost of a carbon regeneration system.

Plot

$$\log \frac{x}{m} \quad \text{vs} \log C$$

$$\text{Slope} = \frac{1}{n}$$

$$\text{Intercept} = \log K$$

From Fig. 12,

$$\text{Slope} = \frac{1}{n} = 0.85$$

therefore, $n = 1.18$.

$$\text{Intercept} = \log K = \log 0.008$$

therefore, $K = 0.008$.

Table 5
Operating and Capital Costs of South Lake Tahoe Carbon Adsorption System (1969–1970)

Operating costs	$/d
Electricity	47.34
Operating labor	24.53
Maintenance labor	3.27
Repair material	1.15
Instrument maintenance	4.24
Total operating cost	80.53
Total cost	**$/million gallons**
Operating[a]	10.74
Capital[b]	16.30
Total	27.04

[a] Total operating cost shown is based on a flow of 7.5 MGD. Total operating cost per million gallons of water treated, including the 7.5 MGD plant influent plus recycle streams, would be $8.77/million gallons.

[b] Includes initial carbon charge. All capital costs were amortized at 5% for 25 yr.

Table 6
Operating and Capital Costs of South Lake Tahoe Carbon Regeneration System (1969–1970)

Operating costs	$/d
Electricity	2.23
Natural gas	6.15
Makeup carbon	70.39
Operating labor	91.90
Maintenance labor	16.21
Repair material	1.17
Instrument maintenance	1.90
Total operating cost	189.95
Total cost	**$/million gallons**
Operating[a]	25.33
Capital[b]	5.20
Total	30.53

[a] Total operating cost shown is based on a flow of 7.5 MGD. Total operating cost per million gallons of water treated would be $19.28/million gallons including 7.5 MGD plant influent, plus recycle flows. Contactors are designed for 8.2 MGD.

[b] Capital cost were adjusted and amortized at 5% for 25 yr.

9.2. *Example 2 (Powdered Activated Carbon Adsorption Tests)*

A wastewater contains 75 mg/L of TOC following biological treatment. Effluent TOC guidelines require that the waste must contain no more than 15 mg/L TOC prior to discharge. An

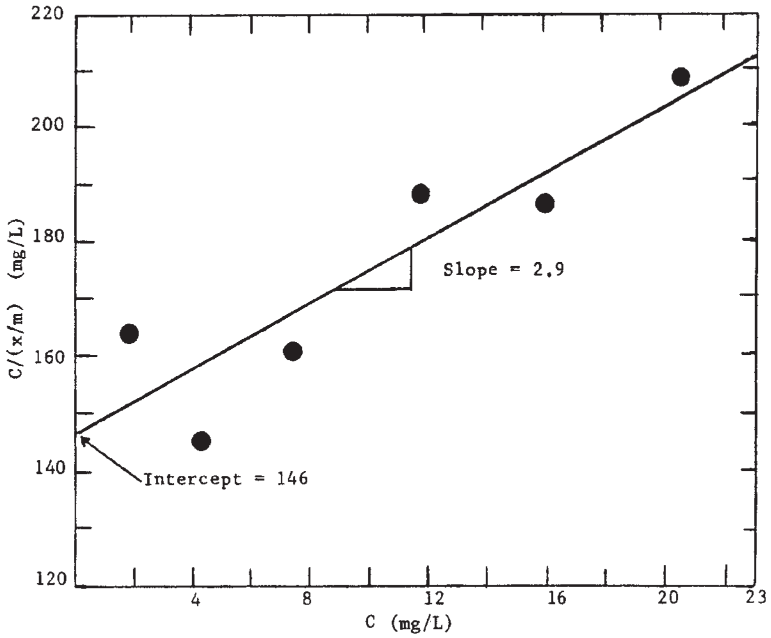

Fig. 11. Determination of Langmuir constants.

adsorption test was conducted with the data given in columns 1 through 4 in the following table. Use the Freundlich isotherm to:

1. Determine if the desired effluent TOC concentration can be achieved by carbon adsorption.
2. Determine the adsorptive capacity of the carbon at this TOC concentration.
3. Determine the ultimate capacity of the carbon for treating this wastewater.
4. Calculate values of the constants *K* and *n*.

1 Flask no	2 *m* Weight of carbon (mg)	3 Volume of solution in flask (mL)	4 *C* Final TOC concentration (mg/L)	5 *x* Weight of adsorbate absorbed (mg)	6 *x*/*m* Adsorbate adsorbed per unit wt of carbon (mg/mg)
1	0	200	75	—	—
2	50	200	44	6.2	0.124
3	100	200	30	9.0	0.089
4	200	200	17.5	11.5	0.0575
5	500	200	6.75	13.65	0.0272
6	800	200	3.9	14.22	0.0177
7	1000	200	3.0	14.4	0.0144

Solution

1. Determine if the desired effluent can be achieved by carbon adsorption. From inspection of the data, an effluent value of 15 mg/L can be obtained by adsorption, since a value of 3 mg/L was achieved in the test.

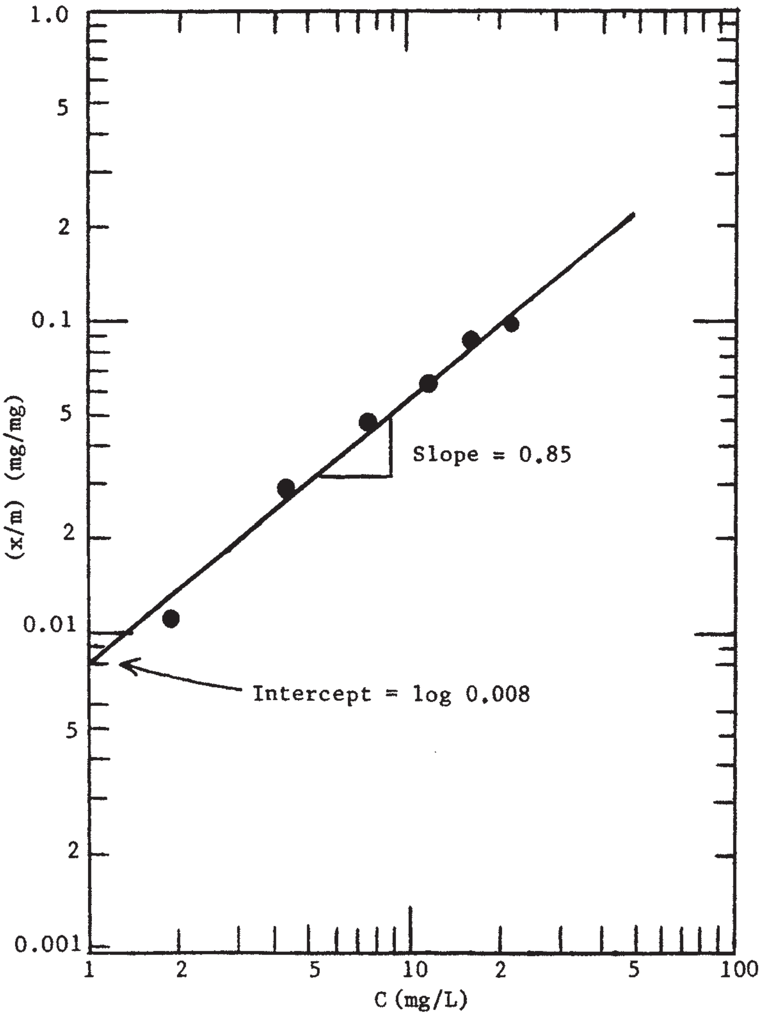

Fig. 12. Determination of Freundlich constants.

2. Determine the adsorptive capacity of the carbon at an effluent value of 15 mg/L by plotting the Freundlich isotherm.
   The Freundlich isotherm is

$$\log \frac{x}{m} = \log K + \frac{1}{n} \log C$$

   Plot values of x/m vs C on log-log paper to obtain the isotherm shown in Fig. 13.
   (a) Draw a vertical line from a C value of 15 mg/L of TOC to intersect the isotherm line.
   (b) The value of x/m obtained is the adsorptive capacity of the carbon for this equilibrium effluent concentration of 15 mg/L. From Fig. 13, read

$$\frac{x}{m} = 0.051 \text{ mg/mg}.$$

3. Calculate the ultimate capacity of the carbon for this waste. The ultimate capacity is the amount of adsorbate adsorbed when the carbon is in equilibrium with the maximum (influent) TOC concentration of 75 mg/L.

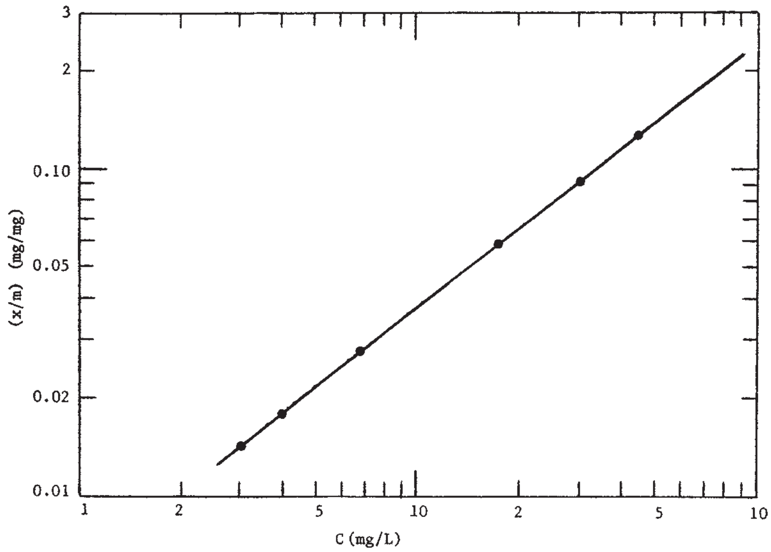

Fig. 13. Freundlich isotherm.

(a) Draw a vertical line from the C value of 75 mg/L of TOC to intersect the isotherm line.

(b) The x/m value obtained is the ultimate capacity of the carbon. From Fig. 13, read

$$\frac{x}{m} = 0.186 \text{ mg/mg}$$

4. Calculate the value of the adsorption constants K and n.

(a) Calculate the value of the constant K from the linearized Freundlich equation:

$$\log\frac{x}{m} = \frac{1}{n}\log C + \log K$$

When $C = 1$, then $\log C = 0$;
therefore

$$\log\frac{x}{m} = \frac{1}{n}\log K$$

$$\frac{x}{m} = K \text{ at } C = 1$$

From Fig. 13, the intersection of $C = 1$ and isotherm lines gives

$$\frac{x}{m} = 0.006$$

therefore, $K = 0.006$

(b) Calculate the value of n, the slope of isotherm line is $1/n$

$$\frac{1}{n} = \frac{\log\frac{x}{m} - \log K}{\log C} = \frac{\log\left(\frac{(x/m)}{K}\right)}{\log C}$$

At $x/m = 0.10$, $C = 34.5$ mg/L

$$\frac{1}{n} = \frac{\log\left(\frac{(0.10)}{0.006}\right)}{\log 34.5} = \frac{1.22}{1.537} = 0.793$$

therefore, $n = 1.26$.

9.3. Example 3 (Design and Applications of Physicochemical PAC Process Systems)

9.3.1. Types of Physicochemical PAC Process Systems

Powdered activated carbon (PAC) is used in water and wastewater treatment facilities to adsorb soluble organic materials and to aid in the clarification process. PAC is fed to a treatment system using chemical feed equipment similar to those used for other chemicals that are purchased in dry form. The spent carbon is removed with the sludge and can then be discarded or regenerated. Regeneration can be accomplished in a furnace or wet air oxidation system. There are seven types of physicochemical PAC process systems (21–24,36,37,45,46,52):

1. Continuous physicochemical PAC process systems involving the use of gravity settling basins for clarification (Figure 14).
2. PAC sequencing batch reactor involving the use of gravity settling basins for clarification.
3. Continuous physicochemical PAC process systems involving the use of dissolved air flotation (DAF) clarifiers for clarification.
4. PAC sequencing batch reactor involving the use of DAF clarifiers for clarification.
5. PAC sequencing batch reactor involving the use of centrifuges for clarification.
6. Upflow fluidized-bed PAC adsorber.
7. Upflow PAC-coated filters (Roberts-Haberer PAC Process).

When PAC is dosed to a DAF system for both adsorption and flotation, the combined process is called adsorption flotation (30,36).

9.3.2. Applications and Performance of Physicochemical PAC Systems for Potable Water Treatment

For water treatment, PAC can be added to the mixing chamber for removal of color, taste, toxic organics, and heavy metals. The amount of powdered carbon fed to a system greatly depends on the characteristics of the water and the desired effluent quality. However, powdered carbon will generally be fed at a rate between 50 and 300 mg/L. Limited pilot and field scale data are available for PAC addition to potable water treatment units and its use in municipal water treatment systems. However, the PAC applications are well established, and accepted by American Water Works Association (AWWA) (27). PAC points of application customarily are (a) before the rapid mix process, (b) after rapid mixing but before flocculation, or (c) after flocculation and before clarification (either sedimentation or dissolved flotation) (52,53). Figure 14 shows a schematic diagram of a typical physicochemical PAC process system for potable water treatment (53). A dissolved air flotation clarifier can also be used to replace sedimentation clarifier in Fig. 14. Adding PAC to water treatment systems (either sedimentation–filtration plants or flotation–filtration plants) can greatly improve their performance in removing certain organic chemicals (31,47,51–55). The upflow fluidized-bed PAC adsorber that processes water through flocculated PAC (53) has been applied to potable water treatment. There are full-scale upflow PAC-coated filters (Roberts-Haberer PAC Process) operating in Africa and Europe, including a 9.5 MGD

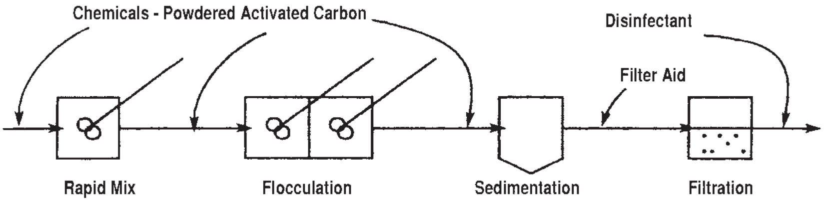

Fig. 14. Schematic of a typical physicochemical PAC process system for potable water treatment (Source: US EPA).

Table 7
Performance of Physicochemical PAC Process System for Wastewater Treatment (28)

Average process treatment results	Raw wastewater	Chemical effluent	Neutralized chemical effluent	Plant effluent
Turbidity, JTU	33	4	4	3
Suspended solids, mg/L	87	14	10	5
Total P, mg/L P	4.50	0.29	—	0.20
Soluble total P, mg/L P	3.16	0.14	0.15	0.11
Total PO_4, mg/L P	2.82	0.10	0.06	0.11
Soluble, PO_4, mg/L P	2.25	0.04	0.05	0.08
COD, mg/L	136	—	55	14

plant in Wiesbaden, West Germany, that has been in operation since 1970. More data on water treatment using PAC can be found from another chapter (55).

9.3.3. *Application and Performance of Physicochemical PAC Systems for Wastewater Treatment*

For physicochemical wastewater treatment, the same flow diagram shown in Fig. 14 can also be adopted (43–45). The nation's largest physicochemical wastewater treatment plant (72 MGD) is the Niagara Falls Wastewater Treatment Plant, in the state of New York (47–49). Its flow diagram is similar to Fig. 14, using GAC filtration. In any type of wastewater plants, PAC can be fed to primary clarifiers directly or to a separate sludge recirculation type clarifier that enhances the contact between the PAC and the wastewater. PAC can also be fed to tertiary clarifiers to remove additional amounts of soluble organics. PAC, when added to a sludge recirculation type clarifier, has been shown to be capable of achieving secondary removal efficiencies. The PAC physicochemical systems have been used in the clarifiers to adsorb soluble organic materials, for removing BOD_5 and COD, as well as some of the many toxic materials. The amount of powdered carbon fed to a system greatly depends on the characteristics of the wastewater and the desired effluent quality. However, powdered carbon will generally be fed at a rate between 50 and 1000 mg/L. Table 7 presents the PAC physicochemical process system's performance data for wastewater treatment (28).

9.3.4. *PAC and Process Equipment*

PAC can be fed in the dry state using volumetric or gravimetric feeders or can be fed in slurry form. There are at least three major PAC producers, over 50 manufacturers of volumetric and gravimetric feeders, and over 50 manufacturers of slurry feeders (24–26). There are also many manufacturers of sequencing batch reactors (SBR) (22), dissolved air flotation (DAF) clarifiers (30), and centrifuges.

9.3.5. Process Limitations and Environmental Impact

The PAC physicochemical process will increase the amount of sludge generated. At higher dosages, regeneration will be necessary in order to maintain reasonable costs. Most PAC systems will require postfiltration to capture any residual carbon particles. A flocculating agent such as an organic polyelectrolyte is usually required to maintain efficient solids capture in the clarifier.

About a pound of dry sludge will be generated per pound of carbon added. If regeneration is practiced, carbon sludge is reactivated and reused with only a small portion removed to prevent buildup of inert. PAC physicochemical process systems are reasonably reliable from both a unit and process standpoint. In fact, PAC systems can be used to improve the process reliability of existing systems. Readers are referred to recent reports for additional information (29,30).

9.4. Example 4 (Design and Applications of Combined Biological and Physicochemical PAC Process Systems)

9.4.1. Types of Combined Biological and Physicochemical PAC Process Systems

The PAC activated sludge system is a modified activated sludge process. PAC is added to the aeration tank where it is mixed with the biological solids. The mixed liquor solids are settled and separated from the treated effluent in a gravity clarifier. Polyelectrolyte will normally be added prior to the clarification step to enhance solids–liquid separation. If phosphorus removal is necessary, alum is often added at this point. Even with polyelectrolyte addition, tertiary filtration is normally required to reduce the level of effluent suspended solids. The clarifier underflow solids are continuously returned to the aeration tank. A portion of the carbon-biomass mixture is wasted periodically to maintain the desired solids inventory in the system.

There are six types of combined biological and physicochemical PAC process systems (20–23,30–32,36):

1. Continuous combined biological and physicochemical PAC process systems involving the use of gravity settling basins for clarification.
2. Combined biological and physicochemical PAC sequencing batch reactor involving the use of gravity settling basins for clarification.
3. Continuous combined biological and physicochemical PAC process systems involving the use of dissolved air flotation (DAF) clarifiers for clarification.
4. Combined biological and physicochemical PAC sequencing batch reactor involving the use of DAF clarifiers for clarification.
5. Continuous combined biological and physicochemical PAC process systems involving the use of membrane filters (MF) for filtration.
6. Combined biological and physicochemical PAC sequencing batch reactor involving the use of membrane filters (MF) for filtration.

When PAC is dosed into an activated sludge process for combined adsorption and biochemical reactions, the combined process is also called the PACT process, in which PAC still stands for powdered activated carbon, while ACT stands for activated sludge.

9.4.2. Applications and Performance of Combined Biological and Physicochemical PAC Process Systems

The combined biological and physicochemical PAC process systems can only be used for wastewater treatment. The addition of PAC to plug flow and complete mix suspended growth reactors is a more common process modification for industrial wastewater treatment, and has

Table 8
Summary of Combined Biological and Physicochemical PAC Process Systems Using Wet Air Oxidation for PAC Regeneration (34,39)

				Permit Limits		
Facility	Current/Design Flow (m^3/s)	PAC/WAR[a] status	Reason for PAC[b]	BOD_5 (mg/L)	TSS (mg/L)	NH_4^+–N (mg/L)
Vemon, CT	0.18/0.28	MA	C	10	20	—
Mt. Holly, NJ	0.11/0.22	MA	C,S	30	30	20
E. Burlington, NC	0.31/0.53	MA	C,N,T	12–24	30	4.0–8.0
S. Burlington, NC	0.30/0.42	AS	C,N,T	12–24	30	4.0–8.0
Kalamazoo, MI	1.1/2.4	MA	C,N,T	7–30	20–30	2.0–10.0
Bedford Hts., OH	0.15/0.15	NAC	N,S	10	12	5.1
Medina Co., OH	0.31/0.44	MA	N	10	12	1.5–8.0
N. Olmsted[c] OH	0.26/0.31	AS	N,S	30	30	2.3–6.9
Sauget, IL	0.70/1.2	AS	T	20	25	—
El Paso, TX	0.20/0.44	MA	N,O			

[a] MA = Modified operation and/or design for ash control. AS = Converted to conventional activated sludge. NAC = Converted to the use of nonactivated carbon without regeneration.

[b] C = Color Removal; S = Space; N = Nitrification; T = Toxics; O = Organics.

[c] Plan to convert to NAC without regeneration.

been applied to municipal systems in some instances. Demonstrated advantages of adding PAC to suspended growth reactors include improved solids settling and dewatering characteristics; the ability of PAC to adsorb biorefractory materials and inhibitory compounds, improving effluent quality and reducing the impact of organic shock loads; reduction in odor, foaming, and sludge bulking; and improved color and $CBOD_5$ removal (33).

Because PAC is wasted with excess biomass, virgin or regenerated PAC addition is required to maintain the desired concentration in the biological reactor. This can represent a significant cost factor for the system. When carbon addition requirements exceed 900–1800 kg/d (2400–4000 lb/d), wet air oxidation/regeneration (WAR) is claimed to represent an economical approach to carbon recovery and waste biomass destruction. However, an ash separation step is needed in this case, affecting the economics of carbon regeneration and recovery (34). The economic analysis is further clouded by the inability to analytically differentiate powdered carbon from background refractory volatile materials, thus making it difficult to quantify the value of the volatile suspended material recovered after WAR. Although ash separation processes have been reported to be effective in at least two municipal PAC–activated sludge plants, the economics of complete PAC/WAR systems relative to other activated sludge nitrification systems are unclear (34–37).

In the United States, PAC–activated sludge systems for nitrification generally has been applied at municipal treatment plants where industrial sources contribute a significant fraction of the incoming wastewater. In all instances, PAC regeneration was included in the flowsheet (38). A summary of selected municipal PAC facilities is presented in Table 8.

The procedure to follow in designing PAC–activated sludge systems for nitrification involves a modification to those for complete mix or conventional plug flow systems (39) in order to account for the effects of the addition of PAC. According to major suppliers of the technology (38–42), most PAC process systems are designed at MLSS concentrations of approx 15,000 mg/L. The mixed liquor is composed of volatile activated carbon, biomass, nonvolatile PAC ash, biomass decay components, and influent inert material. The relative proportions of these materials are strongly influenced by whether carbon regeneration is practiced via wet air oxidation and a return of this material to the aerator. The intent is to maintain the PAC concentration at approx 1.5 times the biomass level in nitrification PAC reactors (38–40). The most appropriate PAC concentration will be dictated by the specific wastewater characteristics and often cannot be specified without bench or pilot scale studies. The PAC concentration to be added will depend on the design solids retention time, the hydraulic retention time, and the required PAC concentration in the reactor. According to the US Environmental Protection Agency (39), for practical engineering design considering the loss, the PAC concentration to be added can be calculated from an equation modified from Eq. (7):

$$\mathrm{PAC_I} = \mathrm{PAC_E} + \frac{\mathrm{PAC_R}\Theta}{\Theta_\mathrm{C}} \tag{8}$$

where $\mathrm{PAC_E}$ = effluent PAC concentration, mg/L. The value of $\mathrm{PAC_E}$ in Eq. (8) can be estimated by assuming that the carbon fraction in the effluent TSS is the same as the fraction of PAC in the MLSS.

PAC–activated sludge nitrification systems are normally selected when the municipal wastewater contains compounds originating from industrial operations, as stated previously. Nitrifiers are susceptible to a number of organic and inorganic inhibitors found in many industrial wastewaters (39). Researchers have provided evidence that the addition of PAC to nitrifying activated sludge systems receiving industrial wastewaters improved nitrification rates (39–42). More recent studies have been completed with the goal of determining the mechanism of nitrification enhancement in PAC activated sludge systems in the presence of adsorbable and nonadsorbable inhibitors (42). The results indicated that the addition of the proper amount of PAC can completely nullify the toxic effects of an adsorbable nitrification inhibitor. A minor positive effect on nitrification rates was observed when PAC was added to a nitrifying activated sludge system receiving nonadsorbable inhibitors. The activated sludge used in these studies was not acclimated to the inhibiting compounds.

9.4.3. *PAC and Process Equipment*

PAC can be fed in the dry state using volumetric or gravimetric feeders or can be fed in slurry form. There are at least three major PAC producers, more than 50 manufacturers of volumetric and gravimetric feeders, and more than 50 manufacturers of slurry feeders (24–26). Additionally, there are many manufacturers of sequencing batch reactors (SBR) (22), dissolved air flotation (DAF) clarifiers (36), and membrane filtration (MF) reactors (31).

9.4.4. *Process Limitations and Environmental Impact*

The process limitations and environmental impact of combined biological and physicochemical PAC process systems are identical to those of the PAC physicochemical process. Readers are referred to Section 9.3.5. Additional information on carbon adsorption and combined biological and physicochemical PAC process systems may be found in the literature (43–51).

NOMENCLATURE

a	Constant, L/(mg/L)
b	Value of x/m when monolayer has been completed, mg/mg
BAC	Biological activated carbon
BOD	Biochemical oxygen demand
C	Equilibrium concentration of adsorbate, or concentration of solute in solution, mass/volume, mg/L

C_s	Concentration of adsorbate at saturation of all layers, mg/L
COD	Chemical oxygen demand
GAC	Granular activated carbon
JTU	Jackson turbidity units
K	Constant related to energy of interaction between adsorbent and adsorbate
$\mathrm{MLSS_C}$	Aerator mixed liquor suspended solids due to carbon, mg/L
$\mathrm{MLVSS_C}$	Aerator mixed liquor volatile suspended solids, mg/L
n	Constant, $n > 1$
PAC	Powdered activated carbon
$\mathrm{PAC_I}$	Influent PAC concentration, mg/L
$\mathrm{PAC_R}$	Mixed-liquor PAC concentration in the reactor, mg/L
$\mathrm{PAC_E}$	Effluent PAC concentration, mg/L
Θ	Hydraulic retention time (HRT), d
Θ_c	Design solids retention time (SRT), d
TOC	Total organic carbon
x	Mass of adsorbent, mg
X_C	Carbon dosage, mg/L
$\left(\frac{x}{m}\right)$	Mass of solute adsorbed per unit mass of adsorbent, mg/mg

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5
Diatomaceous Earth Precoat Filtration

Lawrence K. Wang

CONTENTS

1. INTRODUCTION

Filtration is the process by which particles are separated from a fluid by passing the fluid through a permeable material (1). The filtrations discussed in this chapter concern the removal of suspended solids, including some semi-colloids, from liquids. Ideally the liquid goes through and solids remain, building a permeable cake on the screen. With large, incompressible particles, this ideal situation can be approached. In practice, however, finer solids often pass through with only larger solids remaining on the screen. If the latter are at all compressible, the liquid flow is reduced to an uneconomical level and the solids stick to the screen, making it very difficult to clean. These difficulties occur in almost all organic liquid and food product filtrations. Diatomaceous earth filter aids, properly used in a diatomaceous filtration system as outlined in this chapter, offer practical and economical solutions to these filtration operational difficulties.

Diatomaceous earth filtration (or precoat filtration), accomplishes particle removal by physically straining the solids out of the water. The thickness of the initial layer of diatomaceous earth (DE) filter medium is normally about 1/8-in. (3 mm), and the water

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passageways through this layer are so small and numerous that even very fine particles are retained.

In water supply, diatomaceous earth filters are effective in removing *Giardia* cysts, algae, iron, manganese, coliform bacteria, turbidity, and asbestos. For water supplies with low amounts of suspended solids, DE filters have lower initial costs than conventional rapid sand filtration systems. In comparison with other types of filtration systems (such as conventional sand filtration, direct filtration, slow sand filtration, package filtration, and cartridge filtration), DE filters are especially effective against *Giardia* cysts and *Cryptosporidium* (3–6).

While this DE technology has been used extensively in specialized applications, such as swimming pools and military mobile water and wastewater applications (7–10), DE filtration is a "new" technology for municipal water supply treatment.

Diatomaceous earth filter plants have been chosen for projects with limited initial capital, and for emergency or standby capacity to service large seasonal increases in demand. Because these systems are most suitable for applications where influent is low in turbidity and bacterial counts, water supplies presently receiving just chlorination may consider using diatomaceous earth to meet the filtration requirements of the Surface Water Treatment Rules (SWTR) (2).

Since 1949, more than 170 potable water treatment plants utilizing DE filtration have been designed, constructed, and operated in the United States (10,11). About 90% utilize surface water supplies and 10% groundwater supplies. The largest existing plant is a 20-MGD system in San Gabriel, CA, (11).

2. PROCESS DESCRIPTION

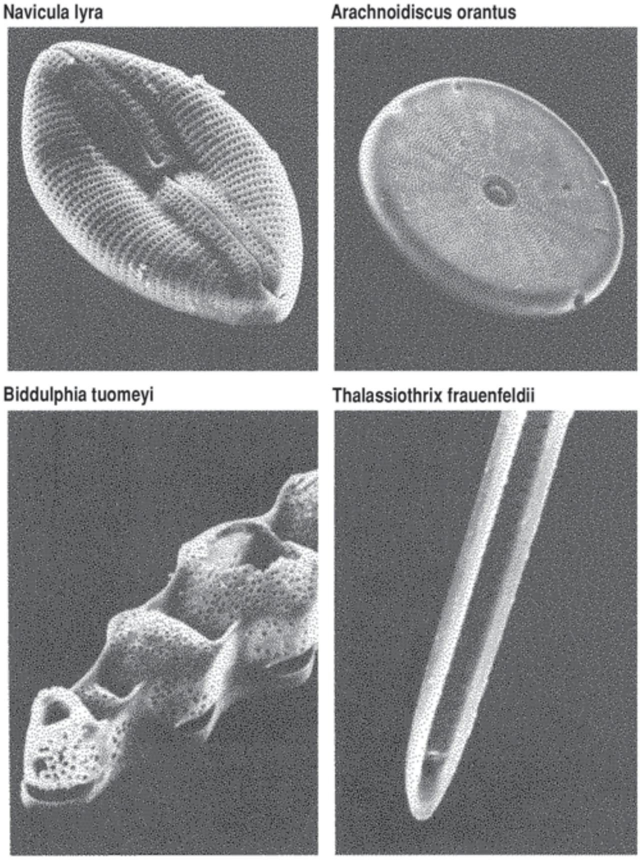
2.1. Diatomaceous Earth

Diatomaceous earth is the skeletal remains of tiny aquatic plants called diatoms, shown in Fig. 1. They flourished in prehistoric waters over what is now Lompoc, CA. Over millions of years, their skeletons formed a deep deposit on the ocean floor, which then rose to become part of the land mass. The diatomaceous earth deposit is distinguished by high purity and an almost infinite variety of diatom shapes and sizes, due to unusual natural circumstances (5).

2.2. Diatomaceous Earth Filtration and Filter Aid

Diatomaceous earth filtration, also known as precoat filtration or diatomite filtration, relies on a layer of diatomaceous earth about 0.3-cm (1/8-in.) thick placed on a septum or filter element. The septums may be placed in pressure vessels or operated under vacuum in open vessels. A schematic diagram of a typical pressure system is shown in Fig. 2.

The diatomaceous earth filtration uses filter aids in two-step operation. Figures 2 and 3 show how a diatomaceous earth filter (DE filter or precoat filter) works. First, a thin protective layer of filter aid (the precoat) is built up on the filter septum by recirculating a filter aid slurry. After precoating, small amounts of filter aid (body feed) are regularly added to the liquid to be filtered. As filtering progresses, the filter aid, mixed with the suspended solids from the unfiltered liquid, is deposited on the precoat. Thus, a new filtering surface is continuously formed; the minute filter aid particles provide countless microscopic channels that entrap suspended impurities but allow clear liquid to pass through, without clogging.



Navicula lyra

Arachnoidiscus orantus

Biddulphia tuomeyi

Thalassiothrix frauenfeldii

Fig. 1. Diatoms: the skeletal remains of tiny aquatic plants.

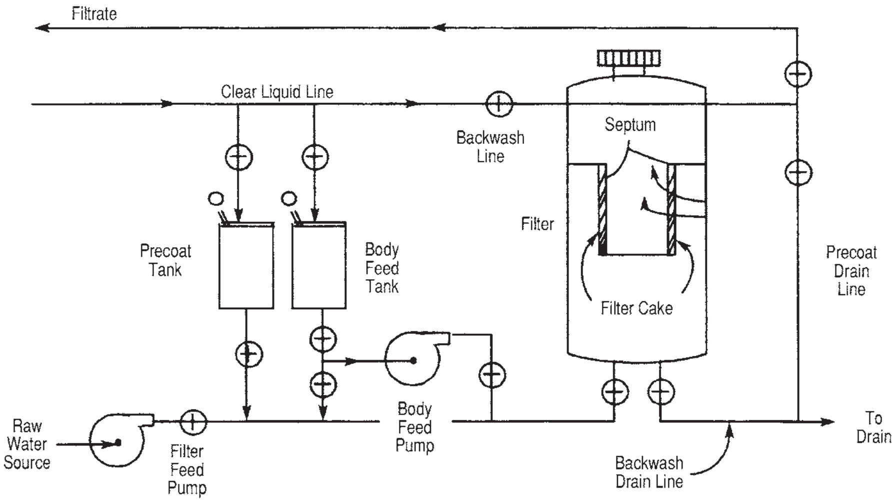


Fig. 2. Flow diagram of a diatomaceous earth filtration system.

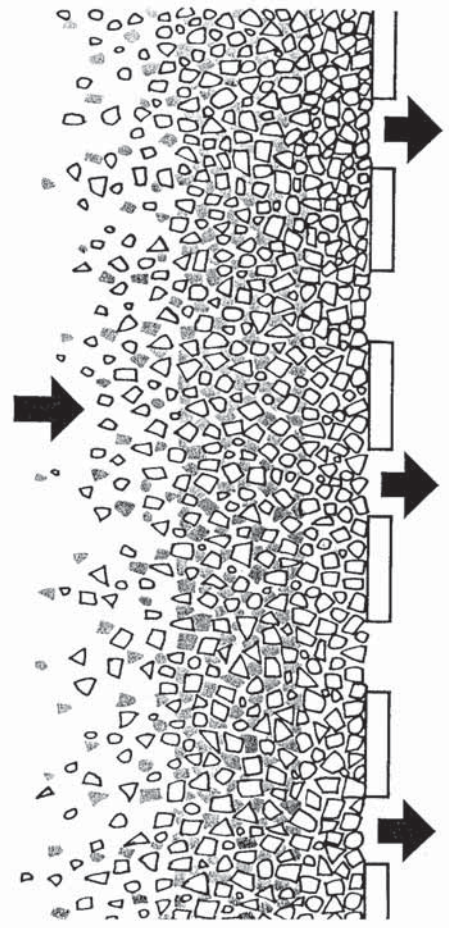


Fig. 3. Schematic of filter cake and precoat.

Any substances that can enhance the filtration efficiency are termed a filter aid. Diatomaceous earth is the most common filter aid for the precoat filtration system. An efficient, economical filter aid must (a) have rigid, intricately shaped, porous, individual particles; (b) form a highly permeable, stable, incompressible filter cake; (c) remove even the finest solids at high rates of flow; and (d) be as chemically inert and essentially insoluble in the liquid being filtered. Commercial diatomaceous earth, such as Celite diatomite, meets these requirements due to the wide variety of intricately shaped particles and inert composition that makes it practically insoluble in all but a few liquids.

The manufacturer of filter aids produces filter aid grades in a wide range of particle sizes to meet practically any industrial filtration requirement. The relative flow rates of these grades are determined by a standard filtration test and are shown in Fig. 4. Typical properties of some commercial filter aids are shown in Tables 1–3. Filter Cel, the finest grade, shown in Fig. 4, giving the highest clarity and lowest flow rate, is a natural diatomite, which has been selectively quarried, dried, milled, and air-classified. To make coarser, faster flow rate filter aids, Filter-Cel is calcined and air-classified. These straight

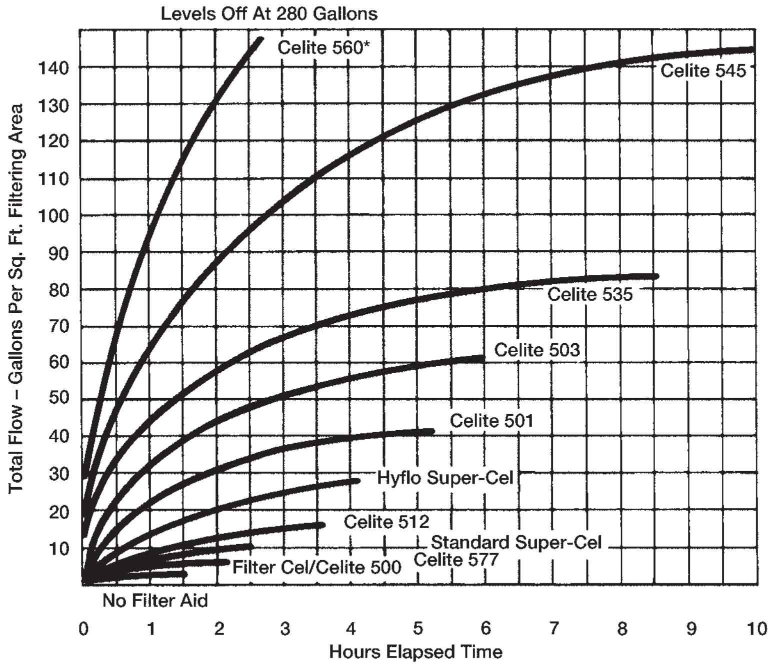


Fig. 4. Hydraulic characteristics of various diatomaceous earth filter aids.

calcined grades are Celite 577, Standard Super-Cel, and Celite 512. To obtain still larger particles, a flux is added before calcination giving the flux-calcined or white grades of filter aids, which include those from Hyflo Super-Cel to Celite 560, the coarsest.

It is axiomatic in the use of filter aids that the ability of the filter aid to remove small particles of suspended matter decreases as the particle size, and thus the flow rate, increases. Conversely, as filter aid particle size, and therefore the flow rate, decreases, the ability of the filter aid to remove small particles of suspended matter increases. The extent to which this takes place will depend very much on the type and particle size distribution of the undissolved solids being removed.

In most instances, the particle size range of undissolved solids is such that a fine grade of filter aid, right down to the finest, will improve clarity. If, however, a given filter aid grade will remove 100% of the suspended solids, a finer grade, while giving a lower flow rate due to its finer structure, will not give increased clarity.

Therefore, the selection of the proper filter aid grade is a compromise between high clarity and low flow rate, and lower clarity and higher flow rate. The best filter aid is that grade which provides the fastest flow rate (or greatest throughput per dollar's worth of filter aid) while maintaining an acceptable degree of clarity, which must be determined and specified by the filter aid user, or selected by a consulting environmental engineer (18).

For a given liquid, clarity of filtrate is governed principally by: (a) grade and amount of filter aid for body feed; (b) grade and amount of filter aid for precoat; (c) length of cycle; and (d) filtration rate.

Table 1
Typical Particle Size of Diatomaceous Earth

Weight % finer than micron size																					Median particle size in microns
Micron size	0.5	0.7	1.2	1.5	2.0	2.5	3.5	5	5.5	8	12	15	17	25	40	60	90	125	175	250	
Celite 500	0	1	7	10		22	31	41		58	72		82	89	96	99	99	99	100		7.5
Filter Cel					10				50			90									7.5
Celite 577		0	1.3	3		10	14	26		40	51		61	81	94	98	99	99	100		12
Standard Super-Cel		0	0.3	0.6		6	13	24		40	66		81	91	97	98	99	99	100		14
Celite 512				0		2	6	14		33	53		72	84	95	97	98	99	99	100	15
Hyflo Super-Cel				0		1	4	9		24	43		55	74	87	92	94	95	99	100	18
Celite-501							0	2		10	15		30	35	61	85	93	96	99	100	20
Celite-503							0	1		3.5	14		29	53	78	91	96	98	99	100	23
Celite-535							0	1		3.5	12		24	46	73	86	93	96	97	100	25
Celite-545								0		2	8		20	44	71	85	92	95	96	100	26

Source: Johns Manville.

Table 2
Typical Physical Properties of Diatomaceous Earth*

Grades	Color	Fibra-Cel/ diatomite blend equiv- alent**	Median pore size in microns	Approx. ΔP@ 1 gal/ ft^2/min with 0.15 lb/ ft^2 precoat	Estimated gal/ft^2/hr water; 6 in. precoat 24 in. Hg ΔP	Perme- ability Darcies*	Denisty lb/ft^3		150 Mesh % retained	% Mois- ture as shipped	pH	% Solubles
							Dry	Wet				
Celite 500	Gray	1	1.5	3.2	***	0.057	7.0	16	2	3.0	7.0	0.15
Filter Cel	Pink		2.5		***		7.5	17	1	1.0	8.0	0.20
Celite 505	Pink	3		2.0	***	0.068	8.0	23		1.0	7.0	0.15
Celite 577	Pink	2	2.5	1.2	***	0.16	8.0	18	2	0.5	7.0	0.10
Standard Super-Cel	Pink	5	3.5	0.7	10	0.28	8.0	18	4	0.5	7.0	0.10
Celite 512	Pink	6	5.0	0.4	20	0.53	8.0	19	7	0.5	7.0	0.10
Hyflo Super-Cel	White	7	7.0	0.1	50	1.2	9.0	18	6	0.1	10.0	0.15
Celite 501	White	8	9.0	0.07	65	1.4	9.5	18	8	0.1	10.0	0.15
Celite 503	White	9	10.0	0.06	130	2.0	9.5	18	9	0.1	10.0	0.15
Celite 535	White	10	13.0	0.03	240	3.1	12.0	19	10	0.1	10.0	0.15
Celite 545	White	11	17.0	0.02	370	4.8	12.0	19	12	0.1	10.0	0.15
Celite 560	White	13	22.0	0.005	1400	30.0	19.5	20	40	0.1	10.0	0.15

* As expressed, these are *typical* or estimated physical properties, *not specifications*, and should be used accordingly.

** Fibra-Cel grades are designated by a number plus a letter (i.e., Fibra-Cel 7F). The number refers to the equivalent grade of Celite filter aid and the letter to the percent Cellulose in multiples of 2 1/2%; i.e., A = 2 1/2%, B = 5%, C = 7 1/2%, etc.

***Not applicable.

Source: Johns Manville.

Table 3
Typical Chemical Analysis of Diatomaceous Earth

Grades	Ignition loss %	SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	TiO_2	CaO	MgO	$Na_2O + K_2O$
Celite 500	3.6	85.8	3.8	1.2	0.2	0.2	0.5	0.6	1.1
Filter Cel	1.5	89.0	3.3	1.4	0.3	0.2	0.8	0.6	1.0
Celite 505 Celite 577	0.5	91.5	4.0	1.1	0.2	0.2	0.6	0.6	1.2
Standard Super-Cel	0.5	91.1	4.0	1.3	0.2	0.2	0.5	0.6	1.1
Celite 512	0.5	91.1	4.0	1.3	0.2	0.2	0.5	0.6	1.1
Hyflo Super-Cel	0.2	89.6	4.0	1.5	0.2	0.2	0.5	0.6	3.3
Celite 501	0.2	89.6	4.0	1.3	0.2	0.2	0.5	0.6	3.3
Celite 503	0.2	89.6	4.0	1.3	0.2	0.2	0.5	0.6	3.3
Celite 535	0.2	89.6	4.0	1.3	0.2	0.2	0.5	0.6	3.3
Celite 545	0.2	89.6	4.0	1.3	0.2	0.2	0.5	0.6	3.3
Celite 550 Celite 560	0.2	89.6	4.0	1.3	0.2	0.2	0.5	0.6	3.3

(1) The soluble portion of celite filter aids is extremely low.
Source: Johns Manville.

The desired clarity, or the amount of acceptable suspended solids in the filtrate, can be determined in a number of ways:

(a) visual examination of a sample of filtrate;
(b) comparing a sample of filtrate with a standard;
(c) the use of electronic turbidity instruments;
(d) filtering a sample of filtrate on a fine white or black filter paper, such as a membrane filter, and observing the impurities on the paper;
(e) chemical or biological analysis; and
(f) gravimetric analysis.

It is extremely difficult to state the particle size of the solid that will be removed by any given grade of filter aid. This depends upon the method used for measuring the particle size of the contaminant, the type of liquid involved, the shape of the particle, the filtration conditions, and the particle characteristics. For example, a needlelike particle might easily be removed if it approaches the filter cake sideways, while it could pass right through if it approaches on end. A mushy, soft particle might worm its way through a filter cake, whereas a rigid particle of the same size and shape would not. Variations in pressure, vibration, and air bubbles may also affect water clarity.

An approximation of the degree of clarity obtainable by any one grade of filter aid can be gained by running filtration tests using proper techniques on a Buchner funnel. These tests will not be exact because in an actual filtration, as the cycle progresses, the filter cake tends to become partially plugged or "tightened" by the particles of suspended solids being removed. This tightening of the filter cake produces a filtrate of progressively higher clarity. It may be advisable, therefore, if filtrate from the whole length of the cycle is blended, to consider average clarity, rather than spot clarities. Possibly, this may allow the use of a faster grade of filter aid.

3. DIATOMACEOUS EARTH FILTRATION SYSTEM DESIGN

The majority of the minimum design criteria in the Ten State Standards for diatomaceous earth (DE) systems meet the SWTR (2). However, two design criteria in addition to the Ten State Standards are necessary to meet current regulations: (a) The minimum amount of filter precoat should be 1 kg/m^2 (0.2 lb/ft^2) to enhance *Giardia* cyst removal; and (b) the minimum thickness of the precoat should be increased from 0.3 to 0.5 cm (1/8 to 1/5 in.) (found to be more important than the size graduation of the diatomaceous earth), also to enhance *Giardia* cyst removal.

An additional recommendation is to use coagulant (alum or a suitable polymer) to coat the body feed to improve the removal rate for viruses, bacteria, and turbidity. Adding these chemicals to the coating does not improve *Giardia* removal rates.

4. DIATOMACEOUS EARTH FILTRATION SYSTEM OPERATION

The essentials of a filter aid filtration system are shown in Fig. 2. These consist of the filter, the filter feed pump, tanks containing filter aid for precoating and body feed addition, and the body feed pump for continuous addition of filter aid. Note also the lines for filling the body feed tank and precoat tank with filtered liquid, and for circulating clear or filtered liquid containing filter aid between the precoat tank and the filter. The system may also include a precoat circulating pump and auxiliary lines for blowing back the filter heel to the feed tank, and for filling and recirculating wash liquid, as well as vent lines and lines for blowing the filter cake dry with air, inert gas or steam (3,4).

Continuous addition of filter aid (body feeding) is accomplished either by feeding filter aid as a slurry or by dry feeding. Slurry feeding is usually done with plunger or diaphragm pumps. If filtration is a batch process, the filter aid can be added directly to the batch.

In the operation of a filtration system, the filter is first precoated by circulating a mixture of filter aid and clear or filtered liquid from the precoat tank through the filter and back to the precoat tank. This is continued until all the filter aid is deposited on the filter. The body feed injection system is then started and the filter is changed over, with minimum fluctuations in pressure, from precoating to filtering.

4.1. Precoating Operation

4.1.1. Purpose and Function

The first step in the use of DE filter aid is to build up a “precoat” of the filter aid on the filter medium. The purpose of the precoat is threefold: (a) To prevent the filter septum from becoming clogged by impurities, thus prolonging septum life, (b) to give immediate high clarity, and (c) to facilitate cleaning of the septum at the end of the cycle.

Precoating is accomplished by circulating a slurry of filter aid and filtered or clear liquid between the filter and the precoat tank. Since most of the filter aid particles are smaller than the openings in the septum, they must form the precoat by bridging these openings. These bridges can be upset by air bubbles, sudden changes in pressure, or vibrations, causing the filtrate to become turbid until the upsetting influences have been corrected. If flow distribution in the filter is good, the filter may be filled with clear precoat liquid; and a concentrated slurry of filter aid, other than cellulose may then be pumped or educted into the filter followed by recirculation.

4.1.2. Precoat Quantity

The amount of precoat should be from 10 to 15 lb of filter aid per 100 ft^2 of filter area (4.5–6.8 kg per 9.29 m^2), the higher amount being used when distribution of flow in the filter is poor, or in starting up new filters. If it is perfectly distributed, 10 lb (4.5 kg) of filter aid per 100 ft^2 (9.29 m^2) of filter area will give a precoat of approx 1.46 in. (1.6 mm) in thickness. The use of baffles or precoating at a different rate may be necessary for an even precoat at lower precoat amounts.

Precoat slurry concentration will depend primarily on the ratio of filter area to filter and piping volume. If it is much below 0.3%, precoating may be difficult because the formation of the bridge depends partly on the "crowding" effect of the particles of Celite trying to get through the septum openings.

4.1.3. Precoating Rate

The precoating rate will depend mainly on the viscosity of the liquid used. The rate should be sufficient to keep all the filter aid in suspension but should not be fast enough to cause erosion of precoat in the filter. For water, a typical rate is from 1 to 2 gpm/ft^2 of filter area, or 0.04 to 0.08 $m^3/min/m^2$ of filter area. For viscous liquids, the rate may be as low as 5 gal per ft^2 per hour (gph/ft^2), or 0.02 $m^3/h/m^2$. A general rule for precoating is to precoat at that rate that gives a differential pressure of approx 2 psi (13.8 kilopascals). For water, an upward velocity of at least 4.5 ft/min (1.4 m/min) is required for proper filter aid suspension. The suspension of filter aid can be improved in the tank, or pressure leaf filter, by recirculating part of the inlet flow from the top of the filter back to the precoat tank.

4.1.4. Precoat Operation Troubleshooting

Precoating filtrate should clear up in from 2 to 5 min. However, this does not mean the precoat is all in place. Continue precoating until the liquid in the filter shell is relatively clear. This usually takes place in 10–15 min at most. Lack of clarity of filtrate could be caused by any of the following: improper venting of filter; precoat erosion caused by too high a circulation rate; blinding of filter septum; insufficient precoat at top of leaves caused by too little circulation; tears in septum; old screens with worn and/or separated wires; leaks between septum and rim of leaf; worn gaskets between leaf discharge nipple and discharge manifold; wrinkles in septum; negative pressure on discharge manifold causing flashing inside the leaf.

4.2. Filtration Operation

4.2.1. Filtration Function

After the precoating filtrate has cleared up, the filter is put on-stream by starting the body feed pump, opening the line from the filter feed pump, and simultaneously closing the line from the precoat circulating pump so that flow through the filter is continuous and without sudden fluctuations in pressure. If the filter is precoated with filtered liquid, the precoat tank is best refilled immediately by directing all or part of the filtrate to it. The precoat tank may be filled at the end of the cycle but this may cause problems, because flow through the filter may drop off suddenly, requiring too long a time for filling.

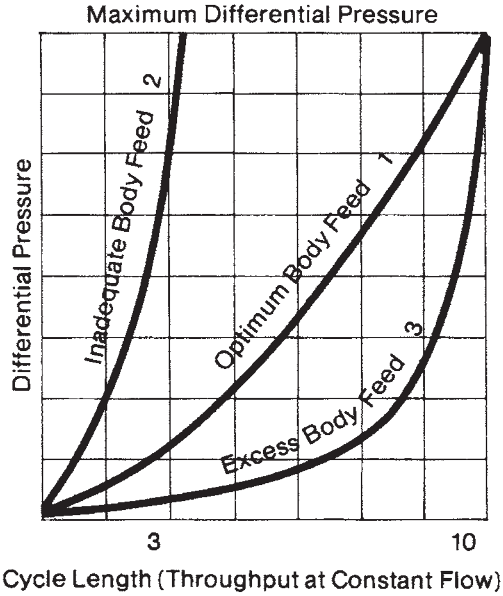


Fig. 5. Filtration cycle length affected by body feed.

It is possible to remove precoat liquid from the filter by using air to blow the liquid through a drain valve at the bottom of the filter tank, while blowing air through the leaves at the same time to hold the precoat in place. It is hydraulically impossible to blow any significant amount of liquid through the leaves. The precoat may also be held in place by vacuum while the filter is drained. After all precoat liquid is blown from the filter, it can be filled with unfiltered liquid and filtration can then proceed.

4.2.2. Amount of Body Feed Addition

The effects of varying the amount of body feed addition are illustrated in Figs. 5 and 6. Figure 6 shows total throughput on the vertical axis versus percentage of body feed on the horizontal axis. As can be seen, the addition of too small an amount of body feed merely reduces the total throughput because the body feed is completely surrounded by undissolved solids and does not, therefore, increase cake permeability. This only increases the cake thickness without adding anything to its porosity. From this point, as body feed is increased, throughput also increases slowly, then rapidly for a short span of time. The rate of increase then tapers off, reaching a peak, after which it actually decreases once again because cake permeability is no longer increased with additional amounts of body feed.

The effects of excessive body feed are shown on Fig. 5. The sudden increase in pressure shown on curve 3 is the result of bridging of the cake between the leaves. This causes a sudden decrease in filter area. It can also result in severe damage to the leaves and loss of clarification.

4.2.3. Filtration Rate

Figure 7 shows the effects of flow rate on cycle length. For instance, at a flow rate of 0.1 gal/ ft^2/min, the filter will run for 480 min to a pressure of 30 lb. At twice that rate, the

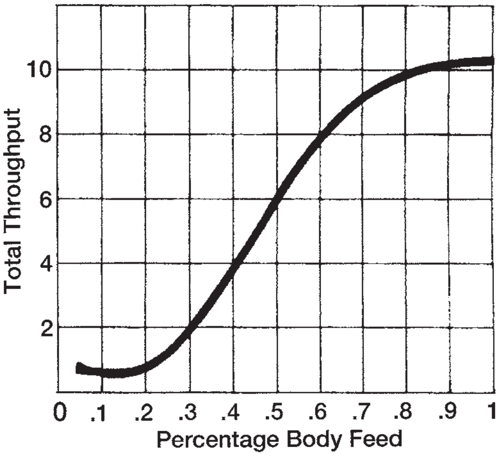


Fig. 6. Flow of same solution with different amounts of filter aid.

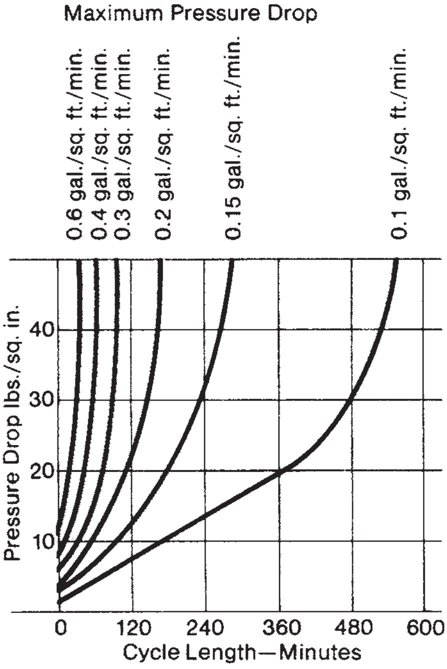


Fig. 7. Effect of flow rate on cycle length.

cycle length will be approx 150 min, slightly less than that dictated by filtration theory. When the maximum pressure drop of 50 lb per ft^2 is reached, the cycle is ended.

4.2.4. Bridging of Leaves and its Effects

Should cake bridging occur between leaves in pressure filters, unequal pressures on the leaves can cause severe warping. The amount of filter aid that can be added without bridging can be calculated from the cake capacity of the filter (area times cake thickness, allowing at least 0.25–0.5 in. between cakes) and the density of the filter aid and cake. For most filter aids use a density figure of 20 lb per ft^3 (320 kg per m^3) for diatomite. This will also equal the cake density because the solid impurities being removed will fit into the interstices of the filter aid particles. In almost all filtrations, except those removing activated carbons or clays, the cake density calculations will not be affected.

4.2.5. Filtration Troubleshooting

When the filter is put on-stream, clarity of filtrate should be immediate. If not, the trouble may be caused by any of the following conditions: (a) partially blinded septa; (b) air in feed liquid, loss of flow during switch-over from precoating to filtering, resulting in disruption of precoat; and (c) improper formation of precoat due to reasons given under Section 4.1.

Short cycles can be caused by temporary or permanent stoppage of body feed addition, blinded septa, changes in characteristics of the liquid being filtered, entrapment of air in the filter, which will decrease the filter area, and too high a filtration rate.

If baffling is nonexistent, or poorly designed, excessive turbulence may occur at localized areas on the septum, preventing formation of the precoat in these areas.

Flashing is the formation of bubbles at the septum–precoat interface causing a continual disruption of the precoat and resultant bleed through of filter aid. Flashing may be due to localized boiling or release of dissolved gases.

Excessive backpressure decreases the amount of pressure drop that should be available for filtration appreciably reducing cycle length. High backpressure may be avoided by the use of take-away pumps on the filter outlet. Care should be taken, however, to ensure that the take-away pump is not creating negative pressure on the outlet of the filter.

If inlet lines are too small, friction losses in these lines reduce the effectiveness of the feed pump. If outlet lines are too small, the same friction losses create excessive backpressure.

Care should be exercised particularly when filtering chilled aqueous solutions where ice may be formed or product can solidify in the outlet lines.

During any filtration, 100% solids removal is never accomplished on the first pass. After the precoat is formed, if recirculation is continued for an excessive period of time, more and more particles are taken out. These particles collect at the surface of the precoat and may in time form an impervious layer reducing off flow and increasing pressure.

4.3. Filter Cake Removal

At the end of the filtration cycle, the filter cake can be removed (Fig. 8) by one of the following methods:

(a) Backwash or bumping (for tubular element filters), see Fig. 8.
(b) Sluicing.
(c) Dry cake discharge by tapping or scraping the leaves or by mechanical vibration, after the filter heel has been blown from the filter and the cake blown dry.
(d) A combination of dry cake discharge and sluicing.
(e) For viscous liquids that are filtered hot, hot air or gas should be used to extract a maximum amount of liquid from the cake.

Whatever method of cake removal is used, it is extremely important that it be complete-otherwise septa will blind and the result will be inadequate filter performance. Practical

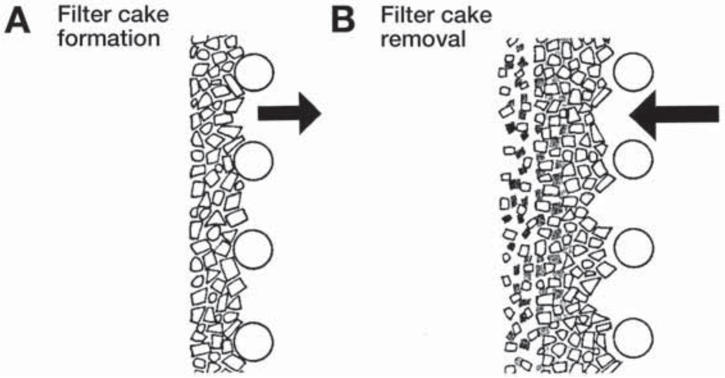


Fig. 8. Filter cake formation and its removal by backwash.

suggestions for cleaning clogged filter septa may be obtained by consulting your Filtration Specialist.

A wide variety of industrial filters are available for use with filter aids, each with its advantages and disadvantages. These all fall, however, into one of two basic classifications: (a) those which operate under pressure and (b) those which operate under vacuum.

5. DIATOMACEOUS EARTH FILTRATION SYSTEM MAINTENANCE

Operating a diatomaceous earth filter requires

- Preparation of filter body feed (diatomaceous earth) and precoat
- Verification of proper dosages
- Periodic backwashing
- Disposal of spent filter cake
- Periodic inspection of filter septum for cleanliness and damage
- Verification of the effluent quality

A common operating difficulty is maintaining a complete and uniform thickness of diatomaceous earth on the filter septum.

In some cases, alum precoating of the diatomaceous earth can improve performance. Typical alum doses range from 1% to 2% by weight (1–2 kg/100 kg of diatomaceous earth applied). Typical precoats of diatomaceous earth of 0.49–0.98 kg/m^2 (0.1 to 0.2 lb/ft^2) are applied to prepare the filter. These filters also require a continuous supplemental body feed of diatomite because the filter is subject to cracking. If the filter has no body feed, there will be rapid increases in headloss due to buildup on the surface of the filter cake. Body feed rates must be adjusted for effective turbidity removal. Diatomaceous earth filters do not need a filter-to-waste cycle, because of the precoating process.

Regular cleaning will maintain up to 95% of the filter septum area available for filtration after 100 filter runs. The filter cake drops off the septum during an interruption in flow, such as occurs during cleaning. During operating interruptions, clean diatomaceous earth and filter water should be used to recoat the filter to reduce the potential for passage of pathogens.

Filter runs typically range from 2 to 4 d. The rate of the body feed and the diatomite media size are critical in determining the filter run length. Shorter filter runs will minimize

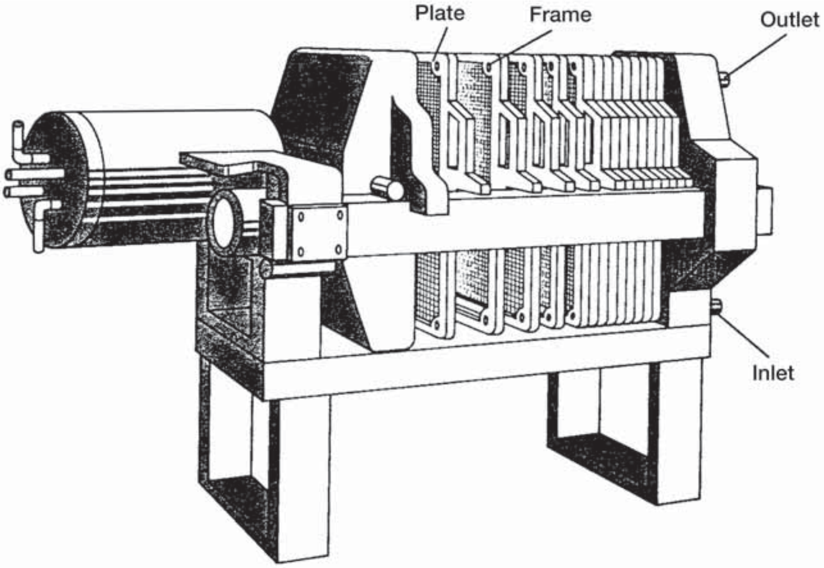


Fig. 9. Plate and frame filter.

filtered water odor and taste problems stemming from the decomposition of organic matter trapped in the filter.

Vacuum diatomaceous earth filters are a variation of this technology that offer the advantages of visibility during backwashing and of not requiring pressure vessels. Their primary disadvantage is that they run an increased risk of the release of gases in the filter cake that shorten filter runs.

6. TYPES OF PRECOAT FILTERS

6.1. Plate and Frame Filters

These filters (Fig. 9) have the advantages of low cost, near indestructibility, and ease of internal inspection. They have the lowest liquid volume-to-area ratio, which makes them most efficient for the washing of filter cakes. Because of this low ratio, they will also have the smallest unfiltered heel remaining at the end of the cycle.

Plate and frame filters (Fig. 9) are made in every conceivable combination of inlet and outlet positions; but for good precoating and filter aid suspension, they should have a bottom inlet and a top outlet, and in the larger sizes these should be at opposite ends of the filter. It is absolutely necessary that all air be purged from the filter before precoating is completed. This may be particularly difficult if gasketed filter septa are used. The Filtration Specialist can give the user details as to how to do this.

The capacity of these filters can frequently be increased by the installation of perforated metal or plastic sheets between the plates and septa. Either cloth or paper may be used for the latter. If paper is used, it is usually disposed of at the end of the cycle. The perforated sheets serve to keep the septum from sagging into the drainage grooves in the plate where it will reduce the capacity of the filter. Plate and frame filters are available with gasketed surfaces and mechanical leaf moving devices.

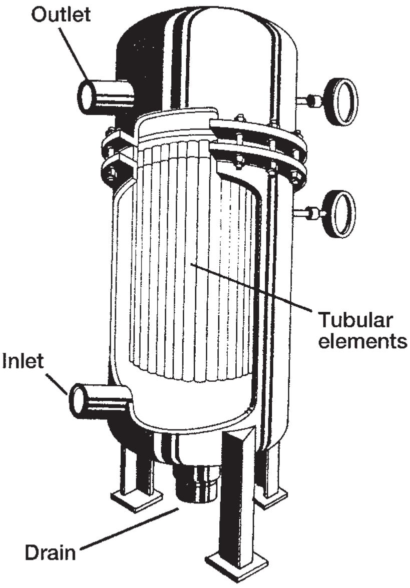


Fig. 10. Tubular filter.

The following pressure filters, varying in type and arrangement of elements, are those in which the elements are contained in a pressure vessel. They offer the advantages of lower labor costs and less opportunity for leakage, when compared to plate and frame filters.

6.2. *Tubular Filters*

Tubular filters (Fig. 10) offer low cost construction and high hydraulic capacities. They are made with both rigid and flexible tubes. Celite is used on the rigid tube filters in the usual combination of precoat and body feed. With flexible tube filters, instead of body feed, an extra heavy precoat [25–30 lb (11.4–13.6 kg) filter aid per 100 ft^2 (9.29 m^2) filter area] is used. After filter pressure has reached a maximum, the precoat is "bumped" from the tubes, re-slurried, then re-deposited. This sequence is repeated until pressure is no longer reduced significantly, at which time the "precoat" is discarded and a new one applied.

6.3. *Vertical Tank–Vertical Leaf Filters*

Among the pressure leaf filters, vertical tank–vertical leaf type (Fig. 11) is lowest in cost and has the lowest volume-to-area ratio. They are available for wet and dry cake discharge. Wet discharge is effected by means of a sluice, which in some filters oscillates to give more complete leaf coverage at the top of the leaves. Dry discharge is effected by blowing liquid from shell and cake, followed by removal of the cake from the leaves and filter. Vibrators may be used for this purpose. Large diameter, quick-opening doors are available for removal of the dry cake from the bottom of the filter. Whether the cake is sluiced or discharged dry, cake discharge lines should be large enough to prevent the cake from hanging up in the filter shell after it has been removed from the leaves.

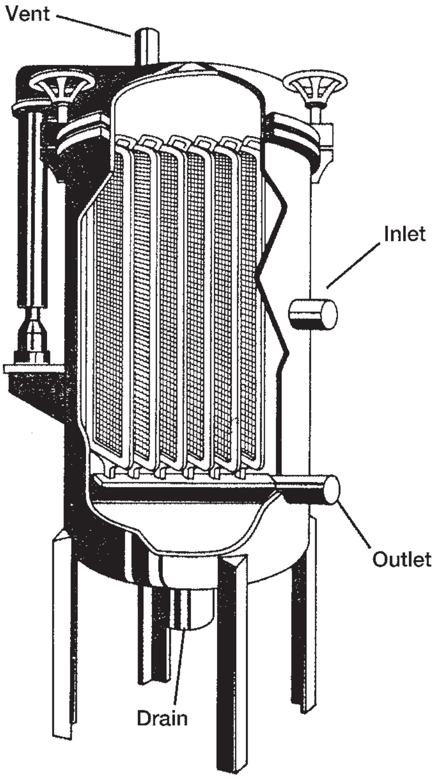


Fig. 11. Vertical tank–vertical leaf filter.

6.4. Horizontal Tank–Vertical Leaf ("H" Style) Filters

Because these filters (Fig. 12) are made so that the leaves can be rolled from the filter quickly, they can be easily inspected for tears in the septum, leaks around the edges of the screens or around the gaskets in the manifold, improper precoating, and so forth. If the cake is blown dry in the filter before the leaves are removed from the filter shell, the cake will usually remain on the leaves so that it can be discharged either manually or by means of a vibrator. Hydraulic capacity of the leaves is usually not a problem, because their size need not be excessively large for the larger areas.

For more efficient leaf cleaning, horizontal tank–vertical leaf filters are made with various types of movable sluices.

6.5. Rotating Leaf Filters

The rotating leaf filter (Figure 13) is particularly adapted for installations where the cake is very difficult to remove by sluicing. It is designed so that the leaves can be rotated with the sluice sprays on, allowing the entire area of the leaf to receive the full force of the sluice jet. If it is undesirable to mix the entire cake with sluice liquid, the bulk of the cake can be vibrated off the leaves first and removed from the filter shell, after which the remaining cake can be sluiced off.

Direct sluicing of all parts of the leaf is also obtained in some filters by the use of moving sluices (Fig. 14).

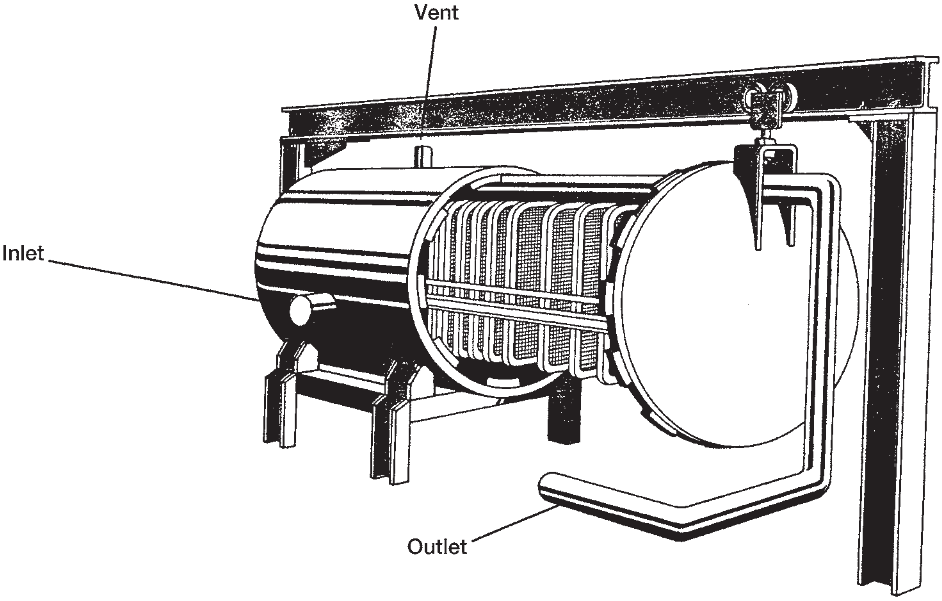


Fig. 12. Horizontal tank–vertical leaf filter.

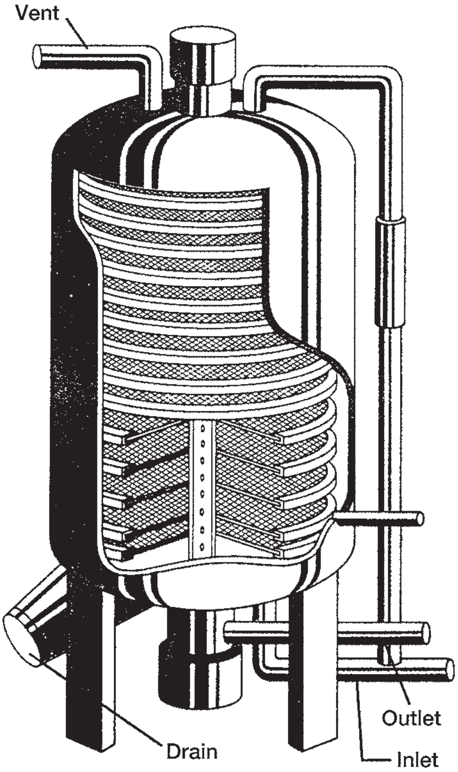


Fig. 13. Rotating leaf filter (centrifugal discharge).

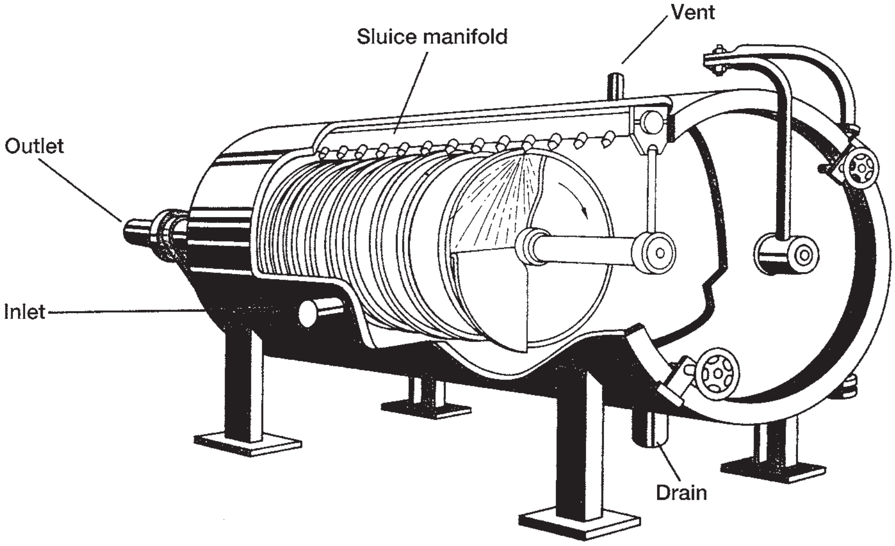


Fig. 14. Rotating leaf filter (sluice type).

6.6. *Horizontal Leaf Filters*

All the filters described so far have the cake held on the filter element by means of a differential pressure across the element, set up by the flow of liquid through the element. Operation must, therefore, be continuous for good filtration. Where operation is intermittent, the horizontal leaf filter can be used to advantage. This filter may be designed so that the leaves and septa are assembled as a unit outside the filter, or with rotating leaves in the filter for discharge by a stationary sluice. In the former, paper is generally used as the filter septum. This type filter (Fig. 15) is generally used as a polish or guard filter where solids loading is low and cycles are relatively long.

6.7. *Specialty Filters*

There are a number of specially designed filters such as horizontal tray filters with tilting leaves for cake discharge, filter heel filtration with scavenger leaves, and others. These filters are all more expensive than the standard filters but are adapted to certain specialized applications. For instance, scavenger leaves are in general not too successful because they usually become so coated with sediment that it takes too long to filter the liquid heel through them. During this time, of course, the entire filter is tied up. A better solution, if the unfiltered heel cannot be blown back to the filter feed tank, would usually be to employ a small plate and frame filter for this purpose.

There are two types: (a) the vacuum leaf filter and (b) the rotary vacuum precoat filter (Figs. 16 and 17).

6.8. *Vacuum Leaf Filters*

This filter has leaves, or tubes, arranged vertically in an open tank, and connected to a discharge manifold. Liquid is drawn through the filter elements by a pump connected to the discharge manifold. Vacuum leaf filters have advantages of low cost (no pressure vessel) and ease of inspection.

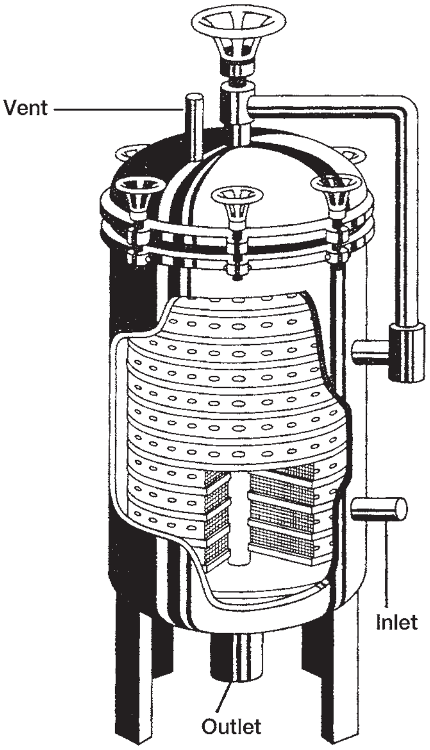


Fig. 15. Horizontal leaf filter.

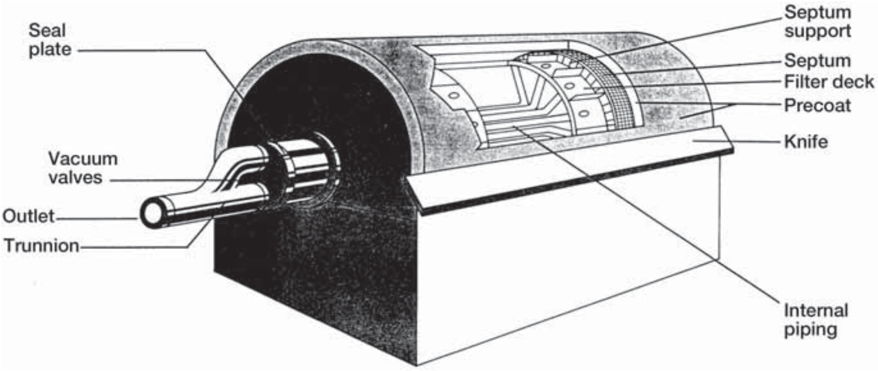


Fig. 16. Rotary precoat filter.

6.9. Rotary Vacuum Precoat Filters

There are some liquids with solids so slimy that it is impossible to filter them on a pressure or vacuum leaf filter. Other liquids contain such a high volume of solids that the filters described previously would quickly become filled with cake, resulting in an uneconomical amount of time spent in cleaning and precoating. The rotary vacuum precoat filter was designed to meet these conditions.

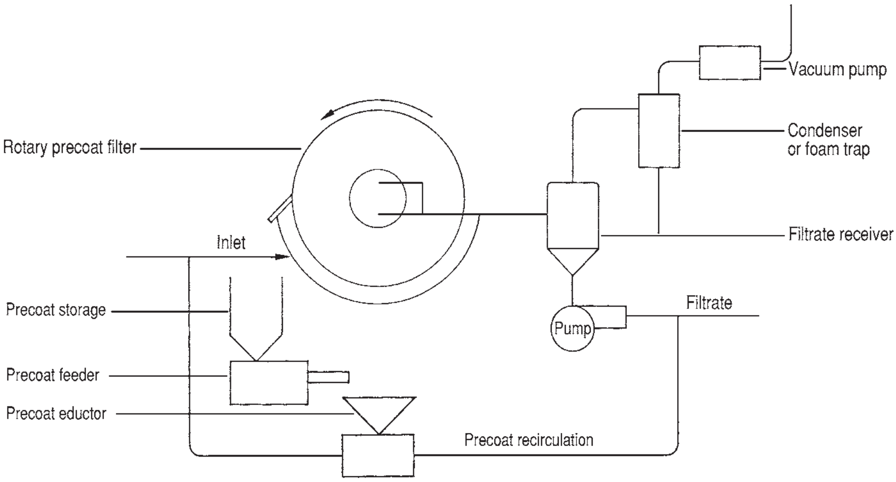


Fig. 17. Schematic of rotary precoat filter system.

6.9.1. Precoating the Rotary Vacuum Precoat Filter

Precoating techniques recently developed by Manville can substantially increase filtration efficiency in terms of reduced precoat usage and increased flow rate.

The filter consists of a horizontal drum, 30–50% of which is submerged in the unfiltered liquid. The drum is covered with a septum capable of retaining filter aid. Vacuum is applied to the surface of the drum by means of internal piping, which emerges through the drum trunnion and valve on one end of the filter.

From the valve, the filtrate goes to a receiver where liquid and air (or other gas) are separated, the liquid usually being removed by a centrifugal pump on the bottom of the receiver, and the gas by a vacuum pump and/or condenser.

6.9.2. Operating the Rotary Vacuum Precoat Filter

In operation, a precoat of filter aid up to 6 in. thick is built up on the drum by pumping a slurry of filter aid from a precoat tank through the filter and either back to the precoat tank or on to the process. After the precoat is built up, unfiltered liquid is introduced into the filter. As the drum rotates, a blade running across the face of the drum above the liquid level continually advances toward the drum, peeling off solids plus a very small amount of precoat. This continues until the knife is within 1/4–3/8 in. (6.3–9.5 mm) of the drum, at which time the drum is cleaned and precoated again.

For the most economical operation of a rotary precoat filter, a number of factors must be considered:

A. Drum speed
B. Drum submergence
C. Drying time
D. Differential pressure
E. Knife advance rate
F. Filteraid grade
G. Cake filterability
H. Liquid viscosity

Variables A, B, and C are closely related and should be optimized as a group. During filtration, as the drum rotates, filtered solids build up on the surface of the precoat forming a cake. The thickness and, therefore resistance of the cake will be inversely related to drum speed. The filtration rate is inversely related to cake thickness. Thus, the higher the drum speed the lower the cake resistance and the higher the filtration rate. For any given drum speed, the submergence should be at the maximum level that will result in a dry cake or that is permitted by the filter design.

Higher drum speeds, however, mean more frequent shaving of the precoat by the blade. To maintain rates, the precoat must be cut to a depth below that which solids have penetrated, and therefore partially blinded, the precoat. A grade of precoat material must be selected, then, to minimize this cake penetration. If this is done, it is possible to take a small enough cut to maintain precoat filter aid economy at high drum speeds and filtration rates.

With the correct combination of these variables, it is frequently possible to increase filtration efficiency severalfold.

7. AUXILIARY PARTS AND EQUIPMENT

7.1. Precoat Filter Leaves

The shape and construction of filter leaves varies widely. Basically, there are two types: three-ply and five-ply. The three-ply leaf consists of a center drainage member (which may be a coarse wire mesh screen or any of a variety of expanded or punched metals) covered by a metal or cloth septum on each side. The five-ply leaf consists of a heavy backing material with a finer mesh screen or perforated metal sheet on either side covered by a cloth or metal septum. The following precautions must be made:

- Leaves should be rigid and free from flexing as filtration pressure increases. Any movement of the leaf during filtration will form cracks in the filter cake and permit unfiltered liquid and filter aid to bypass the precoat.
- The filter septum should be applied tightly (especially in the case of wire cloth) so that no wrinkles or movement of the septum can occur during filtration.
- The septum should be securely attached to the edge of the leaf so that bypassing of unfiltered liquid cannot occur and so that the septum cannot work loose.
- Leaf design should provide for good drainage at the edge of the leaf to prevent accumulation of solids inside the leaf, and for adequate discharge capacity so as not to form more than 0.5 psi backpressure during normal precoating and filtration rates.

The main function of the septum, or screen, is to support the filter aid, which, as we have seen, actually does the filtering. A heavy dense septum is therefore not necessary except where there may be cake instability due to pressure fluctuations or other outside influences. If the cake is discharged dry and is thick or heavy, a strong septum should be used.

Septa are made in such a great variety of materials that a discussion of all available types is beyond the scope of this chapter. In general, septa should have:

- Good dimensional stability.
- Adequate strength to bridge over openings in the backing screen or plate without stretching.
- Uniform openings of larger cross section than the precoat channels or openings.

Septa may be made of metal, natural, or synthetic yarns. Plain, twill, and dutch weaves are available in the metal cloths. In the natural and synthetic fiber cloths, plain, twill, chain, and satin weaves in monofilament, multifilament, and staple yarns have been used.

Generally, any septum having an opening of less than 0.005 in. should be satisfactory for the medium flow rate filter aids. In metal cloths the most commonly used weave is 24 × 110 single dutch with 0.016 in. × 0.011 in. wire. A 60 × 60 twill with 0.011 in. wire and a 70 × 80 twill with 0.007 in. wire are also satisfactory. Keep in mind that mesh does not necessarily indicate the size opening; it also depends upon the wire diameter.

With natural and synthetic fibers, going from plain through twill to satin weave, cake retention is increased. Discharge characteristics, resistance to blinding, and flow rate decrease in the same order. The same order of events also takes place when going from monofilament through multifilament to staple yarn.

7.2. Filter Feed Pumps

Centrifugal pumps are almost universally used for feeding filters because they produce no pulsations to disturb the filter cake. These pumps, however, have two disadvantages: (a) their high speed (which tends to break down any large flocculated solids, making them more difficult to filter) and (b) their decrease in delivery as pressure increases.

To minimize degradation of impurities, low-speed (1800 rpm) pumps with open impellers should be used. Where solids are large and floc-like, it may be advisable to use a recessed impeller centrifugal pump or a multistage piston pump with suitable air-cushioning chambers. Reciprocating pumps should have ball valves. Gear or rotary pumps may be used where solids are not abrasive and filter aid is not present.

All filter feed pumps should operate under a positive head to prevent suction of air into the filter feed liquid.

7.3. Precoat and Body Feed Tanks

These tanks should be equipped with sweep-arm agitators rotating at approx 50 rpm or slow-speed, large-bladed, propeller-type agitators. Filter aid, once in suspension, is easy to keep in suspension. Tanks should have dished, coned, or slanted bottoms so that all liquid can be drained from the tank and so that in the precoat operation a minimum heel can be maintained during circulation of liquid between the precoat tank and the filter.

Precoat tanks should be 125% of the filter's volume (including connecting piping) so that a small heel, giving rapid turnover, remains in the tank after the filter is filled with precoat slurry. The return line from the filter to the precoat tank should be to the bottom of the tank to prevent aeration of the heel. Baffles should be installed, if necessary, to prevent vortexing so that air will not draw back into the filter. The tank should be high enough above the precoat circulating pump, and the line to the pump should be large enough to provide positive pressure on the suction side of the pump.

7.4. Body Feed Systems

Body feed addition may be dry or in slurry form. Slurry concentrations can be as high as 18% but are best kept at 5–10% for lowest pump maintenance. Whatever system is used, it should have the following properties:

- Low maintenance.
- Constant feed rate from minute to minute.

- Have a means of regulating the rate of body feed addition while the system is running. Feed rate should be constant at each setting.
- No degradation of the filter aid. (Systems which require constant recirculation of slurry over long periods of time are likely to do this and are, therefore, not recommended.)

Body feed pumps work best if run continuously, recirculating back to body feed tank only when the filter is off-stream for cleaning. Piston pumps should have ceramic pistons, and flush-out connections on packings may be desirable. Outlets on single outlet diaphragm pumps should be at the bottom of the diaphragm chamber to prevent accumulation of filter aid in the chamber.

7.5. Automation Equipment

With equipment now available, it is possible to completely automate a filtration station. By simply pressing a button, the filter can be

- Precoated and drained
- Filled
- Put on-stream
- Drained with cake in place after differential pressure reaches a predetermined limit
- Filled with wash liquid and the cake washed
- Drained
- Cleaned of cake by any of the methods previously discussed

During the operation, protection can be provided against the following contingencies, among others:

- Incomplete filling in any phase of the filter operation
- Filter going on-stream before precoat clears up
- Poor clarity when on-stream
- Low or high pressures
- Too thick filter cakes
- Power failures

The decision to automate should be based on the same reasoning as was applied to the automation of any other operation. Because automation reduces or eliminates cleaning and precoating labor costs, it may be economical to reduce filter area and go to shorter cycles, increasing throughput per square foot. Against this must be weighed the disadvantages of shorter filtration cycles and higher filter aid costs.

8. BULK FILTER AID HANDLING

Bulk orders of filter aids are shipped in 40-ton to 50-ton pressure differential cars. The filter aid is generally conveyed from the car to a storage tank of from 75 to 100 tons capacity, using a conventional air conveying pressure system. From the storage tank it may be conveyed to any location within several hundred feet.

In California, bulk truck shipments are available. These units are provided with self-contained unloading equipment and can be emptied into a storage silo by the driver. A manufacturer's Filtration Specialist should be available to give customers further information on bulk handling systems and on unloading bulk cars. Additional information may be obtained on request from your filter aids suppliers (6).

Table 4
2005 Capital and Operation and Maintenance Costs of Diatomaceous Earth Filtration for Water Treatment

Category	Plant capacity, MGD	Average flow, MGD	Capital cost, $1000	Operation and maintenance costs $1000/yr[a]	Operation and maintenance costs ¢/1000 gal	Total costs, ¢/1000 gal
1	0.026	0.013	442	12	354	1346
2	0.068	0.045	570	16	88	454
3	0.166	0.130	748	40	84	270
4	0.50	0.40	1140	60	42	134
5	2.50	1.30	3146	256	54	132
6	5.85	3.25	5076	428	36	86
7	11.59	6.75	8866	738	35	75
8	22.88	11.50	21,426	1524	34	74
9	39.68	20.00	31,964	2330	32	73
10	109.90	55.50	75,466	5460	27	70

[a] Processes include pressure diatomaceous earth filtration units, diatomaceous earth feed equipment; filtered water storage clearwell; and sludge dewatering lagoons. A separate administration, lab, and maintenance building is included in Categories 5 through 10. Sludge pumps are included in the package facilities used in Categories 1 through 4, but separate sludge pumping stations are included in Categories 5 through 10. Categories 8 through 10 include sludge holding tanks, sludge dewatering with filter presses, and hauling of dewatered solids to land disposal.

1 MGD = 0.044 m^3/sec; 1000 gallons = 3.78 m^3.

9. PRECOAT FILTRATION APPLICATIONS, ADVANTAGES, AND DISADVANTAGES

9.1. Municipal and Military Applications

Diatomaceous earth filtration is a well-established water treatment process. It performs well on groundwater with high concentration of iron and manganese, or on surface waters with low influent turbidity, acceptable color, and bacteria levels. Effective removals of viruses and *Giardia* range up to 99.95% and from 99% to 99.99%, respectively.

Costs for diatomaceous earth filters are provided in Table 4. Costs vary depending on plant size.

Some researchers have found that diatomaceous earth filters, with added operational steps, are effective in removing polioviruses. The additional steps include coating the filter surface with filter aid or mixing the filter influent with a cationic polymer. The limited research found

- No viruses were detected in 11 effluent samples from a 12-h run of a filter coated with 1 mg of cationic polymer per gram of diatomaceous earth.
- Only 1 of 12 effluent samples contained viruses during the operation of another filter coated with 1 mg of cationic polymer per gram of diatomaceous earth.
- No viruses were detected in the effluent in 12 samples from another 12-h run of an uncoated filter, and the influent was mixed with 0.14 mg of cationic polymer per liter of water.

Table 5
Comparison of Diatomaceous Earth Filtration with Other Filtration Processes

Technological options to meet regulatory requirements	Stage of acceptability	Size suitability	Comments
Conventional filtration	Established	All	Most common; adaptable for adding other processes
Direct filtration	Established	All	Lower cost alternative to conventional filtration
Slow sand filtration	Established	Especially small, but all sizes	Operationally simple; low cost, but requires large land areas
Package plant filtration	Established	Mostly small	Compact; variety of process combinations available
Diatomaceous earth filtration	Established	Mostly small	Limited applicability; potentially expensive for small systems
Membrane filtration	Established	Mostly small	Expensive
Cartridge filtration	Emerging	Small	Expensive

Accordingly under certain environmental situations, DE filtration can be better than other filtration processes. The US Environmental Protection Agency (3) has reviewed seven filtration options for potable water treatment:

- Conventinal filtration
- Direct filtration
- Slow sand filtration
- Package plant filtration
- Diatomaceous earth filtration
- Membrane filtration (reverse osmosis)
- Cartridge filtration

The performance of each filter type depends on the quality of the influent and proper design and operation. The range of influent characteristics for which various filters are effective has been provided by the US EPA (3) in Tables 5 and 6. According to the two tables, DE filtration is an established process mostly for small water systems with good influent quality (less than 5 NTU turbidity, less than 5 color units, and less than 50/100-mL coliform count) and low influent capacity (below 100 MGD). The removal capacities for *Giardia* cysts and viruses of the above seven filter systems are presented in Table 7. It is important to note that DE filtration is better than conventional filtration and direct filtration in terms of removal efficiency of *Giardia* cyst and viruses.

Diatomaceous earth filtration systems have been successfully adopted by the US Army for both potable water supply and wastewater treatment in the battle field since 1970s (7–9,15,16).

9.2. Industrial Applications

Diatomaceous earth filter aids are widely used in industrial filtration operations, and have evolved as an integral part in many other processes. Besides turbidities naturally occurring as a result of processing, diatomaceous earth filter aids are used to remove

Table 6
Typical Influent Raw Water Characteristics and Capacities of Seven Filtration Technologies for Water Treatment

Filtration Options	Turbidity (NTUs)	Color (in color units)	Coliform count (per 100 mL)	Typical capacity (MGD)
Conventional	No restrictions	<75	<20,000	>All sizes
Direct	<14	<40	<500	>All sizes
Slow sand	<5	<10	<800	<15
Package plant		[depends on processes utilized]		<6
Diatomaceous earth	<5	<5	<50	<100
Membrane	<1	[fouling index of <10]		<10
Cartridge	<2	NA	NA	<1.0

NA = not available.
1 MGD = 0.044 m^3/s.
Source: US EPA.

Table 7
Percent Removal Capacities of Seven Filtration Technologies (Percent Removal) for Water Treatment

Filtration Options	Achievable *Giardia* cyst levels	Achievable virus levels
Conventional	99.9	99.0
Direct	99.9	99.0
Slow sand	99.99	99.9999
Package plant	Varies with manufacturer	
Diatomaceous earth	99.99	>99.95
Membrane	100	Very low
Cartridge	>99	Little data available

Source: US EPA.

catalysts, stabilization chemicals, adsorbents, and turbidity produced as a result of chillproofing. Listed here are just a few of the products that are being filtered by one particular filter aid supplier's products (Celite). No attempt is made to state the grade and amounts of filter aids as these can vary up to 10-fold for the same product at different locations. A Filtration Specialist can assist in determining the type and amount of filter aid for a customer's specific application.

Typical industrial applications of diatomaceous earth and diatomaceous earth filters include:

- Antibiotics
- Fruit and vegetable juices
- Alginates
- Animal oils
- Vegetable oils
- Waxes
- Dairy products
- Gelatin
- Bleaching compounds
- Titanium dioxide muds
- Drycleaning solvents
- Lube oils
- Industrial wastes
- Rolling mill oils
- Cutting oils
- Jet fuels
- Process
- Municipal
- Waste
- Boiler
- Condensate
- Cane sugar
- Beet sugar
- Corn sugar

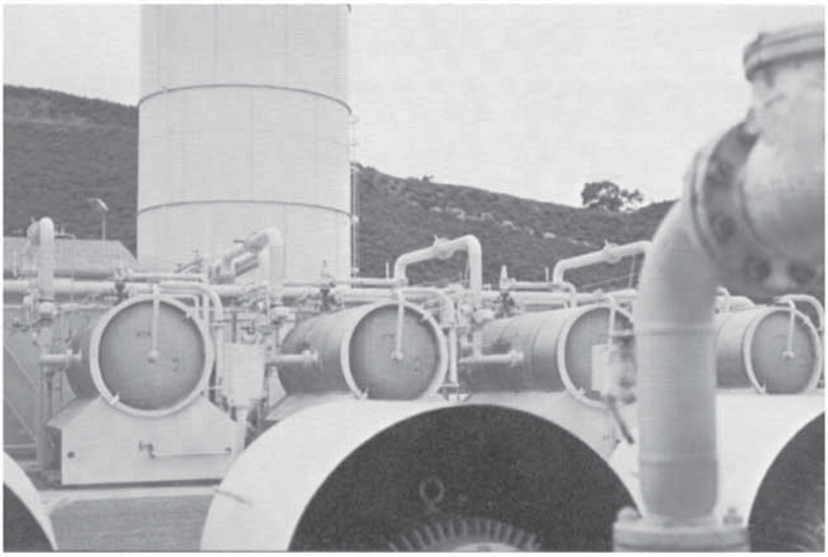


Fig. 18. Multiple DE filtration system filtering water for secondary recovery of oil.

- Inorganic chemicals
- Brine
- Sodium hydroxide
- Gold salts
- Magnesium salts
- Potassium salts
- Organic chemicals
- Acids sulfuric
- Phosphoric
- Varnishes
- Lacquers
- Water
- Beverages
- Beer
- Wine
- Soft drinks
- Fruit juices
- Spirits

Figure 18 shows a full scale multiple unit DE filtration system used for filtering water for secondary recovery of oil. A new DE filtration system has been developed specifically for industrial applications (17).

9.3. *Advantages and Disadvantages*

According to Cleasby and Logsdon (11), where the source water and other conditions are suitable, DE filtration can offer a number of benefits to the user, including the following:

1. Capital cost savings may be possible because of smaller land and plant building requirements.
2. Treatment costs may be slightly less than conventional coagulation/sedimentation/granular media filtration when filterable solids are low (11–13), although sedimentation would not usually be needed for such high-quality source waters.
3. The DE process is entirely a physical/mechanical operation and can attain high log removals of *Giardia* cysts and *Cryptosporidium* oocysts without operator expertise in water chemistry relating to coagulation (3,4,10,11,19–26).
4. The waste residuals are easily dewatered and in some cases may be reclaimed for other uses, including soil conditioning and land reclamation. Research is under way to determine the feasibility of reusing filter medium as body feed (7–10).
5. Acceptable finished water clarity is achieved as soon as precoating is complete and filtration starts. A filter-to-waste period is generally not necessary to bring turbidity of the finished water within acceptable limits.

6. Terminal turbidity breakthrough is not generally observed because precoat filtration is dominantly a surface filtration process.

The disadvantages of precoat filtration are

1. A continued cost is associated with purchase and disposal of the filter medium, which is usually discarded at the end of each filter cycle.
2. DE filtration is less cost-effective for waters that require pretreatment for algae, color, and taste and odor problems or DBP precursor removal. Waters containing only larger plankton such as diatoms can sometimes be treated economically by microstraining prior to the DE filtration.
3. Proper design, construction, and operation are absolutely essential to prevent the filter cake from dropping off of the septa or cracking during operation, which could result in the system failing to remove the target particulates (19–26).

10. SUMMARY

Exposure to microbial contaminants such as bacteria, viruses, and protozoa were the primary remaining health-risk-management challenge for water suppliers and the general public. In a recent US EPA rule, the Interim Enhanced Surface Water Treatment Rule (IESWTR), which was finalized on December 6, 1998, the US EPA acknowledged that public water systems that use surface water or groundwater under the influence of surface waters, must take steps to protect the public. This immediately impacts water systems that serve more than 10,000 inhabitants; however, small communities will need to comply with the Long Term I Surface Water Treatment Rule. Some of the requirements of the IESWTR are (a) Maximum contaminant level goal (MCLG) of zero for *Cryptosporidium;* (b) 2 log *Cryptosporidium* removal requirements for systems that filter; (c) strengthen combined filter effluent turbidity performance standards; and (d) inclusion of *Cryptosporidium* in the definition of groundwater under the influence of surface water.

There are several filtration technologies that can be utilized to meet the US EPA requirements outlined in the IESWTR and what is anticipated to be finalized for small systems. However, DE filtration should be at the top of the list when considering microbial removal, capital costs, operating cost, and ease of operation. DE is a proven and approved technology for the filtration of potable water.

In the US EPA publication “Small System Compliance Technology List for the Surface Water Treatment Rule (SWTR) and Total Coliform Rule (1CR)” (September 1998), DE is a specifically approved filtration technology for compliance with the SWIR. In its comments the US EPA notes that DE is “very effective for the removal of *Giardia* and *Cryptosporidium*” (23).

The US EPA further notes that “since chemical coagulation is not required, DE filtration is very attractive as a small system technology and it has been used successfully by small systems for years.” Although the US EPA defines “small communities” as those with a population of less than 10,000 inhabitants (approx 2 million-gallons per day, or 2 MGD), DE water filtration plants in excess of 10 MGD capacity are operated very successfully (23).

The potential efficiencies of DE filtration for removal of *Cryptosporidium* have been extensively evaluated by many researchers (14–27). The completed study determined that with DE filtration, greater than 6 logs (99.9999%) of reduction in the concentration of *Cryptosporidium* oocysts can be routinely expected (27).

The results of the laboratory study performed by Ongerth and Hutton (22) confirmed that greater than 6 logs (99.9999%) of *Cryptosporidium* oocyst reduction can be achieved not only at the traditional 1 gallon per minute per square foot (gpm/ft^2) operation, but also at a higher rate of 2 gpm/ft^2.

11. GLOSSARY OF DIATOMACEOUS EARTH FILTRATION (PRECOAT FILTRATION) (1,5)

Absolute: A degree of filtration that guarantees 100% removal of suspended solids over a specified particle size.

Absorb: To take up a liquid, like a sponge takes up water.

Activated Carbon: An adsorbent carbon which removes dissolved color, odor and taste, metals, etc., from liquids or gases.

Activated Clay: An adsorbent clay that removes color, odor and free fatty acids, etc., from oils and tallows.

Admix: A substance that is added directly into the batch tank of prefilt to create a permeable filter cake. Usually used in place of body feed.

Adsorb: The act of selectively attracting and holding a gas, vapor, liquid, or colloid onto the surface of a solid.

Amorphous: Noncrystaline. Having no ordered molecular structure of its own.

Area: The surface available in a filter for the passage of liquid and formation of a filter cake. Usually measured in square feet.

Atm: Atmosphere. A measurement of pressure. The air pressure at sea level; 14.7 psi.

Attrition: Breaking down or wearing away by friction. Usually as particle to particle degradation in a diatomite slurry.

Backwash: A reverse flow of liquid to remove solids from the filter.

Baffle: A plate or deflector to provide flow distribution in a filter. Primary functions are to prevent erosion of precoat and setting of body feed in the filter tank.

Blinding: Plugging or sealing of any portion of a filter septum by solids that are not removed during the normal cleaning cycle.

Blind Spots: Any place on a filter septum where liquid cannot flow through due to blinding.

Blowdown: The use of air or inert gas pressure to displace a liquid out of a filter. Usually through the filter cake. Continued blowdown is used to dry a filter cake *in situ*.

Body Feed: A filter aid product, such as CELITE, that is continuously added to the filter while it is on-stream. Its purpose is to create a permeable filter cake.

Bridging: (a) The act of particles forming an arch over the operiihgs on a septum. (b) Filter cakes that have grown to a size where they actually touch each other in the filter.

Cake: The accumulation of solids (and the filter aid, such as CELITE) on the surface of a precoat or septum.

Cake Space: The volumetric space available in a filter to support the formation of a cake.

CELITE: Manville's registered trade name for its line of diatomaceous earth filter aids and fillers (5).

Cellulose: A fibrous material of vegetable origin.

Clarity: Clearness of a liquid as measured by a variety of methods.

Cloth: A type of woven filter septum made from natural or synthetic yarns.

Colloid: Very small, insoluble nondiffusable solid or liquid particles that remain in suspension in a surrounding liquid. Solids usually on the order of 0.2 µm or less.

Compressibility: Degree of physical change in suspended solids (or filter cake) when subjected to pressure.

Contact Time: The length of time an adsorbent is in contact with a liquid prior to being removed by the filter.

Cycle: The length of time a filter is "on-stream" before cleaning is needed. Frequently meant to include cleaning time as well.

D'Arcy: A measurement of filter cake permeability. Named after the French mathematician that first developed the equation.

DE: A commonly used abbreviation for diatomaceous earth.

Deformable: Used to describe suspended solids that extrude into the intersticies of a filter cake and cause rapid filter plugging.

Density: The weight of a given volume of filter aid or its filter cake. Usually measured in pounds per cubic foot (pcf). Can be measured wet or dry.

Diatomite: An abbreviation of diatomaceous earth.

Diatomaceous Earth: The fossilized skeletons of minute, prehistoric aquatic plants.

Differential Pressure: The difference in pressure between the upstream and downstream sides of a filter or filter cake.

Dissolved Solids: Any solid material that will dissolve in the liquid that is being filtered, such as sugar in water. Diatomaceous earth filtration does not remove these solids.

Doctor Blade (knife): A sharp, hard blade that cuts the cake off the surface of a filter. Usually found on rotary vacuum precoat filters.

Effluent: Any liquid that is discharged from a factory, waste treatment facility or filter. Frequently used erroneously to mean filtrate.

Element: Any structural member in a filter on which the septum is supported; may be round, rectangular, or cylindrical.

Feed: The mixture of solids and liquid that enters the filter. Synonyms; prefilt influent and incoming slurry.

Filter: *(Verb)* To pass a liquid containing solids through a filter medium whereby the solids and liquid are separated from each other. *(Noun)* A device for containing the filter media.

Filter Aid: Any material that assists in the separation of solids from liquids. Usually used on difficult filtration applications.

Filter Medium: The permeable material that separates particles from a fluid passing through it.

Filter System: The combination of a filter and associated hardware required for the filtration process.

Filtrate: Any liquid that has passed through the filter media. Sometimes erroneously called effluent.

Filtration: The process by which solid particles are separated from a liquid by passing the liquid through a permeable material.

Filtration Rate: The volume of liquid that passes through a given area of filter in a specific time. Usually expressed as gallons per square foot per minute (or hour).

Flow Rate: The unit rate at which a liquid is passed through a system. Usually expressed in gallons per minute (or hour).

Frazier: A test to measure the air permeability of filter septums. Expressed in cfm or air at a pressure drop of 1/2 in. WC.

Friable: Easily crushed or crumbled.

Gelatinous: Used to describe suspended solids that are slimy and deformable, causing rapid filter plugging.

GSFM: Abbreviation for gallons per square foot per minute. Also GSFH for hour.

GPH: Abbreviation for gallons per hour.

GPM: Abbreviation for gallons per minute.

Heel: (a) The liquid left in a filter shell at the end of a cycle. (b) The precoat left on a RVPF at the end of its cycle.

Hydrophilic: Water accepting.

Hydrophobic: Water rejecting.

Intersticies: Any void spaces in and around solid particles that are packed together.

Leaf: Any flat filter element that has or supports the filter septum.

Liquor: Material to be filtered-as in "feed liquor."

Manifold: A pipe or assembly into which the filter elements are connected to form one common discharge for the filtrate.

Media (medium): The material that performs the actual separation of solids from liquids. Sometimes erroneously used to mean septum.

Membrane: Media through which a liquid is passed; usually associated with a very fine or tight type of filtration.

Mesh: (a) Number of strands in a lineal inch of woven filter fabric. (b) A commonly used synonym for septum, as in wire mesh.

Micron: Now expressed as micrometer (μm). A unit of length; 10^{-6} meters or 39/1,000,000 in.

Monofilament: A single synthetic fiber of continuous length; used in weaving filter cloths.

Multifilament: A number of continuous fiber strands that are twisted together to form a yarn; used in weaving filter cloths.

Nonwoven: A filter cloth or paper that is formed of synthetic fibers that are randomly oriented in the media. Usually held together with a binder.

On-stream: Describes when a filter system is producing a filtered product.

Particle Size Distribution: The distribution obtained from a particle count grouped by specific micron sizes.

Permeability: The property of the filter medium that permits a fluid to pass through under the influence of a pressure differential.

pH: Potential hydrogen. A measurement of the acidity of alkalinity of a substance. A pH of 7.0 is neutral.

Plate: Any flat surfaced filter element. Usually found in horizontal plate filters.

Porosity: The ratio of the void volume to the total bulk volume.

ppm: Parts per million. A unit of concentration; e.g., 3 ppm would be 3 pounds of solids in 1,000,000 pounds of water.

Precoat: The initial layer of CELITE that is deposited on the filter septum. Usually 1/8 in. thick on pressure filters and 2–6 in. thick on RVPF.

Prefilt: Material to be filtered.

RVPF (Rotary Vacuum Precoat Filter): A drum filter that is coated with a thick (up to 6 in.) precoat of filter aid, such as CELITE or equivalent.

Scavenger: A filter, or element in the bottom of a filter, that recovers the liquid heel that remains in a filter tank at the end of the cycle.

Screen: A term commonly used for septum.

Septum: Any permeable material that supports the filter media.

Slurry: Any liquid containing suspended solids.

Sp. G. (Specific gravity): The weight of any substance relative to the weight of water (water Sp. G. = 1.0).

Suspended Solids (S.S.): Solids that do not dissolve in liquid; those solids that remain suspended and can be removed by filtration.

Suspension: Any liquid containing undissolved solids, such as a filter aid (such as CELITE) slurry.

Turbidity: Any insoluble particle that imparts opacity to a liquid.

Voids: The openings or pores in a filter medium.

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6

Tertiary Microscreening

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CONTENTS

1. INTRODUCTION

Wastewater treatment systems can be classified, in addition to pretreatment, as preliminary, primary, secondary, and tertiary (advanced) treatments. Pretreatment of industrial wastewater is required to prevent adverse effects on the municipal wastewater treatment plants. Preliminary treatment is considered as any physical or chemical process that precedes primary treatment. The preliminary treatment processes may consist of influent screening and grit removal. Its function is mainly to protect subsequent treatment units and to minimize operational problems. Primary treatment is defined as the physical or chemical treatment for the removal of settleable and floatable materials. The screened, degritted raw wastewater from preliminary treatment flows to the primary clarification tanks, which are part of the primary treatment facilities. Secondary wastewater treatment is the process that uses biological and chemical treatment to accomplish substantial removal of dissolved organics and colloidal materials. The secondary treatment facilities may be comprised of biological reactor and secondary clarification basins. Tertiary (advanced) wastewater treatment is used to achieve pollutant reductions by methods other than those used in primary and secondary treatments. The objective of tertiary wastewater treatment is to improve the overall removal of suspended solids, organic matter, dissolved solids, toxic substances, and nutrients.

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Several tertiary treatment unit operations have been used to achieve high overall treatment efficiencies beyond the secondary treatment process. Microscreening is one of these treatment units. In this chapter, the tertiary treatment will be focused on microscreening. Microscreening is an effective device to remove additional suspended solids and associated biochemical oxygen demand. It involves the use of variable low-speed, continuously backwashed, rotating-drum screens operating under gravity-flow conditions. To design microscreening units, several factors have to be considered including (1):

1. Characteristics, concentration, and degree of flocculation of suspended solids (including flocs).
2. Capacity to meet maximum hydraulic loadings with critical solids characteristics.
3. Performance requirements over the expected range of hydraulic and solids loadings.
4. Provisions of backwash and cleaning facilities to maintain the capacity of the screens.

Microscreening has mostly been used as a tertiary treatment process for filtering effluents from biological waste treatment systems (2,3). The process has also been used in some other applications such as treatment of combined sewer overflows, aquaculture recycling flow (4), and hatchery wastewater (5), as well as for algal removal in water and tertiary wastewater treatment (6–8). However, algal species change with the seasons. Sometimes they may be collected very well with the microstrainer, while, at other times, the sizes or shapes may result in poor or no collection. It has also been reported that algal cells could clog filter pores in microscreens and thus reduce their run time (8).

2. MICROSCREENING PROCESS

Microscreening is a method of filtration that uses fabric as the filtering medium. Microscreens (microstrainers) usually consist of a special metallic or plastic fabric mounted on the periphery of a revolving drum. The untreated water flows into the drum and radiates outward through the microfabric, leaving behind the suspended solids removed by the cloth. The solids retained on the inside of the rotating screen are carried upward to a row of backwash jets that flush them into a hopper, which is mounted on a hollow axle of the drum, for return to the treatment plant.

Individual microscreening manufacturers have specific designs and sizes for various types of installations, and much of the design information is proprietary in nature. Design elements required for microscreening include (9):

1. Hydraulic loading.
2. Solids inputs.
3. Solids characteristics.
4. Microscreen fabric.
5. Backwash.
6. Head loss.

Tables 1 and 2 (10) summarize the microscreen sizes available from two manufactures. A schematic of a microstrainer appears in Fig. 1.

3. DESIGN CRITERIA

According to The Colorado Department of Public Health (11), the design of microscreening should take the following into consideration:

1. The nature of the suspended matter to be removed.
2. The effect of chlorination, when required as pretreatment.

Table 1
Microscreens Removal from Secondary Effluents

Fabric Aperture (μm)	Anticipated removal (%) Suspended solids	BOD	Flow (gpm/ft^2) of submerged area
23	70–80	60–70	6.7
35	50–60	40–50	10.0

Table 2
Microscreen Sizes from Glenfield and Kennedy

Drum sizes (ft)		Motors (bhp)		Approximate ranges of capacity (MGD)	Recommended maximum flow for tertiary effluent applications (MGD)	
Diameter	Width	Drive	Wash pump		23 μm	35 μm
5	1	1/2	1	0.05–0.5	0.075	0.11
5	3	3/4	3	0.3–1.5	0.20	0.30
7.5	5	2	5	0.8–4	0.70	1.00
10	10	4	7.5	3–10	2.00	3.00

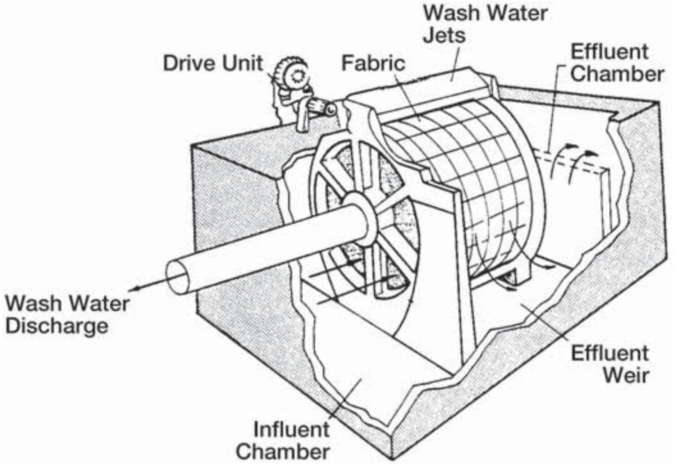

Fig. 1. Schematic of a microstrainer (Source: US EPA).

3. The corrosiveness of the water and the provision of a durable, corrosion-resistant screen.
4. By-pass arrangements.
5. The proper disposal of wash water.

Microscreens have been designed for an application rate not to exceed 10.0 gpm/ft^2 of submerged screen area at design maximum flow (12). Multiple units can be used, and all units should be protected against freezing. Typical opening sizes for microscreens are 23, 35, and 60 μm. In a study at Lebanon, OH (13), suspended solids removals of 89% and 73% were obtained with 23- and 35-μm fabrics, respectively. Studies at the

Table 3
Microscreens Sizes from Zurn Industries

Drum sizes (ft)		
Diameter	Width	Screen area (ft^2)
4	2	24
4	4	48
6	4	72
6	6	108
6	8	144
10	10	315

Chicago Sanitary District (14) reported an effluent suspended solids of 6–8 mg/L and a BOD of 3.5–5 mg/L when applying a good quality (suspended solids = 20–25 mg/L and BOD 15–20 mg/L) activated sludge effluent to a 23-µm screen. Removal efficiencies as recommended for secondary effluents are presented in Table 3 (10). The efficiency of a microstrainer is determined by the hydraulic and solids loadings as well as by the filtering characteristics of the influent. Microstrainers will not remove colloidal material or small (micron-size) algae. Microstrainers are also adversely affected by fluctuations in influent composition and quality.

The allowable head loss and the character and concentration of suspended solids in the feed limit the rate of flow through the screens. Varying the drum speed in proportion to the differential head across the screen hydraulically controls the microscreening units. The controlling speed is commonly set to have 15 ft/min at 3 in. differential and 125–150 ft/min at 6 in. (12). Typical loading rates of 2.5–10 gpm/ft^2 of submerged drum surface area have been reported. The study at Chicago (14) reported an upper limit on hydraulic loading of 6.5 gpm/ft^2. The solids loading was the limiting design factor with an upper limit of 0.88 lb/ft^2/d. Head loss across the microscreening unit, including inlet and outlet structures, is limited to 12–18 in. for normal flows and to 6 in. for peak flows.

The operating drum submergence is related to the effluent water level and head loss through the fabric. The minimum drum submergence value for a given installation is the level of liquid inside the drum when there is no flow over the effluent weir. The maximum drum submergence is fixed by a bypass weir, which permits flows in excess of unit capacity to be bypassed; at maximum submergence, the maximum drum differential should never exceed 15 in.

Effluent and bypass weirs should be designed as follows (12):

1. Select drum submergence level (70–75% of drum diameter) for no flow over the effluent weir.
2. Locate top of effluent weir at selected submergence level.
3. Determine maximum flow rate.
4. Size effluent weir to limit liquid depth in effluent chamber above the weir to 3 in. at the maximum flow rate.
5. Position the bypass weir 9–11 in. above effluent weir (3 in. head on effluent weir maximum flow plus 6–8 in. differential on drum at maximum drum speed and maximum flow).
6. Size bypass weir length to prevent the level above effluent wire flow exceeding 12–18 in. at peak maximum flow or overflowing the top of the backwash collection hopper.

4. BACKWASHING

In backwashing, water jets are pointed against the outside of the microscreen drum as it passes the highest point in its rotation. Half of the flow penetrates the fabric and removes the solids formed on the inside. A hopper inside the drum receives the flushed-off solids. Microscreen effluent can be used for backwashing. The continuous backwashing jets require 3–5% of the total throughput volume. Straining is required to avoid clogging of backwash nozzles. The inline strainers used for this purpose will require periodic cleaning; the frequency of cleaning will be determined by the quality of the backwash water.

In a study (15) the cleaning efficiency was found to be dependent on the fabric nominal size, screen speed, and backwash pressure. Cleaning efficiency was found to increase with increasing fabric nominal pore size to a maximum level of 90–95% at a pore size of 16.5 μm and then to decrease slightly with increasing fabric cleaning efficiency of 85%. Cleaning efficiency was independent of pressure in the range of 15–35 psig and of speed in the range of 14.0–25.8 ft^2/min. In any case, pilot-scale microscreening study is recommended for any specific application in order to develop the needed performance data with the water under consideration.

The backwash system used by Zurn, for instance, employs two header pipes; one operates continuously at 20 psi, while the other operates at 40–55 psi. Under normal operating conditions, these jets operate at 35 psi. Once a day they are operated at 50 psi for 30 min to keep the jets free of slime buildup. Should this procedure fail to keep the jets clean, the pressure is raised to 55 psi. At this pressure the spring-loaded jet mouth widens to allow for more effective cleaning.

Backwash pressure can be increased to compensate for heavy solids loadings, which require higher pressure for thorough cleaning. The superiority of the higher-pressure system is manifested by the following (12):

1. Operation at 50 psi, as opposed to 15 psi, increases the process flow capacity 30%.
2. Suspended solids concentration in the backwash can increase from 260 mg/L at 15 psi to 425 mg/L at 50 psi.
3. Water consumption of the jets as a percentage of process effluent decreases from 5% at 15 psi to 2% at 50 psi. In general, backwash systems are operated at as low a pressure as possible consistent with successful cleaning. High-pressure operation incurs added system maintenance, particularly jet replacement, and is used only as needed.

Operating problems that have been reported for microscreens include slime growths, oil and grease accumulation, and the possible buildup of iron and manganese on the screen. To prevent clogging, cleaning methods in addition to backwashing are necessary. Ultraviolet light, chlorine solutions, acid solutions, and hot water have been used as cleaners (2,9,12,16).

1. *Ultraviolet lamps*. They reduce clogging from algal and slime growth; the use of ultraviolet lamps placed in close proximity to the screening fabric and monthly removal of units from service to permit screen cleaning with a mild chlorine solution is recommended. While most literature sources say ultraviolet lamps are of value, one authority feels these lamps are uneconomical because they require frequent replacement. Zurn Industries claim that, because their screening fabric is completely bonded to the supporting material, crevices where algae become lodged are eliminated and backwashing alone is sufficient to remove algal and associated slime growths.

2. *Hot water.* Where oil and grease are present, hot water and/or steam treatment can be used to remove these materials from the microscreens. Plastic screens with grease problems are cleaned monthly with hot water at 1200°F to prevent damage to the screen material. Downtime for cleaning may be up to 8 hours.

In starting a microscreening unit, care should be taken to limit differential water levels across the fabric to normal design ranges of 2–3 in. For example, while the drum is being filled, it should be kept rotating and the backwash water should be turned on as soon as possible. This is done to limit the formation of excessive differential heads across the screen that would stress the fabric during tank fillup. Leaving the drum standing in dirty water should be avoided because suspended matter on the inside screen face that is above the water level may dry and prove difficult to remove. For this reason, introducing unscreened waters, such as plant overloads, into the microscreen effluent compartment should also be avoided. If the unit is to be left standing for any length of time, the tank should be drained and the fabric cleaned to prevent clogging from drying solids (17).

5. DESIGN OF MICROSCREENS

The design procedure for microscreens is detailed in the following steps (18).

5.1. Input Data

(a) Wastewater flow:
   1. Average flow, MGD
   2. Peak flow, MGD

(b) Suspended solids concentration, mg/L.
(c) Effluent requirements, mg/L.

5.2. Design Parameters

(a) Head loss across microscreen, in., ≈6 in. water.
(b) Initial resistance of clean filter fabric, in ft, at a given temperature and standard flow conditions. Manufacturer's requirements.
(c) Filterability index of influent measured on fabric in use (volume of water obtained per unit head loss when passed at a standard rate through a unit area of standard filter). From laboratory study.
(d) Speed of strainer (number of square feet of effective fabric entering water in given time), ft^2/min (14.0–25.8 ft^2/min).
(e) Constants: $m = 0.0267$; $n = 0.1337$.

5.3. Design Procedure

Utilize the Boucher concept of filterability index (19).

(a) Calculate the effective submerged area of the screen.

$$A = \frac{mQC_f e^{nIQ\times10^6/24(60)S} \times 10^6}{H(24)60} \qquad (1)$$

where A = effective submerged area, ft^2; $m = 0.0267$; Q = total rate of flow through unit, MGD; C_f = initial resistance of clean filter fabric, ft, at a given temperature and standard flow conditions (manufacturer's requirements) (1.8 ft for 23-μm, 1.0 ft for 35-μm screen);

$n = 0.1337$; I = filterability index of influent measured on fabric in use (laboratory) = 0.5; S = speed of strainer, ft^2/min; H = head loss across microscreen, in., ≈6 in.

(b) Calculate hydraulic rate of application.

$$\mathrm{HR} = \frac{(Q)(10^6)}{(A)(24)(60)} \tag{2}$$

where HR = hydraulic rate, gpm/ft^2; Q = total rate of flow through unit, MGD; and A = effective submerged area, ft^2.

(c) Calculate solids rate of application.

$$\mathrm{SR} = \frac{(Q)(C_i)(8.34)}{A} \tag{3}$$

where SR = solids loading rate, lb/ft^2/d; Q = total rate of flow through unit, MGD; C_i = influent suspended solids, mg/L; and A = area submerged, ft^2.

(d) Calculate amount of backwash water.

$$\mathrm{BW} = (3\text{–}6\%)(Q)\ (10^6) \tag{4}$$

where BW = backwash rate, gpd; Q = total rate of flow through unit, MGD.

5.4. *Output Data*

(a) Effective submerged area, ft^2.
(b) Hydraulic rate of application, gpm/ft^2.
(c) Solids rate of application, lb/ft^2/d.

6. ENERGY AND COSTS

The annual energy consumption by microscreens is shown in Fig. 2 (9). Electrical energy requirements include backwash water pumping and screen drive (10).

The microscreens construction and operation and maintenance costs (1979 dollars, Utilities Index = 257.20) are illustrated in Figs. 3 and 4, respectively (9). To obtain the values in terms of the present 2004 US dollars, using the Cost Index for Utilities (Appendix A), multiply the costs by a factor of 506.13/257.20 = 1.97 (20). The costs are based on the following assumptions:

1. Construction costs include tanks, drums, screens, backwash equipment, drive motors, and building.
2. Instrumentation for automatic operation is included. The design basis is as follows:
   a. Hydraulic load = 2.5 gpm/ft^2 at average flow.
   b. Screen mesh = 25 µm.
   c. Peripheral drum speed = 15 ft/min at 3 in. head loss.
   d. Backwash is 3 % of throughput at 35 psi.

7. DESIGN EXAMPLE

(a) Calculate the effective submerged area of the screen (18):

$$A = \frac{mQC_f e^{nIQ\times10^6/24(60)S} \times 10^6}{H(24)60}$$

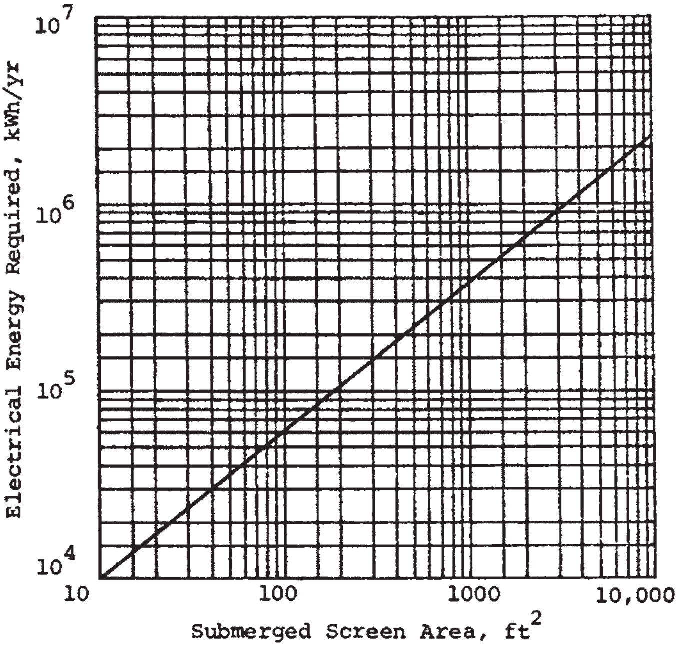

Fig. 2. Microscreens energy consumption (Source: US EPA).

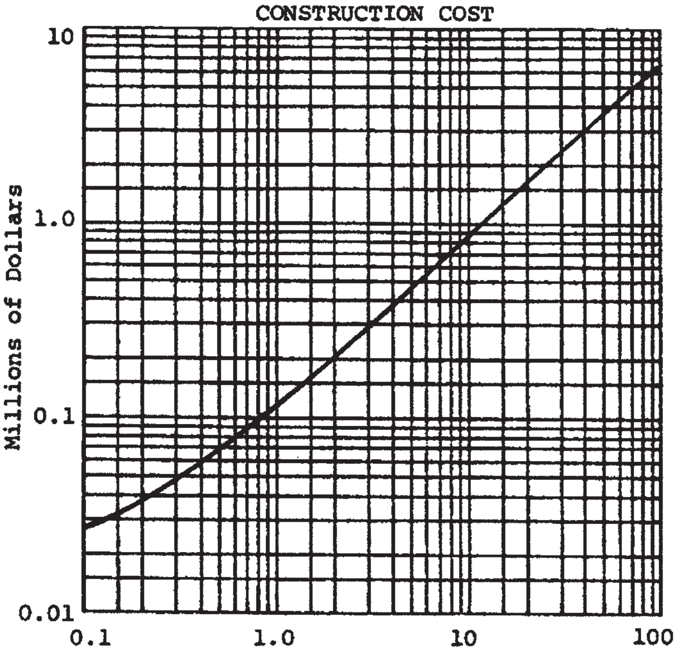

Fig. 3. Microscreens construction cost (Source: US EPA).

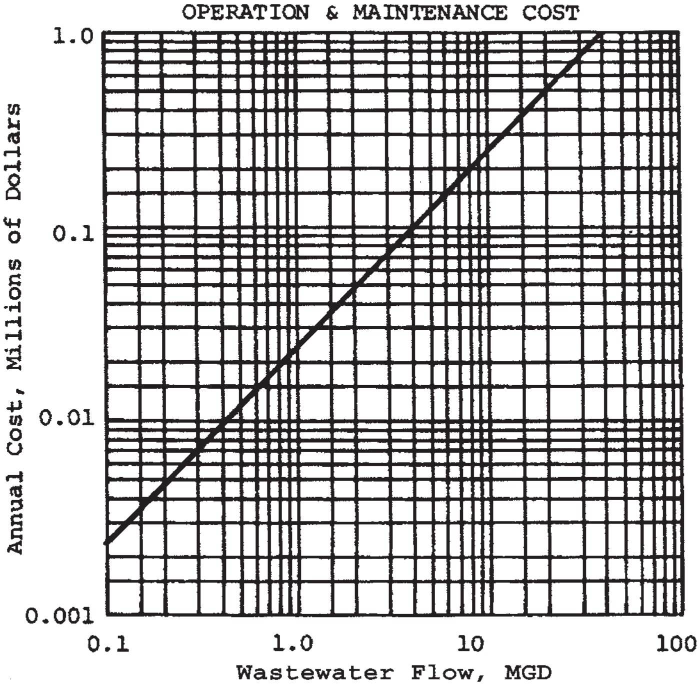

Fig. 4. Microscreens operation and maintenance costs (Source: US EPA).

where A = effective submerged area, ft^2; m = constant, 0.0267; Q = flow, 1 MGD; C_f = initial resistance, 1.8 ft (23-µm fabric); n = 0.1337; I = filterability index, 0.5; S = speed of strainer, 20 ft^2/min; H = head loss across microscreen, in., 6 in.

$$A = \frac{0.0267(1)1.8e^{0.1337(0.5)1\times10^6/24(60)20}\times10^6}{6(24)60}$$

$$= 56.7 \text{ ft}^2$$

(b) Calculate hydraulic rate of application (18):

$$\text{HR} = \frac{(Q)(10^6)}{(A)(24)(60)}$$

where HR = hydraulic rate, gpm/ft^2; Q = flow, 1 MGD; A = effective submerged area, 56.7 ft^2:

$$\text{HR} = \frac{1\times10^6}{56.7(24)60}$$

$$\text{HR} = 12.25 \text{ gpm/ft}^2$$

Note: HR exceeds recommended limit of 6.5 gpm/ft^2; therefore, recalculate area using HR = 6.5 gpm/ft^2.

$$A = \frac{(Q)(10^6)}{(\text{HR})(24)(60)}$$

$$= \frac{(1)(10^6)}{(6.5)(24)(60)}$$

$$= 106.8 \text{ ft}^2$$

(c) Calculate solids rate of application (18):

$$\mathrm{SR} = \frac{(Q)(C_i)(8.34)}{A} \tag{3}$$

where SR = solids loading rate, lb/ft^2/d; Q = flow rate through unit, MGD; C_i = influent suspended solids, 20 mg/L; A = area submerged, 106.8 ft^2:

$$\mathrm{SR} = \frac{1(20)8.34}{106.8}$$
$$\mathrm{SR} = 1.56\ \mathrm{lb/ft^2/d}$$

Note: SR exceeds recommended limit of 0.88 lb/ft^2/d; therefore, recalculate area using SR = 0.88 lb/ft^2/d.

$$\begin{aligned} A &= \frac{Q(C_i)8.34}{\mathrm{SR}} \\ &= \frac{1(20)8.34}{0.88} \\ &= 189.5\ \mathrm{ft^2} \end{aligned}$$

(d) Calculate amount of backwash water (18)

$$\mathrm{BW} = \frac{\%(Q)10^6}{100}$$

where BW = backwash rate, gpd; % = percent, 4; Q = flow, 1 MGD

$$\begin{aligned} \mathrm{BW} &= \frac{4(1)10^6}{100} \\ &= 40{,}000\ \mathrm{gpd} \end{aligned}$$

NOMENCLATURE

A	effective submerged area, ft^2
BW	backwash rate, gpd
C_f	initial resistance of clean filter fabric, ft, at a given temperature and standard flow conditions (manufacturer's requirements)
C_i	influent suspended solids, mg/L
H	head loss across microscreen, in.
HR	hydraulic rate, gpm/ft^2
I	filterability index of influent measured on fabric in use (laboratory)
m	0.0267
n	0.1337
Q	total rate of flow through unit, MGD
S	speed of strainer, ft^2/min
SR	solids loading rate, lb/ft^2/d

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APPENDIX

United States Army Corps of Engineers Yearly Average Cost Index for Utilities (20)

Year	Index	Year	Index
1967	100	1986	347.33
1968	104.83	1987	353.35
1969	112.17	1988	369.45
1970	119.75	1989	383.14
1971	131.73	1990	386.75
1972	141.94	1991	392.35
1973	149.36	1992	399.07
1974	170.45	1993	410.63
1975	190.49	1994	424.91
1976	202.61	1995	439.72
1977	215.84	1996	445.58
1978	235.78	1997	454.99
1979	257.20	1998	459.40
1980	277.60	1999	460.16
1981	302.25	2000	468.05
1982	320.13	2001	472.18
1983	330.82	2002	484.41
1984	341.06	2003	495.72
1985	346.12	2004	506.13

7

Membrane Filtration

J. Paul Chen, Honghui Mou, Lawrence K. Wang,
and Takeshi Matsuura

CONTENTS

1. INTRODUCTION

With the rapid increase of demand in industries and daily life, water has become an increasingly valuable but scarcer resource for human being. Take Singapore as an example. Almost half of its water supply is being imported from Malaysia. The daily water consumption has risen eight times while the population has only grown three times since 1950 (1). This increase has led to a greater pressure on the use of limited raw water resources and the capacity of treatment plants. The potential shortfall between supply and consumption needs to be addressed if domestic and industrial customers are to continue enjoying uninterrupted supply.

Apart from the continuous searching for new water sources from other neighboring countries via diplomatic routes, the Singapore government has already decided to encourage the use of desalinated seawater as an alternative water source in Singapore. However, compared with the seawater desalination, reclamation and reuse of raw wastewater and secondary effluent using membrane technology seems more cost-effective and is becoming a potential challenge to conventional seawater desalination for water production (2).

Today, membrane separation technologies are widely used in many areas of water and wastewater treatment. Membrane processes can be used to produce potable water from

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surface water, groundwater, brackish water, or seawater, or to treat industrial wastewaters before they are discharged or reused. At the same time, membrane technologies have moved into the area of treating secondary or tertiary municipal wastewater and oil field–related water. Membrane separation systems have many advantages over traditional water or wastewater treatment processes, including (1–12):

- Fewer chemicals are used in the process, which helps minimize the negative impacts of those chemicals on the whole process.
- Formation of absolute barriers to particle and pathogens. Microorganisms such as bacteria and viruses can be removed by size exclusion; ultra-pure water can therefore be produced.
- Lower operating and maintenance costs in comparison to conventional systems consisting of coagulation, clarification, and aerobic and anaerobic treatments.
- Membrane separation systems are easy to operate and the performance is more reliable.
- Membrane systems give a compact and modular construction, which occupies less floor space in comparison to the conventional treatment systems. This becomes extremely attractive in the land-scarce countries such as Japan and Singapore.
- Membrane systems followed by an evaporator (for low-volume highly concentrated effluent) can enable industries to achieve zero liquid discharge goals.
- One-stop reduction or elimination of most contaminants (impurities) in the wastewater stream, e.g., total dissolved solids (TDS), chemical oxygen demand (COD), 5-d biochemical oxygen demand (BOD_5), total organic carbon (TOC), color, suspended solids, nitrogen, phosphorus, and heavy metals.
- Permeate can be suitably reused resulting in water conservation, which reduces the intake of raw water and provides savings on raw water processing costs.

Membrane fouling can significantly compromise the performance of the membrane process (4–6,12). Therefore, pretreatment of feed water and cleaning of fouled membranes are important to the overall achievement of the membrane process.

In this chapter, we will introduce fundamental concepts of the membrane and membrane-separation processes, such as membrane definition, membrane classification, membrane formation, module configuration, transport mechanism, system design, and cost evaluation. Four widely used membrane separation processes in water and wastewater treatment, namely, microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO), will be discussed in detail. The issue of membrane fouling together with its solutions will be addressed. Several examples will be given to illustrate the processes.

2. MEMBRANE AND MEMBRANE-SEPARATION PROCESSES FOR WATER TREATMENT

The membrane is essentially a barrier, that separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogeneous or heterogeneous, symmetric or asymmetric, solid or liquid; it can carry positive or negative charges or can be neutral. Transport through a membrane can be affected by convection or by diffusion of individual molecules, and induced by the chemical gradient or electrical gradient.

2.1. *Basics of Membrane and Membrane-Separation Systems*

According to a definition given by the European Membrane Society, the membrane is an intervening phase separating two phases and/or acting as an active or passive barrier

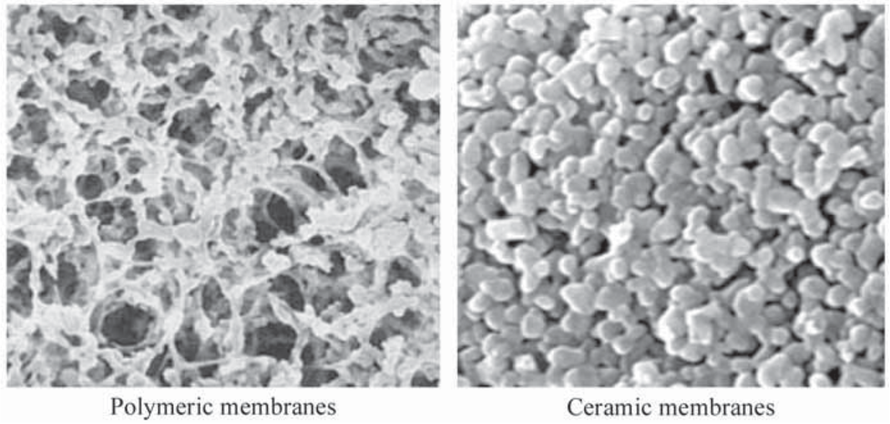

Fig. 1. Pictures of polymeric and ceramic membranes.

to the transport of matter between phases (3). Basically, it is a thin layer that can separate materials depending on their physical and chemical properties when a driving force, either a gradient of chemical potential (concentration or pressure gradient) or electrical potential, is applied across the membrane.

Some basic requirements for membranes are

- High flux of the product
- Good mechanical strength for supporting the physical structure
- Good selectivity for the desired substances

Generally, high selectivity is related to membrane properties, such as small pores and high hydraulic resistance or low permeability. It can be compromised by a broad pore size distribution. The permeability increases with increasing density of pores, and the overall membrane resistance is directly proportional to its thickness. Therefore, a good membrane must have a narrow range of pore sizes, a high porosity, and a thin layer of material.

Membranes can be either dense or porous. Separation by dense membranes relies on physicochemical interaction between the permeating components and the membrane material. Porous membranes, on the other hand, achieve separation by size exclusion, where the rejected material may be either dissolved or suspended depending on its size relative to that of the pore (3).

Membranes can be organic (polymeric) or inorganic (ceramic or metallic), according to its composition, and their morphology is dependent on the nature of the material, as shown in Fig. 1.

A membrane-separation system separates an influent stream into two effluent streams: the permeate and the retentate or concentrate, as shown in Fig. 2. The permeate is the portion of the fluid that has passed through the membrane. The retentate (concentrate) contains the constituents that have been rejected by the membrane.

2.2. *Membrane-Separation Processes for Water Treatment*

There are various types of membrane-separation processes for water treatment, as shown in Fig. 3; the details of the four major processes, MF, NF, UF, and RO, will be

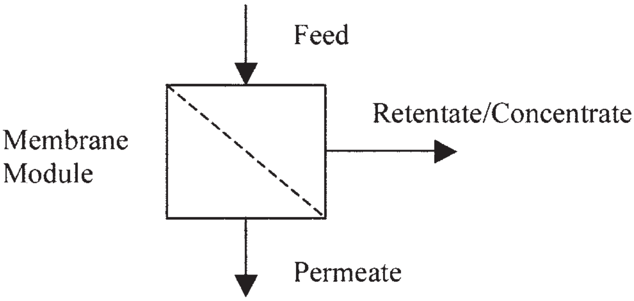

Fig. 2. Basic diagram of a membrane-separation system.

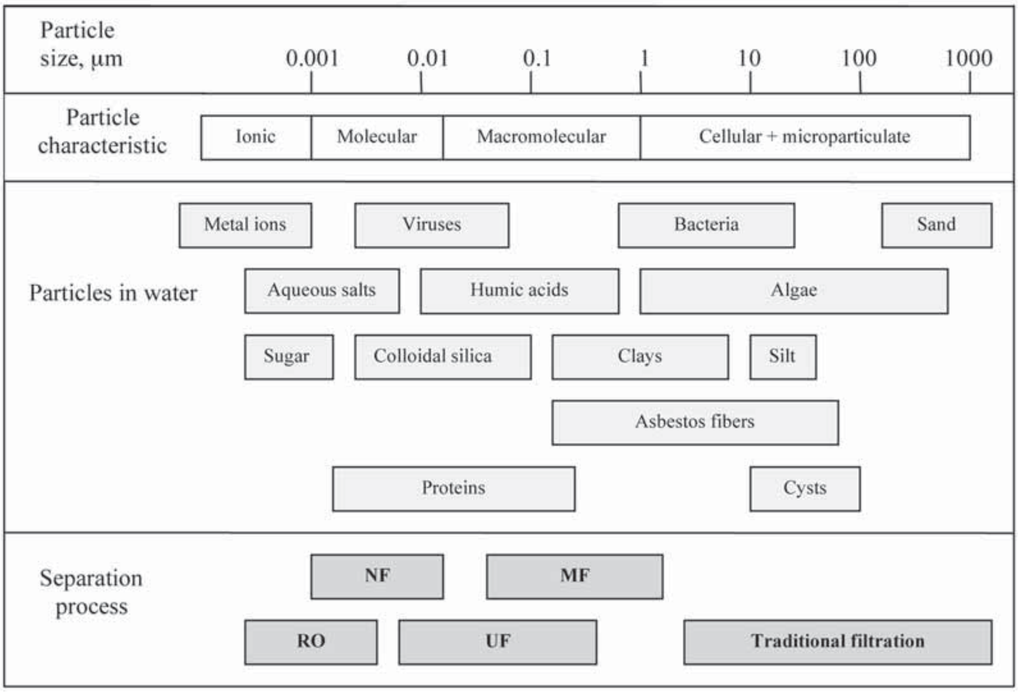

Fig. 3. Application range of various membrane processes.

discussed here. Feed quality and quantity, requirement of products (e.g., permeate or reject), ease in operation, and costs determine the selection of the process (4–24). The applied pressure for typical membrane filtration processes is given in Table 1.

2.2.1. *Microfiltration*

Microfiltration (MF) is a membrane-filtration process that removes micron-sized particles from fluids. MF membrane has pore sizes ranging from 0.1 to 10.0 µm, through which microorganisms cannot pass. As a result, microfilters can be used to disinfect water solutions. For example, the smallest bacterium *Pseudomonas diminuta* with a diameter of 0.3 µm can be disinfected by a MF membrane with smaller pore sizes. On the other hand, both organic and inorganic substances are able to pass through MF membranes.

Table 1
List of Applied Pressure for Typical Membrane Filtration Processes

Membrane processes	Pressure (atm)
RO – Seawater	54.4–68.0
RO – Waste and process	20.4–40.8
RO – Water purification	13.6–23.8
RO – Undersink (home)	3.4
NF	6.8–13.6
UF	1.7–10.2
MF (crossflow)	0.7–1.7

While the mechanism for conventional depth filtration is mainly adsorption and entrapment, MF membranes use a *sieving mechanism* with distinct pore sizes for retaining particles larger than the pore diameter. Hence, this technology offers membranes with absolute rating, which is highly desirable for critical operations such as sterile filtration of parental fluids, sterile filtration of air, and preparation of particulate, ultra-pure water for the electronics industry.

The MF membranes are usually made from natural or synthetic polymers such as cellulose acetate (CA), polyvinylidene difluoride, polyamides, polysulfone, polycarbonate, polypropylene, and polytetrafluoroethylene (PTFE) (13). Some of the newer MF membranes are ceramic membranes based on alumina, membranes formed during the anodizing of aluminium, and carbon membrane. Glass is being used as a membrane material. Zirconium oxide can also be deposited onto a porous carbon tube. Sintered metal membranes are fabricated from stainless steel, silver, gold, platinum, and nickel, in disks and tubes. The properties of membrane materials are directly reflected in their end applications. Some criteria for their selection are mechanical strength, temperature resistance, chemical compatibility, hydrophobility, hydrophilicity, permeability, permselectivity and the cost of membrane material as well as manufacturing process.

Two process modes, namely, dead-end and cross-flow modes, are widely used for microfiltration (14). For the dead-end mode, the entire solution is forced through the membrane. The substances to be separated are deposited on the membrane, which increases the hydraulic resistance of the deposit. The membrane needs to be renewed as soon as the filtrate flux no longer reaches the required minimum values at the maximum operation pressure. This mode is mostly used for slightly contaminated solutions, e.g., production of ultra-pure water. For the cross-flow mode, the solution flows across the membrane surface at a rate between 0.5 and 5.0 m/s, which prevents the formation of a cover layer on the membrane surface. A circulation pump produces the cross-flow velocity or the shear force needed to control the thickness of the cover layer. The system is most widely used for periodic back flushing, where part of the filtrate is forced in the opposite direction at certain intervals, and breaks up the cover layer. The normal operating pressure for this mode is 1–2 bars.

An MF has a wide range of applications in water and wastewater treatment. The most promising opportunity for MF is the treatment of municipal water, allowing it to be disinfected without any disinfectants such ozone and chlorine. A recent study showed that MF membranes can also remove viruses from contaminated surface water. Because viruses are much smaller than the pores in a MF membrane, the finding has been attributed to the viruses being adsorbed on the clay particles, which are large enough to be caught by the microfilter (16). Treatment of municipal sewage is a potential market for MF. Engineers have tried to shift the treatment of sewage to distributed processing, which consists of many small sewage treatment facilities. MF can be used to remove heavy metals from waste streams if pretreatment chemicals are added to precipitate the metals to particles of filterable size. Although conventional methods of wastewater treatment may use a similar pretreatment mechanism, the final solid/liquid separation by gravity settling is usually not as effective as membrane filtration. A promising process for the removal of heavy metal ions from aqueous solutions involves bonding the metals first to a special bonding agent and then separating the loaded bonding agents from the wastewater stream by separation processes. For the separation stage, a new hybrid process of flotation and MF process has been developed by Blocher and co-workers (17), which integrated specially designed submerged microfiltration modules directly into a flotation reactor. This made it possible to combine the advantages of both flotation and membrane separation while overcoming the limitations. MF is applicable in treatment of organic contaminants in groundwater and process water. Cross-flow membrane filtration may be applicable to wastewater containing high-molecular-weight or non-polar organic contaminants, such as polychlorinated biphenyls. A study by Futamura and co-workers showed that an organic wastewater was treated by an activated sludge process, which featured the integrated-type membrane separation (hollow fiber microfiltration membrane) modules, and the treated water quality was favorable (18).

2.2.2. *Ultrafiltration*

Today, ultrafiltration (UF) technology is being used worldwide for treating various waters. It is reported that 50% of the UF membrane plants are being applied on surface waters, including river, reservoir, and lake waters. This technology has been used in municipal drinking water application for more than 10 yr (21). UF is most commonly used to separate a solution that has a mixture of some desirable components and some that are not desirable. It acts as a selective barrier. UF membranes are capable of retaining species in the range of 300–500,000 daltons of molecular weight, with pore sizes ranging from 10 to 1000 Å (0.001–0.1 μm). Typical rejected species include sugars, bio-molecules, polymers, and colloidal particles. They are typically rated by molecular weight cut-off (MWCO), a convenient but fictitious value giving the molecular weight of a hypothetical macrosolute that the membrane will just retain (15). The driving force for transport across the membrane is a pressure difference. UF processes operate at 2–10 bars, although in some cases up to 25–30 bars can be used. The separation is achieved by concentrating the large molecules present in the feed on one side of the membrane, while the solvent and microsolutes are depleted as they pass through the membrane.

To distinguish UF from two related processes, MF and RO, one can use the following example. Consider a solution of protein, water, and salt. The UF process will separate the protein (macrosolute) from the solution. As the water and salts pass through the membrane, the protein is held back. The protein concentration increases and the salts, whose concentration relative to the solvent is unchanged, are depleted relative to the protein. The result is that the protein is both concentrated and purified by the ultrafiltraion. For the RO membrane, it will pass only the water, retaining both salt and protein. The protein is concentrated, but not purified, as the rate of salt to protein remains unchanged. For the MF membrane, it will pass protein, salt, and water all together. Therefore, the protein will be neither concentrated nor purified.

UF usually implies separation of macromolecules such as protein from low-molecular-weight solvents. Pores in the support layer of the membrane are relatively larger than those of the surface layer. Material passing into fine pores can readily be transported through the open-celled, sponge-like structure of the support layer. For example, in electrodeposition paint recovery, the paint, composed of resin, a pigment, and water, is separated into two streams that can be reused. The first stream includes the water and a small amount of paint resin, which can be used to rinse the parts later in the process. The paint pigment is separated from that stream and can be re-used in the paint bath, allowing the bath to be concentrated to a useable level.

Most UF membranes are made from polymeric materials, such as, polysulfone, polypropylene, nylon 6, PTFE, polyvinyl chloride, and acrylic copolymer. Inorganic materials such as ceramics, carbon-based membranes, and zirconia, have been commercialized by several vendors. The important characteristics for membrane materials are porosity, morphology, surface properties, mechanical strength, and chemical resistance. The membrane is tested with dilute solutions of well-characterized macromolecules, such as proteins, polysaccharides, and surfactants of known molecular weight and size, to determine the MWCO.

Most UF processes are operated in cross-flow mode. When the solvent of a mixture flows through the membrane, retained species are locally concentrated at the membrane surface and resist the flow. In the case of processing solution, this localized concentration of solute normally results in precipitation of a solute gel over the membrane. When processing a suspension, the solids collect as a porous layer over the membrane surface. In view of the above, it is clear that the permeate rate can be effectively controlled by the rate of transport through the polarization layer rather than by membrane properties. Hence, UF throughput depends on physical properties of the membrane, such as permeability, thickness, and process and system variables like feed consumption, feed concentration, system pressure, velocity, and temperature.

There are three primary UF module configurations: tubular, spiral wound, and hollow fiber (15). The tubular module is often used for small-scale, high value applications. Because mechanical cleaning is easy for tubular structures, the tubular module is the choice for cases involving severe fouling. The spiral wound module is often used for high volume applications. Its structure is more vulnerable to fouling and mechanical cleaning is difficult to perform. The hollow fiber module consists of a membrane wound into a hollow cylinder with the inside diameters range from 500 to 1000 μm. The choice of diameter value depends on whether the application is high-fouling process or low-fouling process.

UF tests showed good results using the PAN 40 kDa membrane reaching an average copper concentration in the permeate of 2 mg/L and a flux of 135.4 and 156.5 $L/h \cdot m^2$ at 2 and 4 bar, respectively (22). Metal rejection, permeate flow rate, and the possibility of regenerating and recycling the polymer makes the polymer-assisted ultrafiltration process (PAUF) very interesting for metal ion removal from waters. Satisfactory results were also obtained for metal and COD removal from pulp and paper industry wastewater by coupling complexation with water-soluble polymeric ligands and the UF process (23). Some other applications of UF process for water and wastewater treatment include

- Oil emulsion waste treatment
- Production of ultra-pure water for electronics industry
- Reduction of high COD levels in corn starch plants
- Selective removal of dissolved toxic metals from groundwater in combination with chemical treatment
- Treatment of whey in dairy industries
- Wine or fruit juice clarification

2.2.3. *Nanofiltration*

Nanofiltration (NF) is a form of filtration that uses membranes to separate different fluids or ions. NF is typically referred to as “loose” RO owing to its larger membrane pore structure as compared to the membranes used in RO, which allows more salt passage through the membrane. Because it can operate at much lower pressures, normally 7–14 bars, and passes some of the inorganic salts, NF is used in applications where high organic removal and moderate inorganic removals are desired. NF is capable of concentrating sugars, divalent salts, bacteria, proteins, particles, dyes, and other constituents that have a molecular weight greater than 1000.

Membranes used for NF are made of cellulose acetate and aromatic polyamide with characteristics such as salt rejections from 95% for divalent salts to 40% for monovalent salts and an approximate MWCO of 300 for organics. An advantage of NF over RO is that NF can typically operate at higher recoveries, thereby conserving total water usage due to a lower concentrate stream flow rate. NF is not effective on small-molecular-weight organics, such as methanol.

NF membranes can be used to produce drinking water, because they have good molecular rejection characteristics for divalent cations, e.g., calcium and magnesium, and they can effectively remove hardness in place of conventional chemical softening. NF membranes can also reject higher-molecular-weight organics that contribute to taste and odor or that can react with chlorine to form trihalomethanes or other particles, which improves the efficiency of downstream disinfection processes. In Flagler Beach, FL, a study was conducted to evaluate the rejection of six synthetic organic compounds from a potable water sources by a NF membrane process (15). In another study, an NF process was used for recovering tannins and water from exhausted baths and reusing them as tanning agents and washings, and the advantages are particularly significant in terms of reduction of environmental impact (up to 75% of COD reduction of the global effluent), simplification of cleaning-up processes of wastewaters, saving of chemicals and water, easy reuse of sludges and decrease of disposal costs (19). It was also proven by Van der Bruggen and co-workers that, treatment of ground water with NF allows to produce drinking water with outstanding quality at an operating cost that is not excessive (20).

2.2.4. *Reverse Osmosis*

Unlike conventional filtration, which can only remove suspended solids with sizes >1 μm, the reverse osmosis (RO) process is able to eliminate the dissolved solids, bacteria, viruses, and other germs contained in the water. An RO is essentially a pressure-driven membrane diffusion process for separating dissolved solutes. During the process, a pressurized feed solution is passed over one surface of the membrane. As long as the operation pressure, ranges from 10 to 70 bars depending on its application, is greater than the osmotic pressure of the feed solution, water will flow from the more concentrated solution to the more dilute solution through the membrane. An RO is generally used for desalination of seawater for its conversion into potable water. The salient features of the process are that it involves no phase change and it is a relatively low-energy process.

In normal process, solvent (e.g., water) can flow across the semipermeable membrane from a dilute concentration to a more-concentrated solution until equilibrium is reached (15). The application of high pressure to the concentrated side will cause this process to reverse. This results in solvent flow away from the concentrated solution, leaving a higher concentration of solute. In application, the waste stream flows past the membrane; while the solvent (e.g., water) is driven through the membrane, the remaining solutes (e.g., organic or inorganic components) do no pass through, and become increasingly concentrated on the feed side of the membrane.

Almost all RO membranes are made of polymers, cellulosic acetate and matic polyamide types, and are rated at 96–99% NaCl rejection. RO membranes are generally of two types, asymmetric or skinned membranes and thin film composite membranes. The support material is commonly polysulfones, while the thin film is made from various types of polyamines and polyureas.

RO membranes have the smallest pore structure, with pore diameter ranging from approx 5 to 15 Å (0.5 to 1.5 nm). The extremely small size of RO pores allows only the smallest organic molecules and unchanged solutes to pass through the semipermeable membrane along with the water. Greater than 95–99% of inorganic salts and charged organics will also be rejected by the membrane due to charge repulsion established at the membrane surface.

The major advantage of RO for handing process effluents is its ability to concentrate dilute solutions for recovery of salts and chemicals with low-power requirements. No latent heat of vaporization or fusion is required for effecting separations; the main energy requirement is for a high-pressure pump. It also requires relatively limited floor space for compact, high-capacity units, and it exhibits good recovery and rejection rates for a number of typical process solutions (15).

The major problem of RO is its higher potential of fouling. This is caused by particulate and colloidal matters that become concentrated at the feed side of the membrane surface. Fouling of membranes by slightly soluble components in solution or colloids has caused failures, and fouling of membranes by feed water with high levels of suspended solids can be a problem. Pretreatment is used to remove particulate matters from the feed water. A system designed to operate at a high permeate flux is likely to experience high fouling rates and will require frequent chemical cleaning. Limited operational temperature range is another limitation for the RO process. For cellulose acetate membranes, the preferred range is 18–30 °C, lower temperatures will cause decreased fluxes and higher temperatures will increase the rate of membrane hydrolysis, hence reduce system life. These membranes are also chemically sensitive. Strongly acidic or basic solutions, strong oxidizing agents, solvents, and other organic compounds can cause dissolution of the membrane. Poor rejection of some compounds such as borates and low-molecular-weight organics is another problem. Finally, there are some concentrated solutions having initial osmotic pressures, which are so high that they may exceed the available operating pressures and make it uneconomical (15).

The product water from a RO unit will have a low pH and most probably a high concentration of carbon dioxide (15). The carbon dioxide can be removed and the pH of the product increased by use of a decarbonator. A decarbonator is a packed column in which product water is introduced at the top while either forced or induced air is introduced at the bottom. The air and water flow countercurrently over and around the column packing. The carbon dioxide is stripped from the water and exits from the decarbonator at the top in the air stream.

In the last 6–8 yr, the technology has gained industry acceptance as a viable water treatment option for many different fluid separation applications. Low operating costs and the ability to remove organic contaminants and 95–99% of inorganic salts with minimal chemical requirements make RO an attractive technology for many industrial applications.

A study by Chai and co-workers shows that it is successful to remove copper ions from industrial waste water using RO membrane separation on a pilot scale (24). RO also has extensive applications in the following water treatments:

- Boiler feed water and cooling tower blow down recycle for utilities and power generation
- Cleaning of contaminated surface water and groundwater
- Potable water from sea or brackish water
- Pharmaceutical-grade water
- Ultra-pure water for food processing and electronic industries
- Water for chemical, pulp, and paper industry

2.2.5. Other Membrane Technologies

Apart from the above four major separation processes, there are other membrane technology applications in water and wastewater treatment:

1. Dialysis. Dialysis is a process where solutes travel from one side of the membrane to the other side according to their concentration gradients (13,25,26). It uses a semipermeable membrane capable of passing small solute molecules, such as salts and small organic species, while retaining colloids and solutes of higher molecular weight. The transfer through the membrane is by diffusion, rather than by the hydrodynamic flow that would occur in a porous medium. The current applications of dialysis include:

- Hemodialysis
- Purification techniques in pharmaceutical and biochemical laboratories
- Separating nickel sulfate in the electrolytic copper refining industry

2. Electrodialysis. Electrodialysis (ED) is a process in which ions are transported through ion permeable membranes from one solution to another under the influence of a potential gradient (25,26). The electrical charges on the ions allow them to be driven through the membranes fabricated from ion-exchange polymers. Applying a voltage between two end electrodes generates the potential field required for this. Because the membranes used in ED have the ability to selectively transport ions having positive or negative charge and reject ions of the opposite charge, useful concentration, removal, or separation of electrolytes can be achieved by ED. A study by Van der Bruggen and co-workers showed that the separation of monovalent ions and divalent (or multivalent) ions can be done with ED as well as with NF (27). The current applications of ED also include:

- Desalination of seawater and brackish water
- Electroplating rinse water
- Etch bath rinse water
- Removal of organic acids from wine and fruit juices
- Radioactive wastewater treatment
- Regeneration of ion-exchange resins
- Ultra-pure water production

3. Donnan dialysis. Donnan dialysis uses an anion- or cation-selective membrane, which functions similarly to ion-exchange resins (15,25). For an anion-exchange membrane, cations in both solutions are prevented from diffusing through the membrane, but anions will get through until equilibrium is reached. For a cation-selective membrane, cations will diffuse through the membrane while anions will be retained. Potential difference is the driving force behind these separation processes. It is the created by the displacement of the system from the equilibrium ratios, which can be controlled by adjusting solution concentrations. The application for ion exchange includes

- pH control without adding acid or base
- Recovery of acids and bases from salts
- Water softening

4. Membrane bioreactor. Membrane bioreactor (MBR) can be defined as integration of conventional biological degradation and membrane separation into a single process where microorganisms responsible for biodegradation and suspended solids are separated from biologically treated water by a membrane filtration unit. The entire biomass is confined within the system, providing both perfect control of the sludge retention time for the microorganism in the bioreactor and physical disinfection of the effluent (12,28–30).

As the MBR process does not need the secondary clarifier for the solid–liquid separation, it can prevent these “inherited” problems that occur in the conventional processes for the wastewater reclamation (29). The resulting high-quality and completely disinfected effluent means that the MBR process can be used for many purposes, i.e., industrial and municipal wastewater treatment and reuse (30). More important, the land requirement of MBR is much less than that of conventional wastewater reclamation processes.

2.3. *Case Studies on Membrane Applications in Water Treatment*

2.3.1. *Case 1: Desalination of Seawater by RO*

Desalination of seawater is one of the important applications of membrane processes. There are various ways to produce fresh water such as distillation, electrodialysis, membrane distillation, freezing, membrane bioreactor, and reverse osmosis. Among them, distillation is the most used technique, but RO is becoming more popular in the desalination industry. A flow diagram of a single-stage RO system is shown in Fig. 4.

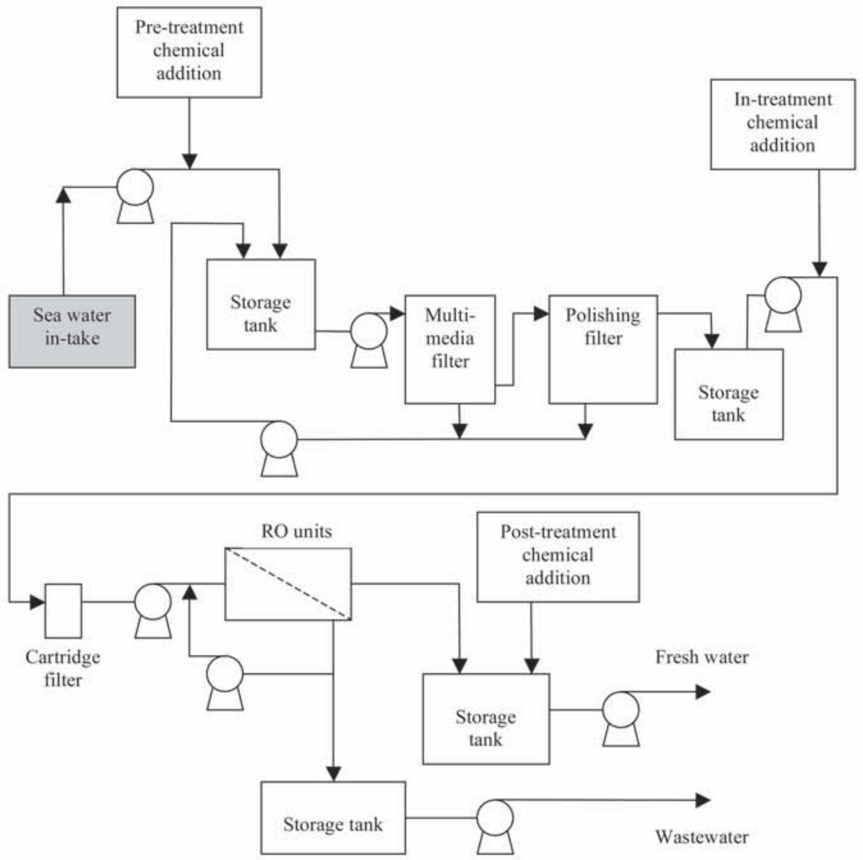

Fig. 4. Schematic diagram of RO system for seawater desalination.

In order to reduce fouling and protect the membrane, pretreatment must be performed for seawater. A pretreatment system removes suspended solids and other potential fouling materials. Flocculation agents such as iron chloride or polyelectrolytes are added in order to remove suspended solids. Chlorine is added to remove bacteria and algae.

The water quality is determined by the membrane materials and configurations. Cellulose acetate membranes can be degraded by the formation of biological slimes on the membrane surface, while polyamide membranes cannot tolerate chlorine. Thus, sodium hydrogen sulfite is normally needed to remove chlorine in the water. Operation at higher temperatures and pressures can cause the compaction of the membrane layer and thus reduce output. A stagnant boundary layer at the membrane surface can cause concentration polarization of salts, increasing the chance of precipitation and reducing output (25,26). The operating brine concentration, pressure, and water conversion factor need to be selected to limit both compaction and concentration polarisation effects.

When a membrane-based desalination process is used, seawater is first collected and pumped to the water-treatment plant. Sodium hypochlorite is injected periodically after the intake pumps to prevent biological growth within the water-treatment system. Suspended solids are retained by sand filters or MF. The filtered water is then acidified,

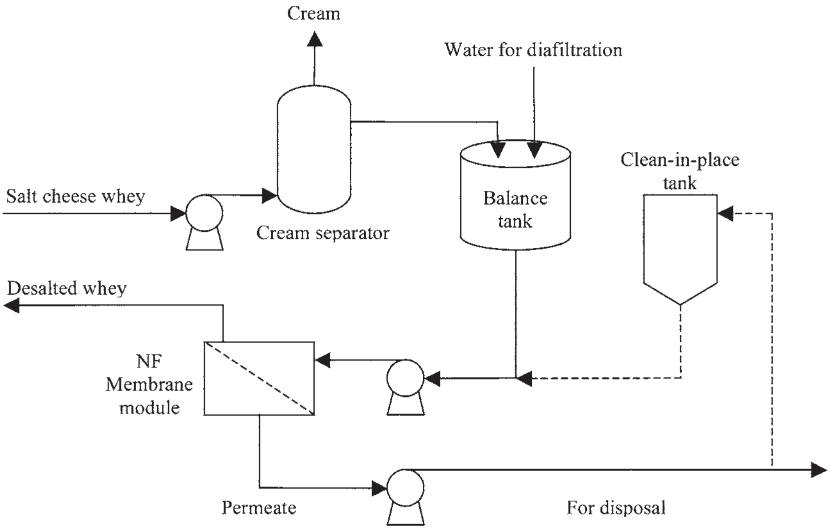

Fig. 5. Removal of salts from cheese whey permeate by NF.

treated with a sequestering agent, and dechlorinated. A security filter precedes the high-pressure pumps that transfer the water to the RO membrane modules. The concentrate leaves the membrane modules via energy-recovery turbines directly coupled to the high-pressure pumps. The product water with a quantity of carbon dioxide and a residual salinity of less than 690 mg/L is led to the degasifier, treated for pH-stabilization, and finally collected in a reservoir.

2.3.2. Case 2: Removal of Salts from Food Processing Water Stream by NF

The single most important food manufacturing application of NF membranes is desalting of whey permeate, as shown in Fig. 5, or other food processing water streams.

Salty cheese whey, for instance, poses a serious waste disposal problem in the food industry (31). The salt content, whey solids content, and biochemical oxygen demand of the salty cheese whey are about 4–6%, 6%, and 45,000 mg/L, respectively. Accordingly, the salty cheese whey can neither be discharged directly into a Public Owned Treatment Works system, nor mixed with normal cheese whey because of its extremely high salt content. The NF system effectively removes sodium chloride as permeate, which is recycled or discharged. The retentate, which is desalted whey, is added back to the normal whey. This is a typical example of cleaner production and cost-saving measurement.

The desalting process system has double benefits. It not only increases profitability, but also solves a tough waste disposal problem. Removal of salts from a food processing water stream can also be accomplished by using electrodialysis or ion exchange. The capital costs of both ED and ion exchange are higher than that of NF.

2.3.3. Case 3: Nutrient Removal from Wastewater Streams by RO

Considering the increasingly stringent industrial effluent standards currently being imposed on industrial effluent pretreatment facilities, specifically allowable concentrations of nutrient-containing substances, the capacity of RO to remove nutrients should be properly documented.

Cellulose acetate (CA) is still considered the preeminent membrane for wastewater treatment because it is capable of producing the highest flux per unit surface area at specified levels of solute rejection. The rejection performance of RO using a 90% sodium chloride rejection CA membrane was studied. Phosphorous removal was greater than 95% in all cases. Ammonia removals were generally in excess of 90%, and nitrite and nitrate removals generally ranged from 84% to 97% (32).

In another study of nutrient removal by RO, similar findings were confirmed: 80–90% separation of sodium nitrate, sodium nitrite, and ammonium chloride were realized, with ammonium chloride rejection significantly better than both sodium nitrate and sodium nitrite. Rejection of phosphate-containing substances were also in agreement with separation efficiency at greater than 98.5% (11).

Meanwhile, many food processing plants, including a major dairy plant in Minnesota, USA, use phosphoric acid in their processes, resulting in over 100 mg/L of phosphate in their wastewater streams. RO is an ideal process unit for recovery and reuse of nutrients as fertilizers.

3. MEMBRANE MATERIALS: PREPARATION AND MODIFICATION

It is essential to understand the basic characteristics of the membrane, such as membrane materials and their formation, so that proper selection of membrane separation processes can be made.

3.1. Membrane Materials

The range of available membrane materials used in water and wastewater treatment is quite broad, but most of them are synthetic membranes. Synthetic membranes can be organic or inorganic; however, the most important class of membrane materials is organic or polymer membrane. The choice of a given polymer as a membrane material is not arbitrary (13). Inorganic materials generally possess superior chemical and thermal stability relative to polymeric materials. However, both types of membranes have different applications. A list of common membranes is shown in Table 2.

3.2. Types of Membrane and Their Formation

3.2.1. Introduction

Symmetric membranes and *asymmetric membranes* are two basic types of membrane based on their structure. *Symmetric membranes* include non-porous (dense) symmetric membranes and porous symmetric membranes, while *asymmetric membranes* include integrally skinned asymmetric membranes, coated asymmetric membranes, and composite membranes. A number of different methods are used to prepare these membranes. The most important techniques are sintering, stretching, track-etching, template leaching, phase inversion, and coating (13,33).

3.2.2. Phase-Inversion Membranes

Generally, in a phase-inversion technique, a polymer transforms from its liquid phase to solid phase in a well-controlled manner. Usually, the process is carried out by starting the transition from one liquid state to two liquid states. One of them has a high polymer

Table 2
List of Commercial Membranes: Compositions and Applications

Membranes	Membrane materials	Applications
Organic membrane	Cellulose regenerated	D, UF, MF
	Cellulose nitrate	MF
	Cellulose acetate	GS, RO, D, UF, MF
	Polyamide	RO, NF, D, UF, MF
	Polysulfone	GS, UF, MF
	Poly(ether sulfone)	UF, MF
	Polycarbonate	GS, D, UF, MF
	Poly(ether imide)	UF, MF
	Poly(2,6-dimethyl-1,4-phenylene oxide)	GS
	Polyimide	GS
	Poly(vinylidene fluoride)	UF, MF
	Polytetrafluoroethylene	MF
	Polypropylene	MF
	Polyacrylonitrile	D, UF, MF
	Poly(methyl methacrylate)	D, UF
	Poly(vinyl alcohol)	PV
	Polydimethylsiloxane	PV, GS
Inorganic membrane		
Ceramic	Metal (Al, Zn, Ti, Si, etc.) oxide	PV, GS
	Metal (Al, Zn, Ti, Si, etc.) nitride	
	Metal (Al, Zn, Ti, Si, etc.) carbid	
Metallic	Metal (Al, Zn, Ti, Si, etc.) oxide	PV, GS
Zeolite	SiO_2	PV, GS

MF = microfiltration; UF = ultrafiltration; NF = nanofiltration; D = dialysis; PV = pervaporation; GS = gas separation; RO = reverse osmosis.

content. At some point during this transition, the polymer-rich liquid phase begins to solidify, forming a solid matrix. The morphology of the membrane can be controlled by adjustment of the initial stage of the phase transition.

There are a number of different techniques belonging to the category of phase inversion: solvent evaporation, precipitation by controlled evaporation, precipitation from the vapor phase, thermal precipitation, and immersion precipitation (13,34–36). The most commercially available membranes are prepared by the last method.

3.2.3. *Spinning of Hollow Fibers*

The spinning of hollow fibers is very often applied as a preparation technique for UF membranes. During the spinning process, nascent hollow fibers must be mechanically self-supporting, which means the spinning solution must have high enough viscosity to support the nascent fiber (37–40). The spinning solution passes through a spinneret with a precision orifice containing a centrally positioned inlet tube for the delivery of the internal coagulation medium. The internal coagulant is required to form the hollow fiber inside bore (37–39). A schematic diagram of the wet spinning apparatus is shown in Fig. 6.

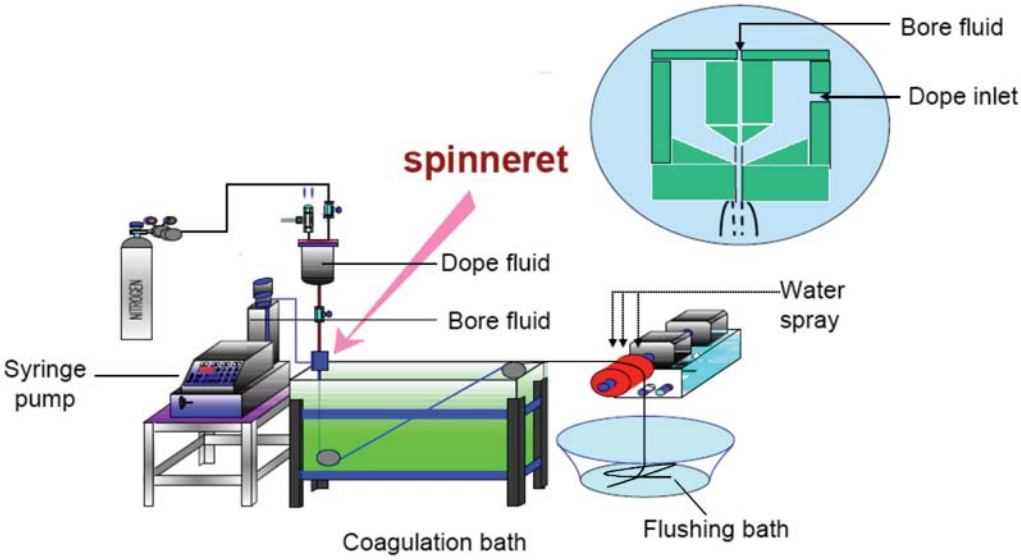

Fig. 6. Schematic diagrams of the wet spinning apparatus.

In the spinning of UF hollow fiber membranes, three options exist for spinneret placement: wet spinning, dry–wet spinning, and dry spinning. The shape and morphological structure of the membranes obtained is related to the rheological characteristics and phase behavior of the polymer solution during spinning. At the bore side, pore structure is determined by the solvent/nonsolvent ratio of the internal bore liquid. For the outer surface, pore structure is mainly dependent on the conditions in the air gap.

Spinning conditions affect membrane physical dimensions and morphology, which in turn influence membrane performance such as permeability. A satisfactory spinning process would produce fibers having the requisite surface pore size and mechanical strength. Parameters involved in a spinning process are:

- Polymer concentration and composition
- Additives
- Velocity of spinning solution through spinneret
- Type and velocity of internal coagulant through the inner tube
- External coagulant
- Spinning temperature
- Distance of the air gap

3.2.4. *Membrane Modification*

In order to enhance the overall performance of the membrane, it is necessary to modify the membrane material or the structure (41). The objectives for modification of the existing membranes are to increase flux, selectivity, and chemical resistance (solvent resistance, swelling resistance, and fouling resistance). Some of the most commonly practiced membrane modification methods are listed in Table 3.

The first reported membrane modification method involved annealing of porous membranes by heat-treatment. Zsigmondy and Bachmann in 1922 demonstrated that

Table 3
List of Membrane Modification Methods

Modification methods	Effects	Applications
Annealing		
• Heat-treatment	Decrease pore size	RO, GS, UF
• Solvent treatment	Eliminate membrane micro-defects	RO, GS, UF
Surface coating	Eliminate membrane defects	GS
	Improve fouling resistance	RO, NF, UF
Solvent exchange	Elimination of membrane defects	GS, UF
Chemical treatment		
• Fluorination	Improve selectivity & reduce flux	GS
• Cross-linking	Improve chemical stability & selectivity	UF
• Pyrolysis	Improve separation performance	RO, GS, PV

UF = ultrafiltration; NF = nanofiltration; PV = pervaporation; GS = gas separation; RO = reverse osmosis.

the pore size of a pre-formed nitrocellulose membrane could be decreased with a hot water or stream treatment (42). An alternative way of annealing is solvent treatment. Micro-defects in a membrane can be eliminated by swelling the thin separating layer with a vapor or a liquid. As a result of swelling, the modulus of the polymer decreases sharply. It has been suggested that capillary forces can pull the swollen polymer layer together, and eliminate the membrane defects (43).

One setback for the production of thin-film composite membranes and integrally skinned asymmetric membranes with separating layer thickness of less than 0.2 μm is the defects. A thin coating of a highly permeable polymer can help eliminate the defects. Surface coatings are also applicable in improving the fouling resistance of membranes for UF or NF applications (44).

Another way to minimize the membrane defects is *solvent exchange*. Typical solvent exchange methods involve replacing water first with iso-propanol and then with *n*-hexane (41). This solvent exchange is essential as collapse of water-wet membranes occurs upon drying. This collapse is due to the strong capillary forces within the finely porous structure during the drying process. According to the Young–Laplace relationship, the capillary pressure is proportional to the surface tension of a liquid and inversely proportional to the pore size. If this capillary force is higher than the modulus of the membrane material, the pores will collapse. As water usually has a very high surface tension, it is often difficult to dry water-wet membranes without destroying the membrane structure. One possible solution is substituting water with liquids having lower surface tension, such as alcohols or aliphatic hydrocarbons, which will maintain the original membrane structure upon drying.

Chemical surface modification methods of gas-separation membranes include treatment with fluorine, chlorine, bromine, or ozone. These treatments result in an increase in membrane selectivity with a decrease in flux. Cross-linking of polymers is often applied to improve the chemical stability and selectivity of membranes for reverse osmosis, pervaporation, and gas-separation applications (41). Mosqueda-Jimenez and co-workers studied the addition of surface modifying macromolecules, and the use of the additive polyvinylpyrrolidone (PVP) (45). Their results showed that membranes prepared with PVP had pure water permeation rates significantly higher than membranes prepared without the PVP additive. The pyrolysis method can lead to significantly improved separation performance of synthetic membranes, especially molecular-sieve membranes made from pyrolized polyacrylonitrile and polyimide (46).

4. MEMBRANE CHARACTERIZATION

Membranes need to be characterized to ascertain which may be used for a certain separation or class of separations (13). Membrane characterization is to measure structural membrane properties, such as pore size, pore size distribution, free volume, and crystallinity to membrane-separation properties. It helps gather information for predicting membrane performance for a given application.

Membrane characterization means the determination of structural and morphological properties of a given membrane. Because membranes range from porous to nonporous depending on the type of separation problem involved, different characterization techniques are required in each case. For example, in MF or UF membranes, fixed pores are present. MF membranes have macropores (pore diameter > 50 nm), while UF membranes have mesopores (2 nm < pore diameter < 50 nm). The pore size (and size distribution) mainly determines which particles or molecules are retained or pass through. On the other hand, for dense or nonporous membranes, no fixed pores are present and the material chemistry itself mainly determines the performance.

4.1. Porous Membrane

Two different types of characterization method for porous membranes can be distinguished (13):

- *Structure-related parameters:* determination of pore size, pore size distribution, top layer thickness, and surface porosity
- *Permeation-related parameters:* determination of the actual separation parameters using solutes that are more or less retained by the membrane

There are a number of characterization techniques available for porous membranes, the following methods are usually used:

- Electron microscopy
- Atomic force microscopy (AFM)
- Bubble point method
- Permeation measurement

The first three methods involve the measurement of structural-related parameters while the last one is a typical permeation-related technique. Both electron microscopy and AFM can provide qualitative measurement of membrane materials. Figure 7 shows the top surface of porous polymeric membrane observed by scanning electron microscopy (SEM). The bubble point method and permeation measurement, on the other hand, provide quantitative information of membrane materials.

4.2. Nonporous Membrane

Transport through nonporous membranes follows the solution–diffusion mechanism, and separation is achieved either by differences in solubility or diffusivity. Therefore,

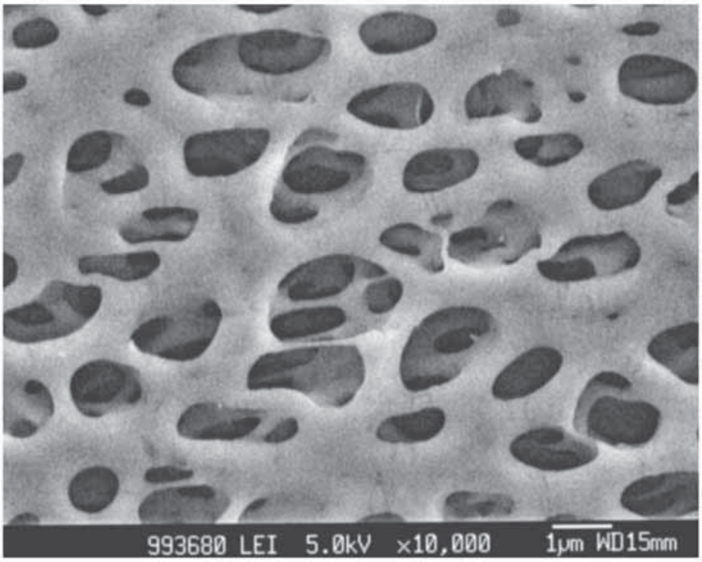

Fig. 7. Visualization of top surface of a porous polymeric membrane by scanning electron microscopy (10,000×).

the characterization method is different from those in the previous section. There are several methods used for nonporous membrane:

- Permeability methods
- Differential scanning calorimetry/differential thermal analysis methods
- Surface analysis (such as X-ray photoelectron spectroscopy)

Details of these techniques will not be discussed in this book, and readers can find relative information in manuals of the respective analytical instruments.

5. MASS TRANSPORT IN MEMBRANES

A membrane can be defined as a barrier between two phases. A molecule or particle is transported from one phase to another through the membrane because a driving force acts on that molecule or particle. This driving force can be chemical potential gradient, e.g., concentration gradient, pressure difference, or electrical potential, or combination of these (10). There is a proportional relationship between the flux and the driving force:

$$\text{Flux} = \text{Proportionality factor} \times \text{Driving force}$$

$$J = A \times X \tag{1}$$

where J is the flux, A is the proportionality factor, and X is the driving force. The proportionality factor (A) determines how fast the component is transported through the membrane, i.e., A is a measurement of the resistance exerted by the membrane as a diffusion medium, when a given force is acting on this component (13). Various models have been established to study both the proportionality factor and the driving force. Among those models, two of the most useful will be discussed next.

5.1. The Solution–Diffusion Model

The solution–diffusion model is currently being used by most of the membrane community. The most general description of the mass transport across a membrane is based on irreversible thermodynamics (10):

$$J_i = L_{ii} X_i + \sum L_{ij} X_j \tag{2}$$

where J_i is the mass flux of component i, mol/m^{2}s, L_{ii}, L_{ij} are phenomenological coefficients, and X_i, X_j are the driving forces. The first term of Eq. (2) shows the flux of the ith component. The second term shows the relation between the flux of the ith component and the forces acting on components other than ith component. It should be noted that L_{ii} is always positive and $L_{ij} = L_{ji}$.

The most appropriate choice of the force X for the molecular diffusion through the membrane under isothermal conditions without external forces being applied to the mass transfer of the ith component is the chemical potential gradient:

$$X_i = -\nabla \mu_i \tag{3}$$

where μ_i is the chemical potential of the ith component, J/mol.

The flux is given by

$$J_i = -L_{ii} \nabla \mu_i \tag{4}$$

In Eq. (4), the second term of Eq. (2) is eliminated, which means that the flow of the ith component is totally decoupled from the flow of other components.

The chemical potential gradient can be described as

$$\nabla \mu_i = RT \nabla \ln a_{im} + V_i \nabla p \tag{5}$$

where a_{im} is the activity in the membrane, mol/m^3, v_i is the partial molar volume of the ith component, m^3/mol, p is pressure, Pa, R is the gas constant, 8.314 J/mol K or 0.08206 atm L/mol K, and T is the temperature, K.

Considering the membrane process as a binary system, the transport of solvent (e.g., water), and solute are involved. Designating solute and solvent by subscripts A and B, Eq. (5) can be written for solvent B as

$$\nabla \mu_B = RT \nabla \ln a_{Bm} + v_B \nabla p \tag{6}$$

Assuming v_B is constant, integration over the membrane thickness yields,

$$\Delta \mu_B = v_B \left(\frac{RT}{v_B} \Delta \ln a_{Bm} + \Delta p \right) \tag{7}$$

(Δ is defined here as "permeate side – feed side.") Assuming further that thermodynamic equilibrium is established at the membrane–solution boundaries, $a_{Bm} = a_B$, where a_B is the activity of solvent (mol/m^3) outside of the membrane. This relationship should be valid on both sides of the membrane. Because the osmotic pressure, Π (Pa), is defined as

$$\Pi = -\frac{RT}{v_B} \ln a_B \tag{8}$$

Eq. (7) can be written as

$$\Delta\mu_B = v_B(\Delta p - \Delta\Pi) \tag{9}$$

For practical purposes, the osmotic pressure of a feed may be estimated by

$$\Pi = R(T+273)\sum M_i \tag{10a}$$

$$\text{or}\quad \Pi = 7720(T+273)\sum M_i \tag{10b}$$

where T is the temperature, °C and ΣM_i is the sum of molalities or molarities of ions and non-ionic compounds, mol/kg or mol/L.

As for solute A, we shall further assume that the activity coefficient remains constant, then Eq. (5) becomes

$$\begin{aligned}\nabla\mu_A &= RT\nabla \ln a_{Am} + v_A\nabla p\\ &= RT\nabla \ln c_{Am} + v_A\nabla p\end{aligned} \tag{11}$$

where a_{Am} is the activity of solute in the membrane, mol/m^3, c_{Am} is the concentration of solute in the membrane, mol/m^3, and v_A is the molar volume of solute, m^3/mol.

Integration over the membrane thickness yields

$$\Delta\mu_A = RT\Delta \ln c_{Am} + v_A\Delta p \tag{12}$$

The second term of this equation can be ignored when the solute concentration at the low-pressure side of the membrane is less than 90% of that at the high-pressure side of the membrane, which is usually the case for the RO process. Therefore, we have

$$\Delta\mu_A = RT\Delta \ln c_{Am} \tag{13}$$

As for L_{ii}, the following physical meaning is usually given to the phenomenological coefficient L_{BB}:

$$L_{BB} = \frac{c_{Bm}}{f_{Bm}} \tag{14}$$

where c_{Bm} is the concentration of the solvent in the membrane, mol/m^3 and f_{Bm} is the friction between a unit mole of the solvent and the membrane material, J s/m^2.

Combining Eqs. (4) and (14) and integrating over the membrane thickness, we obtain

$$J_B = -\frac{c_{Bm}}{f_{Bm}}\nabla\mu_B = -\frac{c_{Bm}}{f_{Bm}}\frac{\Delta\mu_B}{l} \tag{15}$$

where l is the membrane thickness (m). Combining further Eqs. (9) and (15), we obtain,

$$J_B = -\frac{c_{Bm}}{f_{Bm}}v_B\frac{\Delta p - \Delta\Pi}{l} \tag{16}$$

Because the friction f_{Bm} can be given as

$$f_{Bm} = \frac{RT}{D_{Bm}} \tag{17}$$

where D_{Bm} is diffusion coefficient (m^2/s) of solvent in the membrane, Eq. (16) becomes

$$J_B = -\frac{c_{Bm} D_{Bm} v_B}{RTl}(\Delta p - \Delta \Pi) \tag{18}$$

As for the solute, the phenomenological coefficient L_{AA} can be given as

$$L_{AA} = \frac{c_{Am}}{f_{Am}} \tag{19}$$

Then the solute flux can be written as

$$J_A = -\frac{c_{Am}}{f_{Am}} \nabla \mu_A = -\frac{c_{Am}}{f_{Am}} \frac{\Delta \mu_A}{l} \tag{20}$$

Combining Eqs. (13) and (20), we obtain,

$$J_A = -\frac{c_{Am}}{f_{Am}} \frac{RT\Delta \ln c_{Am}}{l} \tag{21}$$

Approximating $\ln c_{Am}$ by $(\Delta c_{Am})/c_{Am}$ and using the relation $f_{Am} = RT/D_{Am}$, we obtain

$$J_A = -D_{Am} \frac{\Delta c_{Am}}{l} \tag{22}$$

Assuming further thermodynamic equilibrium at both sides of the membrane and a proportional relationship between the concentration inside the membrane, c_{Am}, and outside the membrane, c_A,

$$c_{Am} = K_A c_A \tag{23}$$

where K_A is the distribution constant. Hence, Eq. (22) can be written as

$$J_A = -D_{Am} K_A \frac{\Delta c_A}{l} \tag{24}$$

Therefore, the fluxes of the solvent and solute can be described by Eqs. (18) and (24), or

$$J_B = -\frac{c_{Bm} D_{Bm} v_B}{RTl}(\Delta p - \Delta \Pi) \quad \text{and} \quad J_A = -D_{Am} K_A \frac{\Delta c_A}{l}$$

Other than the flux of solvent, the process is also evaluated in terms of solute rejection, R, defined as

$$R = 1 - \frac{c_{AP}}{c_{AF}} \tag{25}$$

where c_{AP} is the concentration of solute in the permeate, mol/m^3 and c_{AF} is the concentration of solute in the feed, mol/m^3.

Because

$$\frac{J_A}{J_B} = \frac{c_{AP}}{c_{BP}} \tag{26}$$

$$R = 1 - \frac{J_A c_{BP}}{J_B c_{AF}} \tag{27}$$

$$= 1 - \frac{D_{Am} K_A RT \Delta c_A c_{BP}}{c_{Bm} D_{Bm} v_B (\Delta p - \Delta\Pi) c_{AF}}$$

$$= 1 - \frac{D_{Am} K_A RT (c_{AP} - c_{AF}) c_{BP}}{c_{Bm} D_{Bm} v_B (\Delta p - \Delta\Pi) c_{AF}}$$

$$= 1 + \frac{D_{Am} K_A RT c_{BP}}{c_{Bm} D_{Bm} v_B (\Delta p - \Delta\Pi)} \frac{c_{AF} - c_{AP}}{c_{AF}}$$

$$= 1 + \frac{D_{Am} K_A RT c_{BP}}{c_{Bm} D_{Bm} v_B (\Delta p - \Delta\Pi)} R \tag{28}$$

Rearranging,

$$R = \left[1 - \frac{D_{Am} K_A RT c_{BP}}{c_{Bm} D_{Bm} v_B (\Delta p - \Delta\Pi)} \right]^{-1} \tag{29}$$

Example 1

The following numerical values were given for reverse osmosis of aqueous sodium chloride solution at 25°C (47).

$$c_{Bm} D_{Bm} = 2.7 \times 10^{-8} \text{ kg/ms}$$

$$D_{Am} K_A = 4.2 \times 10^{-14} \text{ m}^2/\text{s}$$

Calculate the solute separation and water flux, when the feed sodium chloride molality is 0.1 mol/kg and the operating pressure is 4.134×10^6 Pa (gauge). The thickness of the selective layer is 10^{-7} m.

Use the following numerical values:

$$RT = 2.479 \times 10^3 \text{ J/mol for } 25^\circ\text{C}$$

$$c_{BP} = 10^3 \text{ kg/m}^3, \text{ and } \nu_B = 18.02 \times 10^{-6} \text{ m}^3/\text{mol}.$$

From Equation (10),

$$\Pi = 7720 \times (25 + 273) \times 0.2 = 0.460 \times 10^6 \text{ Pa}$$

As $\Pi = 0$ for pure water, first, we can assume pure water on the permeate side. Approximating $\Delta\Pi = (0 - 0.460 \times 10^6) = (0.460 \times 10^6$ Pa, from Eq. (29)

$$R = \left[1 - \frac{(4.2 \times 10^{-14})(2.479 \times 10^3)(10^3)}{(2.7 \times 10^{-8})(18.02 \times 10^{-6})[(-4.134 \times 10^6) - (-0.460 \times 10^6)]} \right]^{-1} = 0.945$$

Then, the sodium chloride molality in the permeate will be

$$0.1 \times (1 - 0.945) = 0.0055 \text{ mole/kg}$$

From Eq. (10), the osmostic pressure of the permeate will be

$$\Pi = 7720 \times (25 + 273) \times 2 \times 0.0055 = 0.0253 \times 10^6 \text{ Pa}$$

Then, the osmotic pressure difference, $\Delta\Pi$, between the permeate and feed will be,

$$\Delta\Pi = (0.0253 - 0.460) \times 10^6 = -0.4347 \times 10^6 \text{ Pa}$$

$$R = \left[1 - \frac{(4.2\times10^{-14})(2.479\times10^{3})(10^{3})}{(2.7\times10^{-8})(18.02\times10^{-6})[(-4.134\times10^{6})-(-0.4347\times10^{6})]}\right] = 0.945$$

Hence, $R = 0.945$ is an accurate answer.
The flux (kg/m^2 s) is calculated from Eq. (18) as

$$J_B = -\frac{(2.7\times10^{-8})(18.02\times10^{-6})[(-4.314\times10^{6})-(-0.4347\times10^{6})]}{(2.479\times10^{3})(10^{-7})}$$
$$= 76.14\times10^{-4}\,\text{kg}/\text{m}^2\text{s}$$

5.2. *The Pore Model*

The fine-pore model was developed assuming the presence of open micropores on the active surface layer of the membrane through which the mass transport occurs (10). The existence of these different pore geometries also means that different models have been developed to describe transport adequately. The simplest representation is one in which the membrane is considered as a number of parallel cylindrical pores perpendicular to the membrane surface. The length of each of the cylindrical pores is equal or almost equal to the membrane thickness. The volume flux through these pores can be described by the Hagen–Poiseuille equation. Assuming all the pores have the same radius, then we have

$$J = \frac{\varepsilon r^2}{8\mu\tau}\frac{\Delta p}{\Delta x} \tag{30}$$

where J is the flux, given in m^2/m s, r is the pore radius, m, ε is the surface porosity and $\varepsilon = n\pi r^2/A$ (A_m is the membrane area, n_p is the number of pores), μ is the fluid viscosity, Pa s, τ is the pore tortuosity, Δp is the pressure difference, Pa (Δ is defined here as "feed side–permeate side"), and Δx is the thickness of the membrane, m.
This equation clearly shows the effect of membrane structure on transport, and indicates that the solvent flux is proportional to pressure difference as the driving force.

Equation (30) gives a good description of transport through membranes consisting of a number of parallel pores. However, very few membranes possess such a structure in reality. Membranes consists a system of closed spheres, which can be found in organic and inorganic sintered membranes or in phase-inversion membranes with a nodular top layer structure. Such membranes can best be described by the Kozeny–Carman relationship:

$$J = \frac{\varepsilon^3}{K\mu S^2(1-\varepsilon)^2}\frac{\Delta p}{\Delta x} \tag{31}$$

where J is the flux, m^2/m s, ε is the volume fraction of the pores, μ is the fluid viscosity, Pa s, S is the specific surface area, m^2/m^3, K is the Kozeny–Carman constant, which is dependent on the pore shape and tortuosity, Δp is the pressure difference, Pa, and Δx is the thickness of the membrane, m.

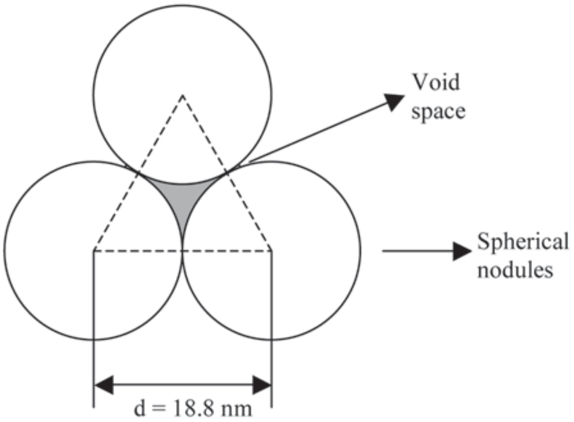

Fig. 8. Schematic diagram for calculating void space between spherical nodules.

Phase-inversion membranes frequently show a sponge-like structure. The volume flux through these membranes is described by the Hagen–Poiseulle or the Kozeny–Carman relation, although the morphology is completely different.

Example 2

Schulz and Asunmaa (48), based on their SEM observation, assumed that the selective layer of an asymmetric cellulose acetate membrane for reverse osmosis consists of closely packed spherical nodules with a diameter of 18.8 nm. Water flows through the void spaces between the nodules. Calculate the water flux by Eq. (30) assuming circular pores, the cross-sectional area of which is equal to the area of the triangular void surrounded by three circles with a diameter of 18.8 nm (as shown in Fig. 8).

(1) Calculate the area of the triangular void space.
(2) Calculate the radius of the circular pore whose cross-sectional area is equal to the triangular area calculated above.
(3) Subtract the thickness of the monolayer of water, 0.28 nm, which is adsorbed at the pore wall and assumed to be immobile.
(4) Calculate the water flux using the relevant data in Example 1, and the following numerical values:
$n_p/A_m = 6.5 \times 10^{15}/\text{m}^2$
$\Delta p = 4.134 \times 10^6$ Pa
$\Delta x = 10^{-7}$ m
$\tau = 2.5$
$\mu = 0.035$ Pa s (viscosity of water that fills nano-sized pores)

Answer

(1) Area of the triangular void space is $9.4^2 \times (\sqrt{3} - \pi/2) = 14.25$ nm^2.
(2) The radius is $\sqrt{14.30/\pi} = 2.13$ nm
(3) The effective radius of the mobile water channel, $r = 2.13 - 0.28 = 1.85$ nm.
(4) Water flux,

$$J = \frac{(6.5\times10^{15})(3.1416)(1.85\times10^{-9})^4(4.134\times10^6)}{(8)(3.5\times10^{-2})(2.5)(10^{-7})} = 141.26\times10^{-7}\,\text{m}^3/\text{m}^2\text{s}$$

Assuming water density of 10^3 kg/m^3, the water flux is 141.26×10^{-4} kg/m^{2}s.

Table 4
Typical Characteristics of Membrane Modules

	Plate and frame	Spiral wound	Tubular	Hollow fiber
Packing density (m^2/m^3)	30–500	200–800	30–200	500–9000
Resistance to fouling	Good	Moderate	Very good	Poor
Ease of cleaning	Good	Fair	Excellent	Poor
Membrane material choices	Many	Many	Few	Few
Relative cost	High	Low	High	Low
Applications	D, RO, PV, UF, MF	D, RO, GP, UF, MF	RO, UF	D, RO, GP, UF

MF = microfiltration; UF = ultrafiltration; D = dialysis; PV = pervaporation; RO = reverse osmosis.

6. MEMBRANE MODULE AND PROCESS DESIGN

6.1. *Introduction*

As we know, large surface areas are required for industrial applications of membrane processes. A practical solution for providing this large surface area is packing the membranes into a small unit called a module, as shown in Fig. 2. The module is the base for membrane installation and process design.

During the process, a stream of feed enters the module with a specific content at a specific flow rate. By passing through the membrane module, the feed stream is separated into two streams, a retentate stream and a permeate stream. The retentate stream is the fraction of the feed that retains in the feed stream and the permeate stream is the fraction that passes through the membrane.

The following membrane modules are largely used for industrial applications, of which typical characteristics are listed in Table 4:

- Plate-and-frame module
- Spiral-wound module
- Tubular module
- Hollow-fiber module

The choice of module configuration as well as the arrangement of the modules in a system are based on economic considerations with correct engineering parameters being employed to achieve this economy, which include the type of separation problem, ease of cleaning, ease of maintenance, ease of operation, compactness of the system, scale, and the possibility of membrane replacement (13). Next, we will discuss these typical membrane modules.

6.2. *Typical Membrane Modules*

6.2.1. *Plate-and-Frame Module*

A schematic drawing of a plate-and-frame module is given in Fig. 9. This type of module appeared in the earliest stage of industrial membrane applications. The structure is simple and the membrane replacement is easy. As illustrated, sets of two membranes are placed in a sandwich-like fashion with their feed sides facing each other. In each

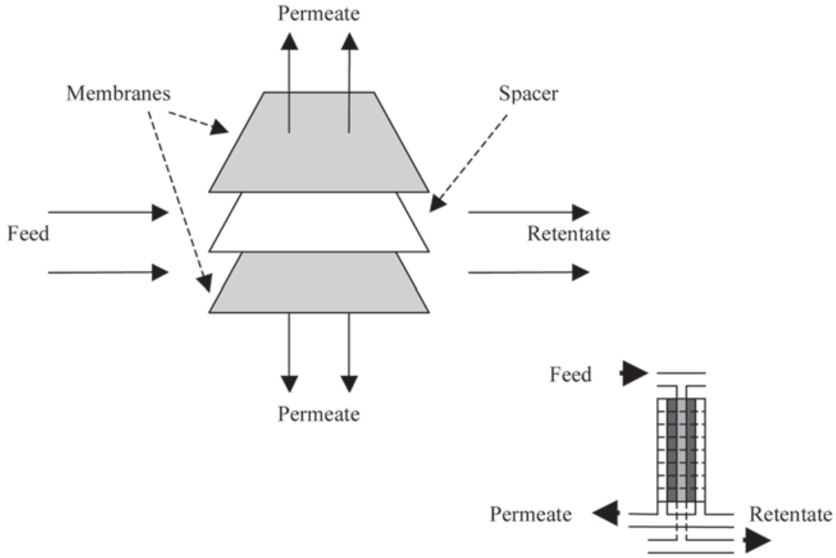

Fig. 9. Schematic drawing of a plate-and-frame module.

feed and permeate compartment, a suitable spacer is placed. The number of sets needed for a given membrane area furnished with sealing rings and two end plates then builds up to a plate-and-frame stack. The membrane permeate is collected from each support plate. The spacer surface is made uneven in order to promote turbulence of the feed fluid and minimize concentration polarization. The module diameter is 20–30 cm. The total membrane area in one module is up to 19 m^2, depending on the height of the module (10).

6.2.2. Spiral-Wound Module

The spiral-wound module is in fact a plate-and-frame system wrapped around a central collection pipe, similar to a sandwich roll. The basic structure of this module is illustrated in Fig. 10. Membrane and permeate-side spacer material are then glued along three edges to build a membrane envelope. The feed-side spacer separating the top layer of the two flat membranes also acts as a turbulence promoter. The feed flows axial through the cylindrical module parallel along the central pipe and the permeate flows radially toward the central pipe. In order to make the membrane length shorter, several membrane envelopes are wound simultaneously. The spiral-wound module is featured by

- A compact structure
- High pressure durability
- Less contamination
- Less pressure drop at the permeate channel
- Minimum concentration polarization

Usually, a number of spiral-wound modules are assembled in one pressure vessel and are connected in series via the central permeate tubes. Some industrial-scale spiral-wound modules are shown in Fig. 11.

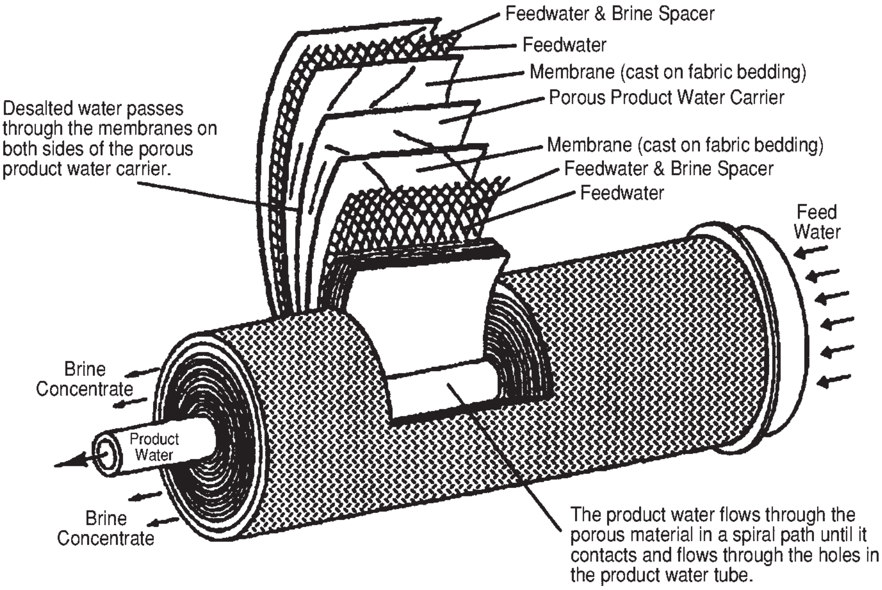

Fig. 10. Schematic drawing of a spiral-wound module.

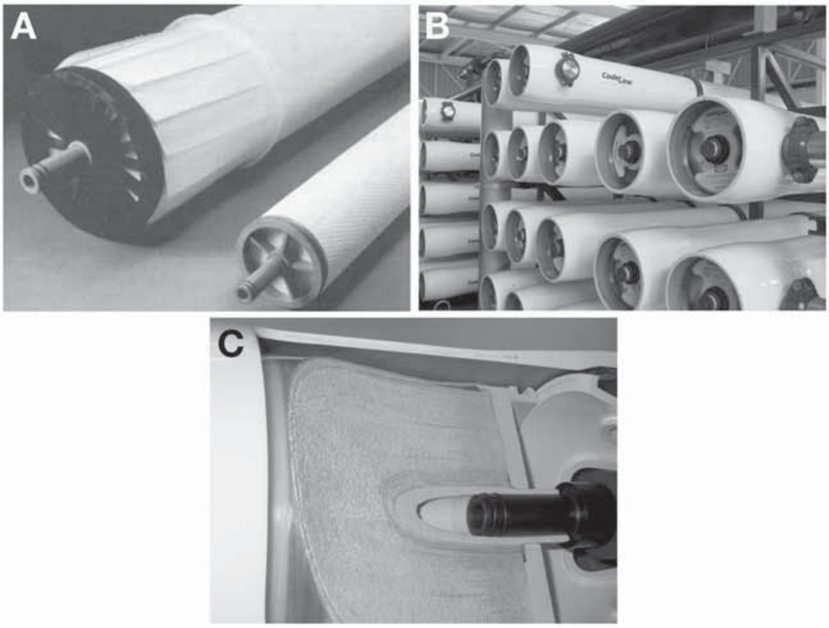

Fig. 11. Industrial scale spiral-wound modules.

6.2.3. Tubular Module

In this type of module, a number of membranes of tubular shape are encased in a container. A schematic diagram is given in Fig. 12. The feed solution always flows through the center of the tubes while the permeate flows through the porous supporting tube into

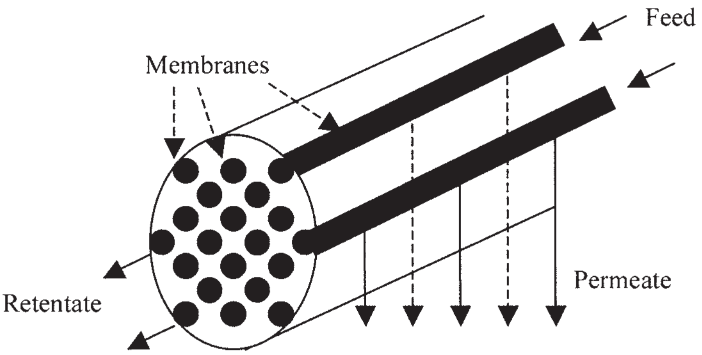

Fig. 12. Schematic drawing of a tubular module.

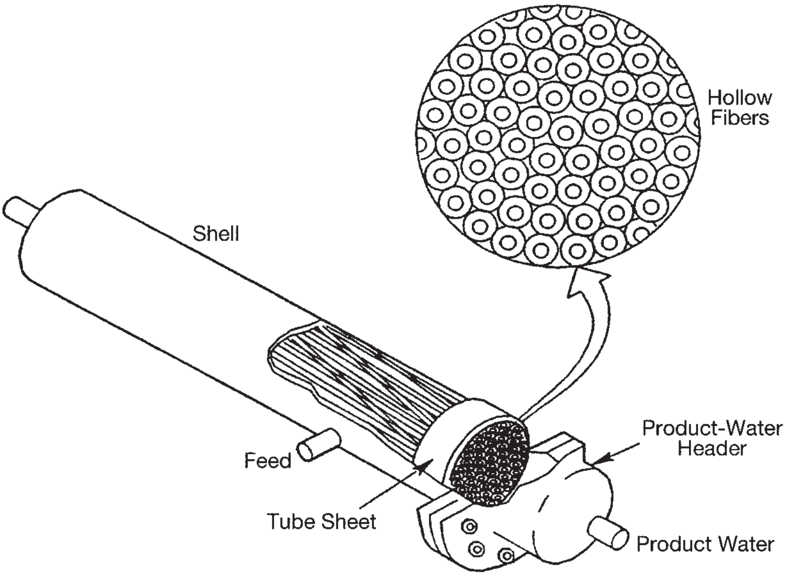

Fig. 13. Cutaway view of hollow-fiber membrane module.

the module housing. Ceramic membranes are mostly assembled in such tubular module configurations. The main features of the tubular module are

- Convenience membrane replacement and easy cleaning of surface contamination
- High energy consumption per unit amount of liquid treated
- High feed flow rate helps reduce the membrane contamination
- Low packing density of the module
- Simple pretreatment of feed liquid

6.2.4. Hollow-Fiber Module

A hollow-fiber module consists of a large number of fibers assembled together in a module, as shown in Fig. 13. The free ends of the fibers are often potted with agents such as epoxy resins, polyurethanes, or silicon rubber. The membranes are

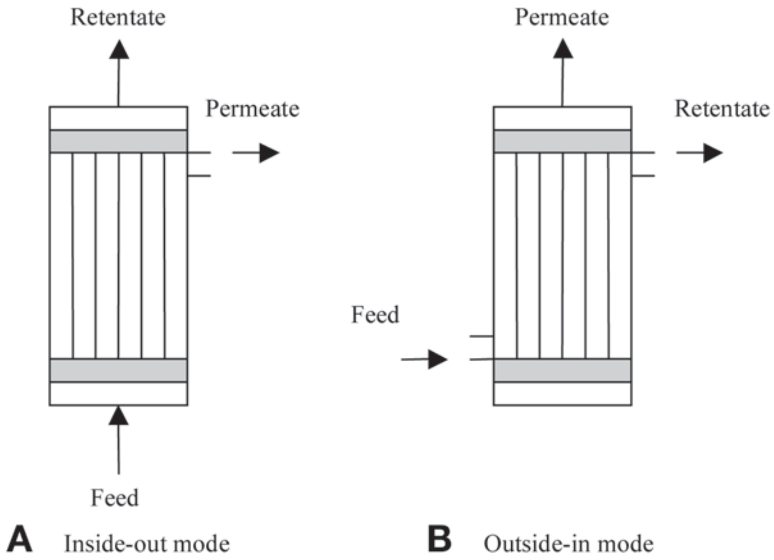

Fig. 14. Schematic drawing of hollow-fiber module operations.

self-supporting for this module. There are two basic types of arrangement for this module:

- *Inside-out*, as shown in Fig. 14A, where the feed solution passes through the bore of the fiber and the permeate is collected on the outside of the fiber.
- *Outside-in*, as shown in Fig. 14B, where the feed solutions enters the module on the shell side of the fibers and the permeate passes into the fiber bore.

The choice between the two concepts is mainly based on some parameters such as operation pressure, pressure drop, or type of membrane available. The fiber wall has a structure of the asymmetric membrane, and the active skin layer being placed to the feed side. The hollow-fiber module is featured by a very high packing density, which can reach values of 30,000 m^2/m^3.

The hollow-fiber module is often used when the feed stream is relatively clean, such as in gas separation and pervaporation. It has also been used in the case of seawater desalination, but pretreatment is needed. The module construction given in Fig. 15A is a typical RO module, where a central pipe is used to uniformly distribute the feed solution throughout the module. This is to avoid the problem of “channelling” in “outside-in” model, which means the feed has a tendency to flow along a fixed path, thus reducing the effective membrane surface area. In gas separation, as shown in Fig. 15B, the “outside-in” model is used to avoid high pressure losses inside the fiber and to attain a high membrane area (13).

6.3. Design Considerations

6.3.1. System Design

The design of the membrane operation system can be very different for different applications and module configurations (13). A number of modules are connected together to form a stage. It is desirable to optimize the whole separation system in order

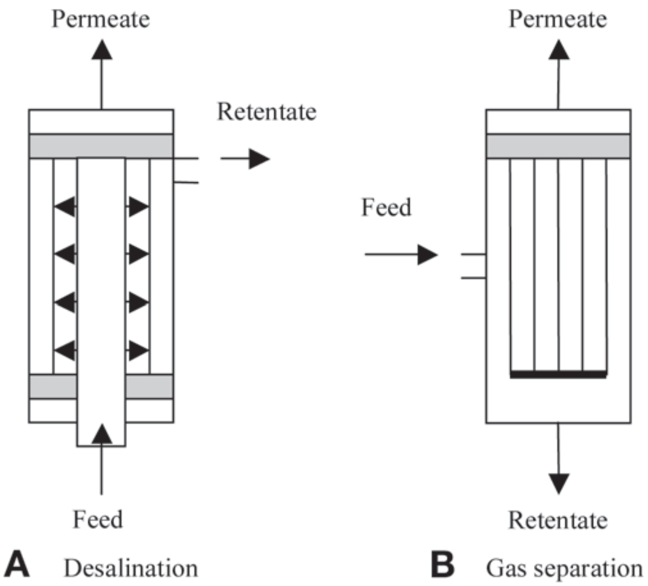

Fig. 15. Hollow-fiber module applications.

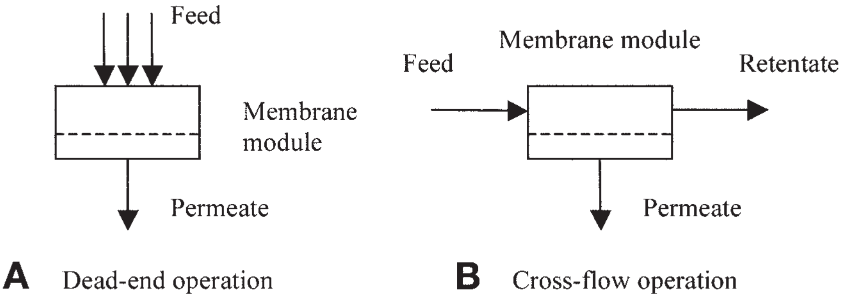

Fig. 16. Schematic drawing of dead-end and cross-flow operation.

to achieve low capital and operational costs and good quantity and quality of treated water. Normally, MF and UF do not require pretreatment units; however, the feed must be pretreated before entering NF or RO unit.

The simplest design is a dead-end operation, as shown in Fig. 16A. As the feed is forced through the membrane, the concentration of rejected components in the feed increases and accumulates at the membrane interface, hence the permeate quality decreases with time. Therefore, for industrial applications, a cross-flow operation, as shown in Fig. 16B, is preferred for its lower fouling tendency comparing to the dead-end mode.

In the cross-flow operation, the inlet feed stream entering the module at a certain composition and it flows parallel to the membrane surface. The composition of the stream changes along the module, and the stream is separated into two parts: a permeate stream and a retentate stream. Flux decline is relatively smaller with cross-flow and can be controlled and adjusted by proper module configuration and cross-flow velocities.

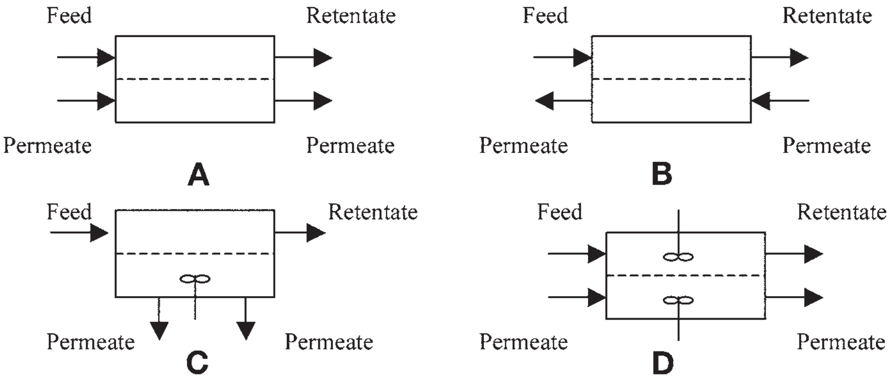

Fig. 17. Schematic drawing of some cross-flow operations: **(A)** co-current; **(B)** counter current; **(C)** cross-flow with perfect permeate mixing; **(D)** perfect mixing.

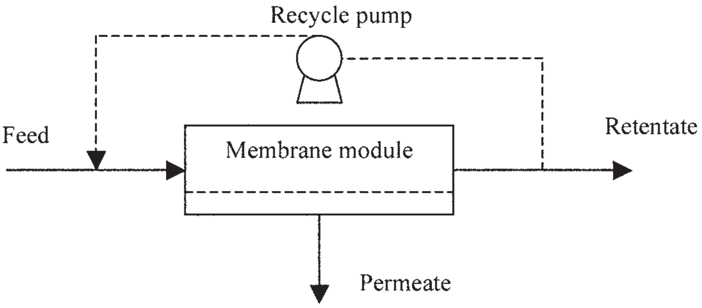

Fig. 18. Schematic drawings of the single-pass and recycling system.

As cross-flow mode is preferred over a dead-end one, the proper choice of the module is the next crucial step. For a given module design and feed solution, the cross-flow velocity is the main parameter that determines mass transfer in the module. Four cross-flow operations shown in Fig. 17 are used:

- Co-current
- Counter current
- Cross-flow with perfect permeate mixing
- Perfect mixing

In co- and countercurrent operations, the feed and permeate stream flow co-currently or countercurrently along the membrane. In the cross-flow mode, it is assumed that mixing occurs so rapidly on the permeate side that the composition distributes equally. Among these modes, countercurrent flow gives the best results, and the perfect mixing gives the worst result.

In practice, systems usually operate in the cross-flow mode with perfect mixing on the permeate side. In general, two basic flow schemes can be used in the system design: (1) a single-pass system, and (2) a recycling system, as shown in Fig. 18.

In the single-pass system, the feed stream passes through the system only once, and there is no recycling. In a recycling system, a recirculation pump is used to recycle the retentate stream. For small-scale applications, a batch system can be used, as shown in Fig. 19.

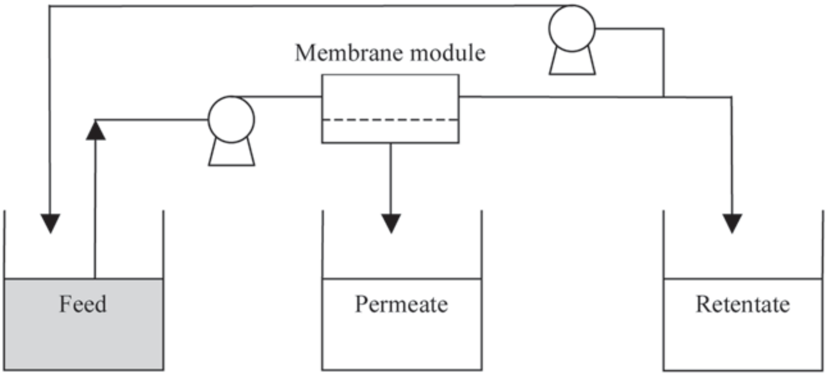

Fig. 19. Schematic drawings of a batch system.

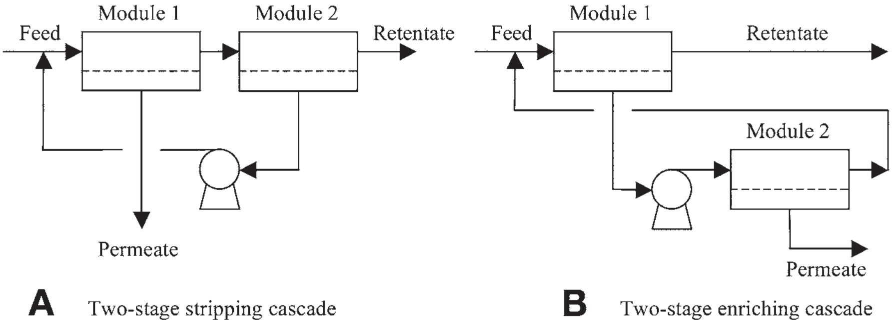

Fig. 20. Schematic drawings for two-stage membrane process.

Usually, a single-stage operation does not give the desired product quality, and a second stage is required. A combination of stages is called a cascade. In a cascade operation, a large number of units are used, and the permeate of the first stage is the feed for the second stage and so on. An example of a two-stage operation process is shown in Fig. 20. When more stages are required, the optimization of the process becomes very complex and difficult.

6.3.2. Nanofiltration and Reverse Osmosis

A typical NF or RO unit includes raw water pumps, pretreatment, membrane modules, disinfection units, storage, and distribution elements (3). The principal design considerations for NF and RO units are:

- *Membrane material*. During the early days, membranes were usually made of cellulose acetate. At present, membranes can also be made from aromatic polyamide and thin-filmed polymer composites. Different membrane materials have their own distinctive characteristics, such as hydraulic resistance, pH range, temperature range, chlorine tolerance, and biodegradation tolerance.
- *Module type*. Spiral wound and hollow fiber are the two membrane modules usually selected for RO systems. The spiral-wound unit clogs less frequently, while the hollow-fiber membrane has much greater surface area per unit volume.

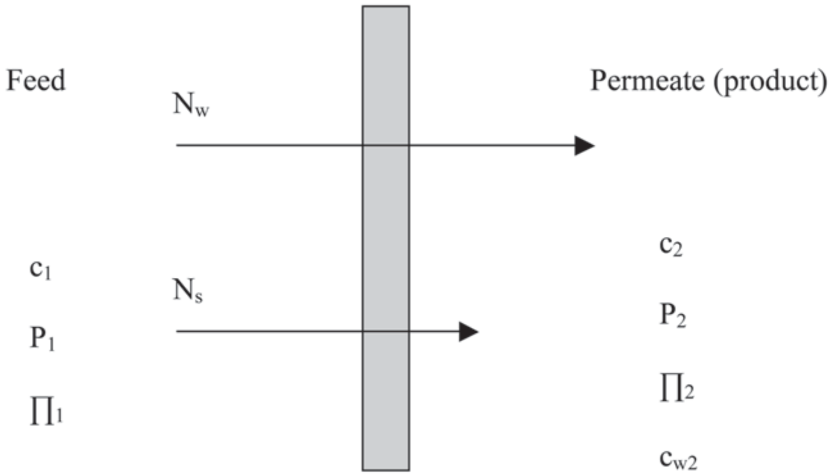

Fig. 21. Mass transfer in RO membrane.

- *Operating pressure*. Applied pressure of NF and RO can be found in Table 1. It is essential to the quantity and quality of water. RO systems operating at pressure less than 17 bars are classified as low-pressure units, while those operating above 24 bars are classified as high-pressure units. High operating pressure can trigger noise, vibration, and corrosion problems, but they are more effective. Recently, developments have been made on new models that perform well at low pressures.
- *Pretreatment requirements*. Pretreatment requirements include: (a) contaminant concentration; (b) ionic size of the contaminants; (c) membrane type; (d) presence of competing ions; (e) suspended solid concentration; and (f) water temperature. Pretreatment is commonly used to prevent fouling of the membrane. Typical pretreatment for NF and RO includes particle removal by filtration, sequestering hardness ions by precipitates, and pH control to prevent clogging.
- *Product conversion rate*. It depends on several factors, mainly ionic charge and ionic size. The higher the ionic charge and the larger the ionic size of the contaminant, the more easily the ion is removed and the more finished water is recovered relative to the amount of reject water.

6.4. Engineering Design

A membrane system can be designed by empirical or semiempirical approaches and computer-simulation models. The former can be found in the literature such as Geankoplis's manuscript (26); the later is illustrated by Judd and Jefferson (3). A frequently used design tool based on a semiempirical approach is given below.

6.4.1. Reverse Osmosic

Mass transfer of substances in a membrane unit can be considered as steady-state diffusion, which can be described by the following equations (6,12,40,49). A conceptual illustration of RO is given in Fig. 21. Noted that 1 and 2 represent feed and permeate (product) sides, respectively.

$$N_w = A_w(\Delta p - \Delta\Pi) \tag{32}$$

$$N_s = A_s(c_1 - c_2) \tag{33}$$

$$\Delta P = P_1 - P_2 \tag{34}$$

$$\Delta \Pi = \Pi_1 - \Pi_2 \tag{35}$$

where N_w is the water flux in kg water/s·m^2, N_s is the salt flux in kg salt/s·m^2, A_w is water permeability constant in kg water/s·m^2·atm, A_s is salt permeability constant in m/s, P_1 is pressure applied on feed solution in atm, P_2 is pressure of permeate (product) in atm, Π_1 is osmotic pressure of feed solution in atm, Π_2 is osmotic pressure of permeate (product) in atm, c_1 is salt concentration in feed solution in kg-salt/m^3, and c_2 is salt concentration in permeate (product) solution in kg-salt/m^3.

Water permeability constant (A_w) is a function of the membrane material such as water membrane permeability and membrane thickness. The presence of salt, however, is less important for the constant. For CA membranes, A_w typically ranges from 1×10^{-4} to 5×10^{-4} kg water/s·m^2·atm. Salt permeability constant depends on the types of salts in the solution. For CA membranes, A_s values range from 1×10^{-7} to 6.0×10^{-7} m/s. The values are 4×10^{-7} m/s for NaCl, 2.2×10^{-7} m/s for $MgCl_2$, 2.4×10^{-7} m/s for $CaCl_2$, 6.0×10^{-7} m/s for KCl, and 4×10^{-7} m/s for Na_2SO_4, respectively.

The solution volumetric flow rate in the feed side is approximately equal to that in the permeate side. Therefore, we have

$$A_m \cdot \frac{N_s}{c_2} = A_m \cdot \frac{N_w}{c_{w2}}$$

where c_{w2} is concentration of water in permeate (product) in kg water/m^3.

Thus, we can have:

$$N_s = \frac{N_w}{c_{w2}} c_2 \tag{36}$$

If the salt concentration in permeate (product) (c_2) is low, its osmotic pressure (Π_2) is normally ignored and the concentration of water in permeate (product) (c_{w2}) is approximately the pure water density that is a function of temperature (Table 5).

Define the salt rejection (R) as

$$R = \frac{c_1 - c_2}{c_1} \tag{37}$$

Combining Eqs. (32), (33), and (37) yields

$$R = \frac{B(\Delta P - \Delta \Pi)}{B(\Delta P - \Delta \Pi) + 1} \tag{38}$$

$$B = \frac{A_w}{A_s c_{w2}} \tag{39}$$

Noted that the newly combined parameter B has a unit of atm^{-1}.

During membrane operations, localized concentration of salt builds up at the boundary layer of membrane. This is called the concentration polarization (40,49). The concentration polarization can be reduced by increasing turbulence.

Table 5
Physical Properties of Pure Water

Temperature (°C)	Density, ρ ($\mathrm{kg/m^3}$)	Specific weight, γ ($\mathrm{kN/m^3}$)	Dynamic viscosity, μ (mPa·s)	Kinematic viscosity, v ($\mu\mathrm{m^2/s}$)
0	999.842	9.805	1.787	1.787
3.98	1,000.000	9.807	1.567	1.567
5	999.967	9.807	1.519	1.519
10	999.703	9.804	1.307	1.307
12	999.500	9.802	1.235	1.236
15	999.103	9.798	1.139	1.140
17	998.778	9.795	1.081	1.082
18	998.599	9.793	1.053	1.054
19	998.408	9.791	1.027	1.029
20	998.207	9.789	1.002	1.004
21	997.996	9.787	0.998	1.000
22	997.774	9.785	0.955	0.957
23	997.542	9.783	0.932	0.934
24	997.300	9.781	0.911	0.913
25	997.048	9.778	0.890	0.893
26	996.787	9.775	0.870	0.873
27	996.516	9.773	0.851	0.854
28	996.236	9.770	0.833	0.836
29	995.948	9.767	0.815	0.818
30	995.650	9.764	0.798	0.801
35	994.035	9.749	0.719	0.723
40	992.219	9.731	0.653	0.658
45	990.216	9.711	0.596	0.602
50	988.039	9.690	0.547	0.554
60	988.202	9.642	0.466	0.474
70	977.773	9.589	0.404	0.413
80	971.801	9.530	0.355	0.365
90	965.323	9.467	0.315	0.326
100	958.366	9.399	0.282	0.294

Pa·s = (mPa·s) × 10^{-3}; $\mathrm{m^2/s} = (\mu\mathrm{m^2/s}) \times 10^{-6}$

Owing to the presence of concentration polarization, Eqs. (33) and (35) will have to be revised as

$$N_s = A_s(\beta\, c_1 - c_2) \tag{40}$$

$$\Delta\Pi = \beta\Pi_1 - \Pi_2 \tag{41}$$

where β is concentration polarization, which normally ranges from 1.2 to 2.0. When the feed solution is well mixed and the salt concentration is about 1 %, the RO membrane filtration unit can be treated as a continuously stirred tank reactor (26).

Example 3

A RO membrane system is used for the desalination of a feed water that contains 2.5 g NaCl/L. The temperature is 25°C and the density of the feed is 999 $\mathrm{kg/m^3}$. The applied pressure (ΔP) is 27.6 atm. The water permeability constant (A_w) and the NaCl permeability constant (A_s) are 4.8×10^{-4} kg/s·m^2 and 4.4×10^{-7} m/s, respectively.

(a) Assume that the concentration polarization can be neglected. Calculate the salt reject, the water flux, and the salt flux through the membrane, and the salt concentration in the permeate.

(b) Owing to the incomplete mixing in the RO module, the concentration polarization can be assumed to be 2.0. What are the salt rejection, the water flux, the salt flux, and the salt concentration in the permeate? Also comment on the applied pressure (ΔP) if the quality of the product water remains the same as in (a).

Solution

(a) According to Eq. (10a), the osmotic pressure in the feed can be determined by:

$$\sum M_i = 2 \times 2.5 / 58.45 = 0.0856\ M$$

$$\Pi_1 = RT \sum M_i = 0.08206 \times (273 + 25) \times 0.0856 = 2.09\ \text{atm}$$

Assume that the salt concentration in the permeate is very low. Therefore, we have

$$\Pi_2 = 0$$

$$N_w = A_w(\Delta p - \Delta\Pi) = 4.8 \times 10^{-4} \times (27.6 - 2.09) = 0.01224\ \text{kg water} / \text{s} \cdot \text{m}^2$$

From Table 5, at a temperature of 25 °C, the water density is 997.05 kg/m^3. Thus, we have

$$c_{w2} = 997.05\ \text{kg} / \text{m}^3$$

$$B = \frac{A_w}{A_s c_{w2}} = \frac{4.8 \times 10^{-4}}{4.4 \times 10^{-7} \times 997.05} = 1.094\ \text{atm}^{-1}$$

$$R = \frac{B(\Delta P - \Delta\Pi)}{B(\Delta P - \Delta\Pi) + 1} = \frac{1.094 \times (27.6 - 2.09)}{1.094 \times (27.6 - 2.09) + 1} = 0.965$$

From $R = (c_1 - c_2)/c_1$, we have

$$c_2 = c_1(1 - R)$$

$$c_2 = 2.5 \times (1 - 0.965) = 0.0865\ \text{g NaCl/L}$$

$$\begin{aligned} N_s &= A_s(c_1 - c_2) = 4.4 \times 10^{-7} \times (2.5 - 0.0865) \\ &= 1.062 \times 10^{-6}\ \text{kg NaCl} / \text{s} \cdot \text{m}^2 \end{aligned}$$

(b) The concentration polarization is 2.0. According to Eq. (41), we have

$$\Delta\Pi = \beta\Pi_1 - \Pi_2 = 2.0 \times 2.09 = 4.18\ \text{atm}$$

$$\begin{aligned} N_w &= A_w(\Delta p - \Delta\Pi) = 4.8 \times 10^{-4} \times (27.6 - 4.18) \\ &= 0.01124\ \text{kg water} / \text{s} \cdot \text{m}^2 \end{aligned}$$

$$R = \frac{B(\Delta P - \Delta\Pi)}{B(\Delta P - \Delta\Pi) + 1} = \frac{1.094 \times (27.6 - 4.18)}{1.094 \times (27.6 - 4.18) + 1} = 0.962$$

$$c_2 = c_1(1 - R) = 2.5 \times (1 - 0.962) = 0.095\ \text{g NaCl} / \text{L}$$

From Eq. (40), we have

$$N_s = A_s(\beta c_1 - c_2) = 4.4 \times 10^{-7} \times (2 \times 2.5 - 0.095)$$
$$= 2.158 \times 10^{-6} \text{ kg NaCl / s} \cdot \text{m}^2$$

From the above calculation, we can find that, owing to the concentration polarization, the salt concentration in the permeate (c_2) is increased by about 10%, the water flux (N_w) is reduced by 8%, and the salt flux (N_s) is increased by 103%. If the applied pressure is increased to overcome the effect of concentration polarization (is increased by 2.09 atm), the same quality of water as in Part (a) can be obtained.

6.4.2 Microfiltration and Ultrafiltration

The water flux of MF and UF can be calculated by Eq. (32). As the membrane is more porous than RO membrane, it is only good for removal of "large" molecules with a molecular weight ranging from 500 to 1,000,000. Thus, it is reasonable to consider that the osmotic pressure ($\Delta\Pi$) is very low and can be ignored. Equation (32) is therefore modified as

$$N_w = A_w \Delta P \tag{42}$$

The concentration polarization is much more severe than RO. Therefore, the pressure drop must be considered in the calculation. The reader can refer to Geankoplis' manuscript for more-detailed information (26).

6.5. Membrane Testing

Before installing a membrane operation system, membrane testing is required to determine the capability of the particular polymer for the separation, optimum membrane configuration in the application, and optimum processing conditions (e.g., pressure, flow rates, and temperature).

In general, every stream must be tested to determine design factors such as the specific membrane polymer, membrane element design, total membrane area, applied pressure, system recovery, flow conditions, membrane element array, and pretreatment requirements.

For an ideal system, all contaminants to be removed are separated by the membrane and exit in the concentrate stream. In reality, no membrane is perfect. The actual quantity of solute that passes through the membrane depends on the chemistry of solute on the feed, the nature of membrane material, and the operational conditions. Cell test, applications test, and pilot test can be used to evaluate membrane technology with a particular stream.

Cell test uses small, approx 100-cm^2 cut pieces, of sheet membrane mounted in a "cell" that exposes the membrane to the test solution by cross-flow mode. This test is effective for quick evaluation of a number of different membrane polymers to determine the degree of separation. However, it cannot determine the long-term chemical effect of a solution on the polymer and does not provide engineering scale-up data.

An *applications* test is quite similar to the cell test. It typically involves the evaluation of treatment efficiency of a sample with a slightly higher volume, such as 100–150 L. The test can be completed within 1–2 h. The test is fast and provides scale-up data such as flow, element efficiency, and pressure requirements. It can also provide an indication

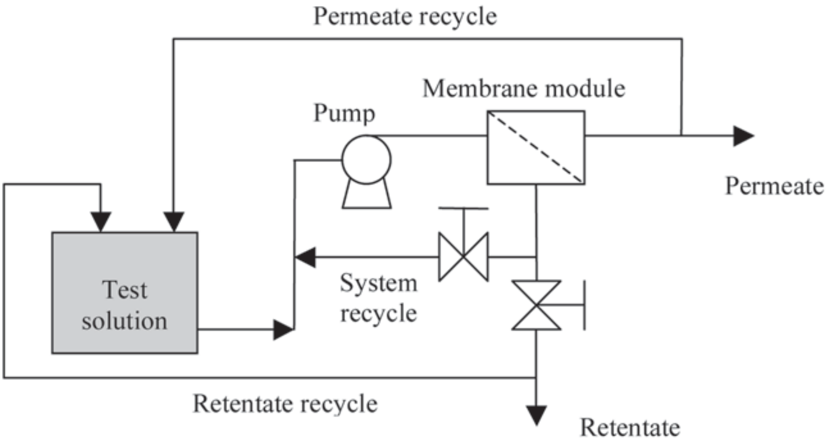

Fig. 22. Schematic drawing of a typical membrane application test.

of membrane stability. However, it provides neither the long-term chemical effects nor sufficient data on the fouling effects of the test solution. Figure 22 illustrates a typical applications test process.

Unlike the above two tests, the *pilot* test can provide more-detailed information. The test has a test machine in the process (similar to that in the applications test), which is operated for a longer period (normally a minimum of 30 d). It provides long-term membrane operation data such as fouling and chemical stability data. However, it can be expensive to perform, in terms of cost of equipment, and daily monitoring.

6.6. Economics of Membrane Processes

Membrane processes are mainly used in processes where very high purity of the component is required. Despite the technical advantages, such as being gentle to the products, the large-scale applications of membranes processes are often affected by their cost. The cost of a given installation is determined by two parts, the capital cost and the operational cost. The capital cost, or the installation investment, can be further divided into three parts:

- Membrane modules
- Costs of piping, pumps, electronics, vessels
- Pretreatment and post-treatment

In order to calculate the cost per unit (volume or mass) of product, the capital costs are depreciated over a period of time, often 10 yr. Interest has to be paid over this time on this amount of money. And the operational cost can be divided into four parts:

- Energy requirement
- Membrane replacement
- Labor
- Maintenance

A more detailed calculation of the cost of membrane operation can be found in some articles and books (50, 51). A computer program, named the Water Treatment Cost Estimation Programme (WTCost) can be used to estimate costs of water treatment

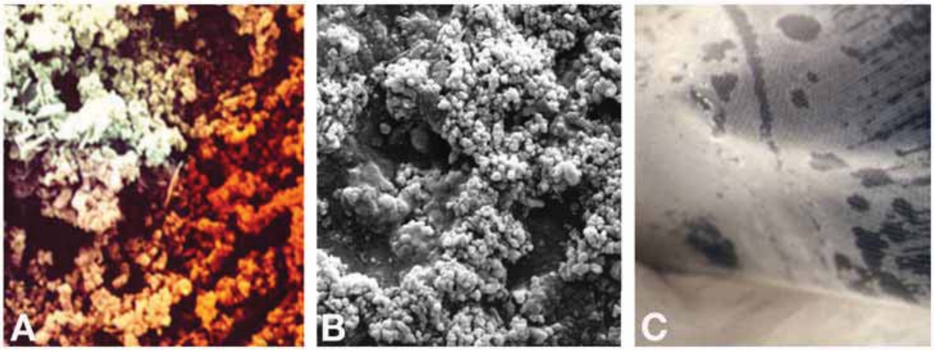

Fig. 23. Visualization of membrane fouling by scanning electron microscopy: **(A)** inorganic fouling due to calcium carbonate, calcium sulfate, silica, iron, barium and strontium sulfate (35,000×); **(B)** organic fouling due to humic acid (35,000×); **(C)** flow channels in membrane fouled with biological growth.

processes employing MF, UF, NF, RO, and ED. The costs of pretreatment and post-treatment unit operations can also be estimated. The WTCost has been tested by industry experts, and it has been shown to accurately project true water treatment costs for a number of plants of different brackish and seawater capacities (51).

7. MEMBRANE FOULING AND PREVENTION

7.1. *Mechanisms*

The major drawback hindering the use of membranes is the reversible and irreversible fouling that impedes the flux of clean water through the membranes (52). The consequence of membrane fouling is a reduction of permeate production rate and/or an increase in solute passage across the membrane with time. Fouling also causes increase in energy consumption as transmembrane pressure can increase substantially due to fouling. In addition, fouling increases downtime and may shorten membrane life span. Figure 23 demonstrates membrane fouling due to the presence of organic compounds, inorganic salts, and microorganisms.

Fouling can be defined as irreversible deposition of materials onto or into the membrane, causing loss of flux and altered rejection (53–55). Membrane fouling can be caused by

- Particulate deposition (colloidal fouling)
- Adsorption of organic molecules (organic fouling)
- Inorganic deposits (scaling)
- Microbial adhesion and growth (biofilm formation)

Colloidal fouling is caused by accumulation of particles and macromolecules on, in, and near a membrane. Materials accumulated at the membrane surface create an additional layer of resistance to permeation. Early work on colloidal fouling of RO membrane used to treat secondary effluents indicated that particles smaller than 5 μm contribute more substantially to fouling than larger particles (56). It was postulated that as particle size increases, it is subjected to higher velocity and shear force at the membrane surface. Therefore, larger particles tend to be swept away in bulk flow rather than deposit on the membrane surface. In addition to surface deposition, some particles may be small enough to penetrate and remain within the pores of the membrane. The tendency of pore blockage is likely to be higher in UF and MF as their pore size is bigger and hence allows more particles to penetrate and deposit in the membrane pores. In another study, factors influencing the flux decline of NF membranes for the treatment of dye bath wastewaters were investigated. It was found that cake layer formation of dye molecules on membrane surface, especially at low salt concentrations was the principal cause of flux decline (57).

The adsorption of organic matter on membrane surfaces is detrimental to permeate flux and affects the salt rejection of membranes (Fig. 23B). The negatively charged functional groups on organic foulants have an affinity for charged membrane surfaces, thereby forming a permeate-resistant layer. Organic foulants also interact with colloidal foulants. Polyphenolic compounds, proteins, and polysaccharides bind colloids and particles and increase their cohesion to the membrane surface (58). It was also found that membrane fouling by natural organic matter (NOM) adsorption is a major factor limiting the use of MF for drinking water treatment (59). UF is commonly used for isolation and fractionation of humic substances. In addition, the biochemical interaction between organics and microorganisms promote biofilm formation and growth. Insufficient knowledge on the composition of dissolved organics in water makes the control of organic fouling difficult.

Inorganic fouling is caused by deposit of iron, silica, aluminum, calcium, phosphorus, and sulfate (Fig. 23A). The fouling mechanism at the membrane surface can be caused by the concentration polarization effect. A concentrated boundary layer is created on the separation surface as product water passes through the membrane. Within this boundary layer, the high concentration causes the salts to precipitate and suspended solids can start to deposit on the membrane surface leading to scaling and fouling (58). Scale deposition on and into RO membranes impairs the hydrodynamic conditions of the feed flow. When fouling conditions are not controlled properly, scaling becomes a self-sustaining phenomenon (60). Under serve concentration polarization, channelling, failure of RO performance and damage to membrane surface occur.

Biofouling is the term given to the adhesion of microorganisms and growth of biofilm on the membrane surface (Fig. 23C). Sewage carries a very high load of potentially pathogenic and nonpathogenic microorganisms in addition to chemical pollutants and nutrients (61). Besides the detrimental effects of increasing transmembrane pressure and decreased permeate flux, biofouling may cause chemical degradation of the membrane material. This could result from direct enzymatic biodegradation of the membrane surface or by generation of extreme local pH that may hydrolyze the membrane polymer (61–63). Such fouling can significantly reduce the membrane lifetime.

The formation of biofilm involves three steps:

1. Formation of a conditioning film composed of macromolecules, proteins, etc.
2. Primary bioadhesion by microorganisms.
3. Biofilm development.

A recent study has shown that some RO membranes are more prone to bioadhesion than others. The study involved a bioadhesion assay, which utilizes a model bacterium, SW 8, known to adhere to membranes. Examination of bacteria adhered to the membranes using optical microscopy revealed that membranes which are less susceptible to bioadhesion are hydrophilic in nature (62,63). Further investigation with municipal wastewater carried out on RO simulators that consisted of flat sheet membranes to simulate spiral-wound module revealed biofilm characteristics under field emission scanning electron microscope. Microorganisms cover the surface of all types of RO membranes used in the experiment to a density of about 2.25×10^8 cells/cm^2 (62). Bacteria of different shapes (mostly rod-shaped) with dimensions between 1 and 3 μm were observed. The organisms appeared to excrete extracellular polymeric substances.

The ratio of carbon to nitrogen to phosphorus (C:N:P) has important effects on the rate of biofilm development. It has been reported that membranes which suffered severe biofouling were found to contain a high percentage (typically >60%) of organics. Laboratory characterization of membrane biofilms found that a typical biofilm contains:

- 90% moisture
- 50% total organic matter
- up to 40% humic substances
- low inorganic content
- high microbiological counts ($>10^6$ cfu/cm^2) including bacteria and fungi

Membrane autopsy of desalination RO membranes that had been in service for 2.5 yr in Saudi Arabia revealed bacterial deposits that are slimy and very adherent (64). This is primarily due to accumulation of extracellular polysaccharides excreted by microorganisms, thus resulting in biofilm formation (54). Bacteria embedded in a biofilm are found to be more resistant to biocides than freely suspended ones (65).

Understanding membrane fouling creates the foundation for researchers to devise an approach to counter or minimize fouling in order to maintain high RO performance. One strategy to alleviate membrane fouling is feed pretreatment to reduce or remove fouling constituents in the feed. A proper membrane cleaning and regeneration protocol to periodically remove foulants from the membrane surface is also essential in maximising RO efficiency.

7.2. Feed Pretreatment

Applicable pretreatment prior to membrane separation are screening, coagulation, flotation, and, in extreme cases, activated carbon or resin adsorption and even ultrafiltraion (66). Economics has a major role to play in deciding the pre-treatment sequence. For example, membrane life estimates may be 1 and 3 yr for minimal and extensive pretreatment, respectively. A study shows prefiltration of the humic acid solution significantly reduced the rate and extent of fouling by removing the large humic acid aggregates/particles from the solution (67).

RO membranes are generally not robust enough to operate directly on feed such as secondary wastewater. The success of RO process is highly dependent on appropriate feed pretreatment. Pretreatment must be effective in reducing RO fouling potential in a reliable and consistent manner. Feed pretreatment continues to be one of the fields that is extensively studied. Water Factory 21, which has been operating for more than two decades, continues to evaluate feed pretreatment to maximize RO efficiency (68). In the development of a pretreatment program, the focus is on removing as much fouling constituents in the feed water as possible before RO processing.

7.2.1. Conventional Pretreatment

Wastewater reclamation was pioneered using advanced conventional treatment processes to upgrade the water quality of wastewater to reusable standards. When RO was first introduced to produce water closer to drinking water quality from wastewater, a conventional treatment process was employed as pretreatment to the RO. A typical conventional pretreatment configuration would include flocculation, lime or alum clarification, recarbonation, settling, filtration, and activated-carbon adsorption. Biological activity is controlled by chlorination.

Water Factory 21, which employs such a train of pretreatment, reported that 26% of TOC was removed by lime clarification. The concentrations of inorganic constituents such as calcium, magnesium, iron, fluoride, and silica were significantly reduced. Over 99% of coliform bacteria were removed and viruses were effectively inactivated by the high pH. Multimedia filtration produced an average effluent turbidity of 0.14–0.16 NTU. Granular activated carbon (GAC) removed 30–50% of the organics. The average TOC concentration of GAC effluent was 5.5 mg/L (69).

Although clarification following lime or alum coagulation is a very effective pretreatment for removing colloidal and suspended matter, the process is expensive, as chemical dosage is required. The process is also difficult to operate because optimum dosage depends on influent quality. Furthermore, the coagulation–clarification process generates solid waste that requires additional handling and disposal. In cases where over-dosage occurs, high metal salt content of the pretreatment water may result in metal hydroxide precipitation on the subsequent RO membranes (70). Another disadvantage of the clarification process is a large requirement in land space.

A simplified process used in smaller systems is in-line flocculation followed by pressure filtration. The simplified process produces water of lower quality than the lime clarification process but the equipment is smaller and simpler to operate (71). Experience with in-line filtration showed that optimal dosage of alum was rarely achieved due to fluctuating influent turbidity (72,73).

Alum, alum–polyelectrolyte, and polyelectrolyte in-line flocculation filtration systems were compared by Cikurel et al. (74). Their results show that high-molecular-weight (2×10^6) branched-chain polyacrylamide at a dosage as low as 0.5 mg/L is more effective at turbidity removal than alum dosed at 10–20 mg/L. The results are consistent at both low (6–12 NTU) and high (20–27 NTU) feed turbidity. The performance of polyacrylamide as primary flocculant was comparable to the alum–polyelectrolyte system. Various polyelectrolytes of different molecular weights (MW) were evaluated. High MW polyacrylamide was more effective than medium and low MW polyamides at same dosage of 0.5 mg/L. Effectiveness of medium MW polyamide increased when dosage was increased above 5 mg/L. Low MW polyamide was not effective in reducing turbidity even at dosage of 7 mg/L. The charge density of the polymers did not play a significant role in particle removal. It was postulated that the main mechanism of high MW polymer is bridging in contrast to adsorption and charge neutralization action of alum.

Studies on in-line filtration showed that effluent turbidity of less than 2 NTU is achievable with alum dosage of 0–8 mg/L and cationic polymer dosage of 0–0.5 mg/L (73). However, the performance of this system is dependent on feed water quality, hydraulic loading rate of the granular media column, and good control over the dosage of alum and the cationic polymer. High feed water turbidity and high polymer dosage have adverse effect on the duration of filtration cycle.

7.2.2. Membrane Pre-treatment

MF and UF membrane processes are increasingly being used in the water and wastewater treatment. The outcome of rapid developments in membrane industry is low-cost high-productivity membranes making membrane processes economically feasible. Numerous studies and site experience have lead to better understanding of process parameters, allowing process optimization making membrane processes more technically feasible.

Water Factory 21 has demonstrated that MF pretreatment can provide good pretreatment for the RO processes with multiple benefits over conventional pretreatment (75). The benefits of MF pretreatment include increased RO flux and overall efficiency, prolonged operation time between cleans, and reduction in operating and chemical costs. Following this successful demonstration at Water Factory 21, the industry is moving from lime clarification toward MF and UF as a pretreatment. There are multiple pilot projects evaluating MF as a pretreatment to the RO process. Pilot study performed in San Francisco utilizes MF as pretreatment to RO for desalination of municipal wastewater for horticultural reuse. The average turbidity removal was 99.4 ± 0.4%. The average Silt Density Index (SDI) was 1.15 ± 0.53.

Pilot plant studies conducted at Canary Islands (Spain) showed that microfiltered secondary effluent from Tías WWTP contained below 1.0 mg/L of suspended solids and turbidity below 1.0 NTU. Total and fecal coliforms were also absent from the microfiltered water. The SDI of the microfiltered water was below 3.0. Average removal achieved for BOD_5, COD, and TOC were 81%, 40%, and 27% respectively. The MF achieved water recovery of about 85% (76).

A study was performed to investigate MF pretreatment performance in treating a broad range of water. Results showed that the performance of MF remains satisfactory when subjected to very cold water (0.2°C), water with high iron content, and water with high organic load and biofouling potential (77). Acid wash has to be included in the operation procedures when treating high iron content water to prolong run time between chemical cleaning. The addition of acid keeps the iron content in the water in a reduced and dissolved form, preventing precipitation and scaling on the membrane.

A lab scale evaluation of pretreatment for RO recycling of secondary effluent from refinery demonstrated that UF is able to provide good pretreatment for subsequent RO process. UF was capable of removing over 98% of suspended solids and colloids. Partial removal (30%) of COD was also achieved. The removal efficiency was consistent and was independent of influent water quality and operating conditions (78). Similar results reported by Qin and co-workers demonstrate that an appropriate UF pretreatment could reduce fouling of RO membrane and increase the flux of RO membrane by 30–50% (79).

Another pilot study on UF-RO membrane treatment of industrial effluent (pulp and paper mill effluent) showed that UF permeate flux increased with temperature of feed water. The fluxes were 1.44 and 1.84 times higher at 30°C and 40°C, respectively compared to flux at 20°C. The improvement in flux was attributed to decreased wastewater viscosity with increased temperature. However, at higher temperatures, more organic matter was able to diffuse through the membrane. Comparison of UF pretreatment at feed pH 2.4, 5.3, and 7.0 showed that higher flux is achieved at pH 7.0 (80).

MF and UF can reduce biofouling tendency in RO membrane as they pose a physical barrier to these microorganisms. MF is capable of removal of protozoa (approx 10µm), coliform (approx 1µm) and cysts (approx 0.1µm). The pore size of UF is smaller and thus can further remove viruses (approx 0.01–0.1 µm) (81). It has been reported that UF showed more than a five-log reduction of microbial content (82). Membranes are attractive as disinfection process because it reduces the dosage of aggressive chemicals such as chlorine and ozone. In addition, undesirable disinfection by-products can be minimized or avoided. The interest in using membrane as part of the disinfection process has intensified with the emergence of chlorine-resistant pathogens. Chlorine-resistant *Cryptosporidium parvum* has been reported to cause outbreak of diarrhea epidemic in US and UK. Water supply authorities are looking to UF and MF application to act as an absolute barrier to *Cryptosporidium* oocysts, which range from 4 to 6 µm (83).

Chlorination of secondary effluent prior to membrane pretreatment may extend membrane run times between clean. Over 90 h of MF operation was achieved with prechlorinated secondary effluent compared to 42 h operation reported when secondary effluent was not chlorinated (72,73). Similar observations were reported with dosage of chloramine prior to microfiltration pretreatment (77). It was speculated that preoxidation due to chlorination altered the chemistry of extracellular polymeric substance (EPS) produced by the microorganisms in the secondary effluent. This could weaken the attachment of the EPS on the membrane and thus offset the detrimental effect on the membrane flux. However, care must be taken to verify compatibility of membrane with chlorination as some membranes are not tolerant to the aggressive action of chlorine.

Although MF and UF membranes have been shown to be a viable option as feed pretreatment for RO, long-term operating and cost data are required to verify that membrane pretreatment is more cost effective than conventional pretreatment.

From a fouling perspective, use of membrane pretreatment has made it possible to segregate flux loss due to colloidal fouling and biofouling from flux loss due to scaling (84). Antifouling strategy can be developed with more focus on the relevant type of fouling. Although microbes can escape defective portions of pretreatment membrane and cause biofouling, the potential and degree of biofouling has been greatly reduced. This can reduce the application of disinfection, increase operation interval between cleans, and prolong membrane life.

Overall, studies on membrane pretreatment demonstrate the following advantages:

- Addition of chemicals is not required
- Effluent quality is independent of feed quality
- Operation at ambient temperature
- Forms an absolute barrier to pathogens
- Space efficient

The simplicity of membrane operation makes it an attractive option in the field of wastewater reclamation.

8. MEMBRANE CLEANING AND FLUX RESTORATION

Fouling is almost an inevitable consequence of the nature of the RO process itself even when good pretreatment is employed. The challenge is therefore to reduce and control fouling sufficiently to minimize the rate of RO flux decline and prolong membrane lifetime. This can be accomplished by a combination of good feed pretreatment and well-developed membrane cleaning programs.

It is essential to have a good knowledge of fouling to successfully clean and regenerate fouled membranes. Types of foulants that could occur on RO membrane surfaces include suspended solids, colloids, metal oxides, scales, biological slime, organics, oil, and grease. The type of fouling that could occur on the membrane surface is a function of the make-up of the feed water, the pretreatment applied prior to the RO membrane, and the interaction between the different foulants. The effects of cleaning parameters (e.g., pH and temperature) can be obtained through factorial design approach as described by Chen et al. (4).

The most dominant fouling that can occur in wastewater reclamation is biological fouling and organic fouling (70). The major factor in controlling fouling on membranes used in secondary effluent treatment is the dissolved organic content of the feed water (56). Dissolved organics such as humic acids, proteins, carbohydrate and tannins in addition to biological growth were the major fouling constituents of RO membranes in wastewater reclamation (85).

8.1. *Chemical Cleaning Methods*

Most membrane manufacturers recommend chemical methods for membrane cleaning and regeneration (70). Chemical cleaning is the most common method to clean NF membranes (86). Chemical cleaning methods depend on chemical reactions to weaken the cohesion forces between the foulants and the adhesion forces between the foulants and the membrane surface. Chemical reactions involved in cleaning include hydrolysis, peptization, saponification, solubilization, dispersion, chelation, sequestering, and suspending (87). It was found that cleaning with strong chelating agents, such as EDTA, most effectively removes the fouling layer and restores permeate flux for NF membranes (88). Chemical used for cleaning membranes should ideally serve the following functions and posses the following desirable properties:

- Loosen and dissolve foulants from membrane surface
- Keep foulants in dispersed and soluble form
- Avoid fresh fouling
- Does not cause damage to membrane material
- Easily rinsed away after cleaning
- Chemically stable before, during and after use
- Cost effective

Table 6 gives a brief description of cleaning action of some chemicals commonly used in membrane cleaning. Important cleaning parameters that vary with foulant and membrane material are type of cleaning agent, pH, concentration, temperature, and time. However, as a rule, mineral deposits are removed by acidic solutions and organic compounds by alkaline solutions (89). The choice of chemical cleaning agents not only depends on type of foulants present in the membrane system but also on the chemical

Table 6
Chemicals Commonly Used in Membrane Cleaning and Their Cleaning Actions

Type of chemicals	Common chemicals used	Typical concentration (%)	Cleaning actions (87)
Acid	HCl	0.1–0.2	• Dissolve precipitation of inorganic salts
	HNO_3	0.3–0.5	
	H_3PO_4	0.3–0.5	
	Citric acid	1.0–2.0	
Carbonate	Na_2CO_3	0.5–1.0	• Buffer pH of cleaning solution
	$NaHCO_3$		
Disinfectant	H_2O_2	0.1	• Inactivate microorganisms
	NaOCl	0.002–0.02	
	Na_2SO_3	0.25	
Enzymes	Lipase protease		• Break down high-molecular-weight organic compounds
Hydroxide	NaOH	0.5–1.0	• Remove organic fouling
	KOH		
Polyphosphate	Polymeric phosphonate		• Act as dispersant • Solubilize carbonates • Bind ion salts • Regulate pH • Emulsify fats • Peptise proteins
Surfactant	$EDTA\text{-}Na_4$ EDTA + NaOH $EDTA\text{-}Na_4$ + NaOH	0.5–1.0	• Increase ease of rinsing • Improve contact between cleaning chemicals and the foulants • Minimize amount of water required • Shorten rinsing time

resistance of the membrane material and the whole system. Caution must be taken in applying these chemicals as the aggressive nature of these chemicals may adversely affect system or membrane integrity when not applied properly. This is especially true for aromatic polyamide membranes, which are less robust than cellulose acetate and polysulfone membranes. For example, some cationic and non-ionic surfactant may be adsorbed onto polyamide membranes and cause a flux decrease.

Polyamide membranes are also not resistant to the strong oxidizing actions of disinfectants such as hydrogen peroxide and hypochlorite. Acids used to the clean membrane system must be rinsed out thoroughly before application of hypochlorite for disinfection as hypochlorite at low pH can cause corrosion in stainless steel. The pH of the chemical cleaning solution must fall within the tolerable range of pH 1–13 for polysulfone membranes and pH 3–8 for CA membranes (87).

In studies to remove organic fouling on RO membranes, it has been reported that several commercial cleaners developed by Pfizer gave excellent results. Differential pressure of the membrane system could be reduced by 42% using a neutral pH liquid formulation (Floclean 107) designed to remove organics, silt, and other particulates from cellulose acetate RO membranes. For polyamide, polysulfone, and thin-film-composite membranes, a high pH commercial cleaner (Floclean 411) was able to recover permeate flow by 23.8% (90). In a comparison study, commercial cleaners proved to perform better than cleaning recipes recommended by membrane manufacturers. Ebrahim and El-Dessouky compared commercial cleaner Floclean 403 and 411 from Pfizer with the membrane manufacturer's recommended recipe of 2% citric acid at pH 4.0 for cleaning seawater RO membranes (91). An improvement of 11.6–30.8 % was achieved.

High biological activity can be expected from secondary effluent due to biological treatment. Bacterial concentrations between 10^3 and 10^4 CFU/mL are common in secondary effluent (92). Biofouled membranes cleaned with a combination of a high pH cleaner designed for biofouled membranes and a low pH cleaner designed for bioslimes reportedly resulted in 76% restoration in permeate flow. This was accompanied by a reduction in differential pressure of 41% (90). Alternating between caustic detergent at pH 12 and peracetic acid and hydrogen peroxide at pH 2 was effective in eliminating sulfate-reducing bacteria on seawater RO membranes (93).

Biocides have commonly been used in the water treatment industry to counter biofouling problems. Unfortunately, the application of biocide to a membrane system has its limitations. Application of biocide such as hypochlorite can remove about 80% of the biofouling layer on a RO membrane. This can result in considerable process improvement in the RO system. However, the remaining 20% of biofilm provide nutrients for rapid regrowth of the biofilm (94).

Systems with chlorination prior to the membrane processes were easier to clean due to the presence of chloramines, which act as a disinfectant and reduce the tendency of biofouling. However, membranes in such systems are more susceptible to structural damage owing to prolong exposure to the aggressive action of the combined chlorine. Cellulose acetate membranes are reported to become more brittle when chlorine dosage was in the range 15–20 mg/L (92). It was also suggested that certain organochlorine derivatives might modify the molecular structure of the membranes, thus resulting in flux decline and decreased salt rejecting efficiency.

Results of a study on regeneration of RO membranes treating brackish water showed that dosing of a high-molecular-weight polymer colloidal solution following high pH alkaline chemical cleaning could reduce salt passage through the membranes. Tannic acid was chosen as the polymer for this study. Average salt passage across the RO membrane was reduced from 14% to 6–10% using this cleaning method (95). However, the system suffered an average of 10% flux loss, which was claimed to be tolerable. It was postulated that a dynamic layer capable of reducing salt passage was formed on the membrane surface during such a polymer post-treatment following chemical clean.

It was reported that a combination of anionic cleaning agent and enzymes could effectively remove biofilm (92). The disadvantage in using enzymes is that they are very costly and formulating enzymes into effective cleaners is very expensive (87). In addition, enzymes are very specific and may not work well in all applications. Enzyme cleaning is dependent on many factors such as temperature and pH. Enzymes act slowly and consequently longer cleaning times are required.

Inorganic fouling in the form of scale formation is generally removed by acidic cleaning (54, 96, 97). Membranes treating water with high inorganic potential, such as a high TDS or hardness level, often include low pH cleaning in their chemical cleaning

Table 7
Chemicals Used in Removing Scale from RO Membranes

Target foulants	Recipe for chemical cleaning	Results	Reference
$CaSO_4$ $CaCO_3$	2% EDTA and citric acid stabilised by ammonia to pH 7	Remove calcium scale effectively	96
Metal hydroxide deposits	Floclean 103A by Pfizer (low pH formulation)	Removed stubborn metal hydroxide deposits 30% improvement in permeate flow 33% reduction in differential pressure	90
Ca and Mg deposits	1% EDTA at pH 10	Remove Ca and Mg deposits effectively Removal is faster in dynamic cleaner than in static cleaning	97
Fe deposits	1–2% sodium hydrosulfite at pH 3.2-3.8	Remove Fe deposits effectively	97

procedures. Table 7 shows a survey of chemical methods used to counter scaling on membrane.

Although chemical cleaning agents are categorized with respect to their action on different types of foulant, their combine effects are much more complex. These cleaning agents may interfere with the cleaning effects of each other. Some may provide efficient control over particular foulants while adversely affecting fouling control of another foulant. For example, some cationic polymers while effective in silica scale inhibition, reduce calcium carbonate scale inhibition by 30–40% (98). Humic and fulvic acids act as good calcium scale inhibitor, but they promote biofouling in the membrane system.

8.2. *Physical Cleaning Methods*

Physical cleaning methods depend on mechanical forces to dislodge and remove foulants from the membrane surface. Physical methods used include forward flushing, reverse flushing, backwashing, vibrations, air sparge, and CO_2 back permeation.

MF and UF used in pretreatment to RO are more frequently cleaned by physical cleaning and less frequently by chemical cleaning. Cleaning frequencies reported in literature varied widely. Physical cleaning frequency is approximately every 40 min with a chemical clean scheduled every 6 mo (98). An air backwash frequency of 15–20 min is sufficient for hollow-fiber MF membranes (77). In a UF evaluation study, backwashing was able to achieve an average flux recovery of 86.5% (99). It was observed in the same study that flux restoration could be achieved even when backwash was reduced from 10 to 1 min.

There has not been adequate investigation into physical and physicochemical cleaning methods for RO membranes (70). It was commented that there is little published information on membrane cleaning and regeneration. Most cleaning studies reported are based on trial and error (4,87). A more systematic approach is required to study the various aspects of fouling control (98). A better understanding of cleaning mechanisms and the effect of different cleaning agents on different foulants and different types of membrane is much needed. Further efforts are needed to develop more feasible and cost-effective cleaning and restoration procedures for different types of membranes.

A new generation of low fouling composite membranes has been introduced. The salt rejection layer on the membrane has been modified to make it more hydrophilic thereby reducing its affinity to organics (98). The novel process is the incorporation of an electromagnetic device, which produces an electromagnetic field surrounding the membrane elements. This electromagnetic field reduces the precipitation of sparingly soluble salts. Organic fouling can also be reduced by this method as the electromagnetic field can neutralize organics and affect their ability to interact with the membrane surface.

9. SUMMARY

In conclusion, the use of membrane technology in water and wastewater treatment has begun to emerge as the most significant advancement in water treatment in the past 20 yr, and its presence is expected to become widely spread in the future.

The potential to use membranes exists whenever they provide the ability to remove contaminants that cannot be removed by other technologies, remove contaminants at less cost than other alternatives, or require less land area than competing technologies. The biggest single technical challenge with the use of membranes for water treatment is the high fouling that occurs universally, which results in an increase in feed pressure and requires frequent cleaning of membranes. This leads to a reduction in overall facility efficiency and a shorter membrane life. Pretreatment prior to membrane filtration is generally required for a full scale plant (100,101).

With extensive research and development efforts on tackling the membrane fouling and emerging of new cleaning technology, membrane technology has become a more promising option for both water treatment (100,101) and wastewater treatment (102) when considering urban reuse, agricultural reuse, industrial recycle, groundwater recharge, salinity barriers, and augmentation of potable water or ultra-pure water supplies. Membrane bioreactor (MBR) is the latest environmental process development which combines both biotechnology and membrane technology together for wastewater treatment (102). Another latest development involves the use of membrane technology for gas separation (37, 103). The future of membrane technology is unlimited.

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ABBREVIATIONS

AFM	Atomic force microscopy
BOD_5	5-d Biochemical oxygen demand
CA	Cellulose acetate
COD	Chemical oxygen demand

ED	Electrodialysis
EPS	Extracellular polymeric substance
GAC	Granular activated carbon
MBR	Membrane bioreactor
MF	Microfiltration
MWCO	Molecular weight cutoff
NF	Nanofiltration
PTFE	Polytetrafluoroethylene
PVP	Polyvinylpyrrolidone
RO	Reverse osmosis
SDI	Silt density index
TDS	Total dissolved solids
TOC	Total organic carbon
UF	Ultrafiltration
WTCost	Water treatment cost estimation program

NOMENCLATURE

A	Proportionality factor
A_m	Membrane area, m^2
A_w	Water permeability constant, kg-water/s -m^2 -atm
A_s	Salt permeability constant, m/s
a_{Am}	Activity of solute in the membrane, mol/m^3
a_B	Activity of solvent outside of the membrane, mol/m^3
a_{Bm}	Activity of solvent in the membrane, mol/m^3
a_{im}	Activity in the membrane, mol/m^3
B	Combined parameter, atm^{-1}
β	Concentration polarization, 1.2–2.0.
c_1	Salt concentration in feed solution, kg-salt/m^3
c_2	Salt concentration in permeate (product) solution, kg-salt/m^3
c_A	Concentration of solute outside the membrane, mol/m^3
c_{AF}	Concentration of solute in the feed, mol/m^3
c_{Am}	Concentration of solute in the membrane, mol/m^3
c_{AP}	Concentration of solute in the permeate, mol/m^3
c_{Bm}	Concentration of the solvent in the membrane, mol/m^3
c_{BP}	Concentration of the solvent in the permeate, kg/m^3
c_{w2}	Concentration of water in permeate (product), kg-water/m^3
D_{Am}	Diffusion coefficient of solute in the membrane, m^2/s
D_{Bm}	Diffusion coefficient of solvent in the membrane, m^2/s
Δ	Quantity difference
ε	Surface porosity
f_{Am}	Friction between a unit mole of the solute and the membrane material, J s/m^2
f_{Bm}	Friction between a unit mole of the solvent and the membrane material, J s/m^2
∇	Gradient
J	Flux, mol/m^2 s (by quantity) or kg/m^2 s (by mass) or m^2/m s (by volume)

J_i	Flux of component i, mol/m^2 s
J_A	Flux of solute, mol/m^2 s
J_B	Flux of solvent, mol/m^2 s
K	Kozeny–Carman constant
K_A	Distribution constant of solute
l	Membrane thickness, m
L	Phenomenological coefficients
M_i	Molalities or molarities of ions and non-ionic compounds, mol/kg or mol/L
μ	Fluid viscosity, Pa s, or chemical potential, J/mol
μ_A	Chemical potential of solute, J/mol
μ_B	Chemical potential of solvent, J/mol
μ_i	Chemical potential of the ith component, J/mol
n_p	Number of pores
N_w	Water flux, kg-water/s m^2
N_s	Salt flux, kg-salt/s m^2
v	Molar volume, m^3/mol
v_A	Molar volume of solute, m^3/mol
v_B	Molar volume of solvent, m^3/mol
v_i	Partial molar volume of the ith component, m^3/mol
p	Pressure, Pa
P_1	Pressure applied on feed solution, atm
P_2	Pressure of permeate (product), atm,
Π	Osmotic pressure, Pa
Π_1	Osmotic pressure of feed solution, atm
Π_2	Osmotic pressure of permeate (product), atm
r	Pore radius, m
R	Gas constant, 8.314 J/mol ^{o}K , or Solute rejection rate
S	Specific surface area, m^2/m^3
T	Temperature, ^{o}C or K
τ	Pore tortuosity
x	Axial coordinate in the pore, m
X	Driving force

Subscripts

1	Quantities concerning feed solution
2	Quantities concerning permeate (product) solution
A	Quantities concerning solute
B	Quantities concerning solvent
F	Quantities concerning the feed
i	Quantities concerning ith component
j	Quantities concerning jth component
m	Quantities concerning inside the membrane or membrane
P	Quantities concerning the permeate, or pore
s	Quantities concerning salt
w	Quantities concerning water

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Ion Exchange

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CONTENTS

1. INTRODUCTION

Several processes can be used to attract soluble ions from the liquid phase to the solid phase and among these is ion exchange, which is arguably the most widely used in the water treatment industry for this purpose (1–4). Ion exchange (IX) provides a means for transferring one or more ionic species from one liquid phase to another via intermediate solid resins. To achieve this, a group of ion species (the target ions) present in a solution is exchanged with another group of ion species belonging to a solid phase (IX resin or IXR). The target ions, which may be toxic, precious, or contaminants affecting water purity, are therefore concentrated on the resin, while nontoxic, precious or contaminating ions are released from the resin to replace them in the solution. The use of a regenerant on the IXR could, subsequently, release the target ions into solution again (i.e., the regenerant) and allow recovery of the IXR's exchange capacity so that it may be applied again on more of the original solution.

The ion-exchange phenomenon was discovered by Thompson and Way in the 1850s, who noted ammonium ions in solution could be replaced by calcium ions after percolating the solution through a tube filled with soil (1). The first industrial application of ion exchange was reported in 1905 where water was softened using sodium–aluminosilicate cation exchange resin (2). The latter was subsequently regenerated with sodium chloride solution. This process is the forerunner and basis for the large-scale use of ion exchange today.

Initially, naturally occurring ion exchangers (called zeolites) were (and are still) used but these are unstable in the presence of competitive substances such as mineral acids.

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Adams and Holmes (1) contributed much to solving this problem by proposing the use of synthesized resins (3). These resins were condensate polymers resulting from the reaction between formaldehyde and phenolic or aromatic amine derivatives. Depending on the nature of the phenolic group, the resins can have either sulfonic ($–SO_3^-$) or amine ($–NH_3^+$) functional groups. It is these functional groups which participate in the reversible exchange of cations or anions.

Subsequently D'Alello developed the polystyrene-based resin in 1944 (4). Two years later, polystyrene anion-exchange resins made by chloromethylation and amination of the matrix were produced. Four principal classes of ion-exchange resins were commercially available by the 1950s. These are the strong-acid, strong-base, and weak-base resins derived from styrene–divinylbenzene copolymers, and the weak-acid resins derived from cross-linked acrylics. To this day, the most widely used ion exchangers are synthetic organic polymer resins based on styrene- or acrylic-acid–type monomers as described by D'Alelio in U.S. Patent 2,3666,007.

The ion-exchange process is typically intended to be a reversible one; thus, the spent resins are expected to be regenerated and reused. Ion exchange resins are water-insoluble solid substances that can absorb positively or negatively charged ions from an electrolyte solution and release other ions with the same charges into the solution in an equivalent amount. According to the charges of the ions exchanged, ion exchangers can be classified as cation or anion exchangers. The so-called amphoteric ion exchangers can exchange both negatively and positively charged ions. While this chapter discusses the purposeful application of ion exchange in industry, it should be noted it is a natural phenomenon that occurs in minerals, soils, waters, and even the tissues of plants, animals, and the human body.

While ion-exchange processes are, in many aspects, analogous to adsorption processes, there are distinct differences. Ion-exchange processes take place stoichiometrically with an effective exchange of ions, whereas adsorption removes dissolved substances from solution with the release of negligible amounts of substances into the solution to replace those removed. However, the two processes cannot be entirely separated in practice and they act together although it is likely one of the two would be the dominant process.

Ion exchange forms the basis of a large number of chemical processes involving substitution, separation, and removal of ions (3–8). In substitution, ions on the resin that are of low or no commercial value are replaced with valuable ions. This represents a process of recovering the valuable ions from solution. In separation, ions are separated according to the affinities between them and the resin as the solution passes through a column packed with the resin. If such columns are packed with a combination of cation and anion resins, then they can remove all ions from solution. Selection of a specific resin for a particular application depends on the ions to be removed and recovered, and the chemistry of the process.

Ion exchange has found applications in industries including water treatment, recovery of by-products and regeneration of spent chemical streams, food manufacturing, and semiconductor and pharmaceuticals manufacturing. Continuing research has been directed at development and discovery of novel ion-exchange resins, and improvements in existing ion exchanger efficiency. This chapter discusses the ion-exchanger material, exchange mechanisms, the ion-exchange processes, the design and operation of the ion-exchange unit process, applications of the process, and the new developments in this subject area.

2. CHARACTERIZATION OF ION EXCHANGERS

Many natural and synthetic substances can function as ion exchangers. Given their different origins, compositions, and structures, differences in their sorption properties can be expected. This would mean these resins are not equally important to a particular industry. For example, synthetic ion-exchange resins are of greatest importance in water treatment. Inorganic ion exchangers, on the other hand, are well received where their mechanical, thermal, and chemical properties are advantageous and this need not necessarily mean the water industry.

2.1. Physical Properties

Many of the physical properties of ion exchangers play key roles in the operation of ion exchange unit processes. Relevant properties include color, density, mechanical resistance, particle size, and porosity. For example, a larger resin particle size would cause lower separation kinetics.

2.1.1. Color, Density, and Mechanical Resistance

Ion exchangers can be categorized according to their colors (4–8). The strongly acidic cation exchange resins and the weakly acidic condensation-type resins are generally brown. Acrylic and methacrylic acid polymers are white. The color of anion exchangers vary from pale yellow to medium brown. Color density depends on the degree of cross-linking in the resin network.

Two material density measurements are relevant to ion exchange resins: the *dry resin density* and the *water-swollen resin density*. The true density of any resin, in its dry or swollen form, will depend on resin type, structure, degree of cross-linking, ionic form, and swelling capacity. The dry and water-free resin density is generally smaller (around 1200 kg/m^3) for anion exchangers than for cation exchangers (around 1400 kg/m^3). However, it is usually more practical to use the water-swollen resin density. The latter is an important consideration when predicting the hydrodynamic behavior of continuous countercurrent systems or combinations of different resin types contained in fixed beds. The density of the swollen resin is around 1300 kg/m^3 for strongly acidic polymerization-type cation exchangers and about 1100 kg/m^3 for strongly basic anion exchangers. Generally, the water content of water-swollen resin is about 40–60%. The latter is important information when IXRs are applied in industry.

The mechanical strength of IXRs varies according to a resin's structure. An IXR's mechanical strength is important because it contributes to wear resistance. An IXR that has low wear resistance would suffer from material losses particularly during the regeneration phase. The air-dry resin readily suffers from attrition caused by friction between particles. Their solidity increases with increasing degree of cross-linking. However, mechanical strength reduces after regeneration with alternate concentrated acid and base. The polymer structure of a resin influences not only its mechanical strength, but also its swelling characteristics, ionic equilibria (e.g., capacity), and kinetic properties.

2.1.2. Particle Size

Ion exchange resins typically have particle sizes in the range of 0.04–1.2 mm; the most common size ranges in large-scale applications are 0.30–0.85 mm (50–100 U.S. mesh) and 0.15–0.30 mm (100–200 U.S. mesh) (7). Owing to the size distribution of IXRs, information on the effective size and uniformity coefficient is provided by manufacturers. Effective size is defined as the screen mesh size that allowed passage of 10% (by weight) of the total quantity while 90% is retained. Uniformity coefficient is defined as the ratio between the mesh size (mm) that allowed passage of 60% of the IXR and the effective size. IXRs typically have uniformity coefficients of 1.4–1.6.

Particle size plays an important role in ion-exchange kinetics, separation efficiency, pressure drop (headloss), liquid velocity, and the hydraulic expansion. Typically, the particle size selected would be the result of an appropriate compromise between the reaction kinetics and hydrodynamics. Ion-exchange kinetic rate is controlled by the mass transfer resistance, which is due to the external mass transfer (sometimes termed as external diffusion) and the internal diffusion. Both internal diffusion and external mass transfer are dependent on the nature of the resins. The external mass transfer is also dependent on the size of the resin particles as well as the flow characteristics. This is supported by the results of experimental studies as well as theoretical analysis (8,9). In general, a larger particle size and lower target ion concentration differential between the resin and liquid phase leads to a lower ion-exchange rate. However, these effects may be less noticeable in certain circumstances such as if the resin particle size is extremely small, the kinetics would then be controlled by the chemical reactions, and therefore the mass transfer resistance becomes less important. For example, Zhao et al., developed a new microporous ion-exchange resin for lead removal and reported that the equilibrium time was only 20 s (10). In addition to its favorable effect on the kinetics, the extremely small resin particle maximizes physical and osmotic stabilities. Nevertheless, if the particles are too small, the hydrostatic resistance (headloss) in fixed-bed columns would become extremely high. This would lead to serious pressure drops and lower liquid flow-through velocities. Resin bed performance can be significantly affected by a resin with a very low content of very large particles or very small particles. Each condition can result in the remaining particles having a disproportionately large effect on performance. To avoid this, the recent trend in the industry is to use resins with uniform particle sizes. With such resins, better separation, lower pressure drop, and higher kinetics can be obtained. It should be noted that the effect of particle size on the pressure drop/headloss becomes irrelevant if batch and/or continuously stirred mixed reactors are employed.

2.1.3. Porosity

Similar to particle size, the porosity of an ion-exchanger particle plays an important role in the exchanger's capacity. Porosity can be defined as a ratio (usually expressed as a percentage) of volume of voids to total volume of the resin. The porosity of conventional resins ranges from 20% to 55% (4–8).

The shape and size distribution of pores in an IXR particle can vary significantly, and this distribution is influenced by the manufacturing process. For the same resin material, different pore size ranges can be incorporated. A large number of smaller pores should be incorporated if a large surface area is the objective. The most substantial contribution to the overall surface area comes from the micropores, which have diameters smaller than 2 nm, followed by the mesopores with diameters ranging from 2 to 50 nm. Large macropores contribute insignificantly to the overall surface area but are important because these pores allow access into the meso- and micropores at reasonably low pressures (3–8,11).

Microporous resins exhibit single-phase homogeneous structures wherein counter ions diffuse uniformly. Pore sizes vary with the degree of cross-linking and the electrolyte of the solution. Lightly cross-linked granular resins (0–6%) offer high microporosity, while macroporosity offers permanent discrete pores. Macroporous resins generally contain a pore phase and a gel phase within each resin bead. Thus, porosity equals the volume ratio between the continuous yet discrete pore phase and the total bead. In addition, porosity depends inversely on cross-linking density in the gel phase. In macroporous resins, porosities range from 5% to 50% by volume (5–8).

Porosity can be determined using a solution containing ions of known size and similarity, and by using capacity measurements. The same measurement can also be made using vapor pressures. It should be noted these methods provide values related to the mean particle size but such information can be useful in both the design and operation of an application.

Porous materials have many applications which rely on intimate contact with a surface that supports the active sites, such as in catalysis, adsorption, ion exchange, chromatography, and solid-phase synthesis (4–8,10–13). The active groups that cause the separation during ion exchange are not only on the surface of the resin particles but also in the capillary channels or pores within the particles. The size distribution of these pores plays an important role in the selectivity of ion exchangers, because different sizes of pores are suitable for reception of ions of different sizes; only ions of smaller size than the pore size can be exchanged, while the larger ions cannot be exchanged (sieve effect) because they could not gain access to the relevant sites. The capacity determined experimentally for specific ions can therefore be considerably lower than the theoretical value estimated from total surface area considerations. It is therefore important to not only have high porosity but to have this porosity contributed by pores with a size distribution appropriate to the target ions. This would ensure both high capacity and separation kinetics can be achieved.

2.2. *Chemical Properties*

The chemical properties of ion exchangers which determine performance include active groups, capacity, selectivity, degree of cross-linking and swelling.

2.2.1. *Active Groups*

According to the chemical strength between the exchangeable ions and the functional groups in the resins, ion exchange resins can be classified as (7,8,12):

1. Cation exchangers: strong and weak-acidic cation resins
2. Anion exchangers: strong and weak-base anion resins

Ion-exchange resins behave like storage batteries, as they must be recharged (regenerated) periodically to restore their exchange capacity. A cation resin is regenerated with a cationic reagent such as an acid, whereas an anion resin is regenerated with an anionic reagent such as a base. The positively charged ions in cationic resins such as hydrogen and sodium ions are exchanged with positively charged ions, such as nickel, copper, and zinc ions, in the bulk solutions, which are toxic according to United States Environmental Protection Agency (US EPA) standards (14). Similarly, the negative ions in the resins such as hydroxyl and chloride ions can be replaced by the negatively charged ions such as chromate, sulfate, nitrate, cyanide, and dissolved organic carbon (DOC).

Both strong-acid cation and strong-base anion resins are high ionized in water; thus, they can work in the entire pH range. The pH does not affect the ion-exchange performances. Conversely, weak-acid cation and weak-base anion resins are more like weak acid (base). For example, their ionization strongly depends on pH. When pH is below 6.0, weak-acid cation resin's performance will be significantly decreased. Similar phenomenon will occur to weak-base anion resin at pH above 7.0.

Different ions are not bound to an ion exchanger resin with the same affinities. Weak-acid resins are more selective for multivalent metal ions than strong-acid resins, making them suitable for the separation of organic bases. However, ion-exchange with weak-acid resins proceeds slowly owing to their less dissociated active groups. Weak-acid cation resins can strongly adsorb hydrogen ions. Therefore, at low pH, the adsorbed metal ions can be easily desorbed from the resin and released back to the solution.

Just like activated carbons and hydrous oxides, potentiometric titration can be used to characterize the acid–base surface properties of the resins (4–8,12,15–19). The ionization reactions and the constants (pK values) can be determined according to the titration data. For example, Chen and co-workers reported a successful case of characterization of a cation resin—a calcium alginate based ion exchange resin (CABIER) (17). The study included three steps:

`- potentiometric titration of a resin and equilibrium experiments (e.g., pH effect and isotherm);
- formulation of reactions that involve ion exchange between the ions in the resins and ions in the solution; and
- modeling simulation

The final step can be performed by numerical solvers, such as *FITEQL 4.0* (19). If inert ions are added in the solution to represent ionic strength during the titration measurement, it is worthwhile to include the possible reactions between these ions and the functional groups, which is similar to the consideration in the study of activated carbon by Chen and Lin (15). The literature arising from Westall and co-workers and Schecher and McAvoy provide many other successful case studies (19,20).

Ion-exchange resins are formed with a cross-linked polymer matrix as a backbone. Numerous charged functional groups are then attached to this. The "backbone" can be polystyrene cross-linked with 3–8% divinylbenzene in order to achieve structural stability. The four functional groups commonly found in the four categories of resins are strongly acidic groups, sulfonate group ($–SO_3^-$); weakly acidic groups, carboxylate group ($–COO^-$); strongly basis groups, quaternary amine group [$–N^+(CH_3)_3$]; and weakly basic groups, tertiary amine group [$–N^+(CH_3)_2$] (7,8,12).

Strong-acid cation exchanger. As the sulfonate group in the resin is strongly acidic, it is ionized throughout the pH range of 1–14. Hence, the resin can split strong or weak salts at any pH. Cationic ions in water such as Ca^{2+}, Mg^{2+}, Na^+, and K^+ are

Table 1
List of Ion-Exchange Resins and Typical Reactions

No	Resins	Typical reactions
1	Strong-acid cation exchanger	(1.1) $Ca(HCO_3)_2 + 2\overline{RSO_3H} = \overline{Ca(RSO_3)_2} + 2H_2CO_3$
		(1.2) $CaCl_2 + \overline{2RSO_3H} = \overline{Ca(RSO_3)_2} + 2HCl$
		(1.3) $MgSO_4 + \overline{2RSO_3H} = \overline{Mg(RSO_3)_2} + H_2SO_4$
		(1.4) $CaCl_2 + \overline{2RSO_3Na} = \overline{Ca(RSO_3)_2} + 2NaCl$
		(1.5) $Ca(HCO_3)_2 + \overline{2RSO_3Na} = \overline{Ca(RSO_3)_2} + 2NaHCO_3$
		(1.6) $NaCl + \overline{RSO_3H} = \overline{NaRSO_3} + HCl$
2	Weak-acid cation exchanger	(2.1) $Ca(HCO_3)_2 + 2\overline{RCOOH} = \overline{Ca(RCOO)_2} + 2H_2CO_3$
		(2.2) $Mg(HCO_3)_2 + 2\overline{RCOOH} = \overline{Mg(RCOO)_2} + 2H_2CO_3$
		(2.3) $NaHCO_3 + \overline{RCOOH} = \overline{Na(RCOO)} + H_2CO_3$
		(2.4) $Ca(HCO_3)_2 + 2\overline{RCOONa} = \overline{Ca(RCOO)_2} + 2NaHCO_3$
3	Strong-base anion exchanger	(3.1) $NaNO_3 + \overline{R_4NOH} = \overline{R_4NNO_3} + NaOH$
		(3.2) $NaNO_3 + \overline{R_4NCl} = \overline{R_4NNO_3} + NaCl$
		(3.3) $H_2SO_4 + 2\overline{R_4NOH} = \overline{(R_4N)_2SO_4} + 2H_2O$
		(3.4) $HCl + \overline{R_4NOH} = \overline{R_4NCl} + HCl$
		(3.5) $H_2SiO_3 + 2\overline{R_4NOH} = \overline{(R_4N)_2SiO_3} + 2H_2O$
		Note: R_4N^+ represents quaternary exchange site, $–N^+(CH_3)_3$
4	Weak-base anion exchanger	(4.1) $HCl + \overline{R_3N} = \overline{R_3NHCl}$
		(4.2) $HNO_3 + \overline{R_3NHCl} = \overline{R_3NHNO_3} + HCl$
		(4.3) $2\overline{R - NH_3OH} + SO_4^{2-} \leftrightarrow \overline{(R - NH_3)SO_4} + 2OH^-$
		(4.4) $2\overline{R - NH_3Cl} + SO_4^{2-} \leftrightarrow \overline{(R - NH_3)SO_4} + 2Cl^-$
		R represents functional group such as $–CH_3$ or $–C_2H_5$

The over-bars denote the ion exchanger (solid phase).

exchanged with the H^+ in the resins as illustrated in Table 1. The resin has a wide range of applications and has been used in both sodium and hydrogen cycle for softening, and in dealkalization and demineralization.

The strong-acid resin has different affinities for different cations as shown below:

Monovalent cation: $Ag^+ > K^+ > NH_4^+ > Na^+ > H^+$

Divalent cations: $Pb^{2+} > Hg^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Fe^{2+} > Mg^{2+} > Mn^{2+}$

Trivalent cations: $Fe^{3+} > Al^{3+}$

Because the exchange reactions are reversible, when the resin capacity is exhausted, it can be recovered through regeneration with a mineral acid (e.g., HCl) or a simple inorganic salt (e.g., NaCl) solution with concentrations ranging from 0.5 to 3.0 *M* (7,8,12). Industrial experience has shown that the strong acid is more effective at regenerating the resin. The acid regenerant has minimal effect on the subsequent stability and effectiveness of the resin. For example, the acid regenerant will cause less swelling (expansion) of the resin than sodium chloride. Because of the robustness of such resins, they can have working lifespans of up to 20 yr with very little loss of exchange capacity.

Weak-acid cation exchanger. This resin is also known as the weak-acid resin. This type of resin is used primarily for softening and dealkalization, and is frequently used in conjunction with a strongly acidic resin. The resin produces treated water of quality that is comparable to that produced by a strongly acidic resin. These resins have the carboxylic acid group (–COOH), which releases the hydrogen ions. As the functional group has a pK_a value of 4.8, it is not ionized at low pH. As a result, it can effectively remove carbonate hardness as shown in Table 1. However, it does not work well at $pH < 4$, at low temperatures, and at low hardness–alkalinity ratios (e.g., ratio < 1.0). It would not be able to effectively remove noncarbonate hardness such as $CaCl_2$ as the solution can become more acidic as shown in the following reaction:

$$CaCl_2 + 2\,\overline{RCOOH} = \overline{Ca(RCOO)_2} + 2HCl \tag{1}$$

Regeneration with an acid would return the exhausted resin to the hydrogen form as shown in Table 1. This IXR is much easier to regenerate than the strongly acidic exchangers and is possibly more economical to do so because it can be regenerated with 110% of the stoichiometric amount of acid as compared with the 200–300% for the strongly acidic cation exchange resin. As the resin can be regenerated with the “spent” acid arising from regeneration of an upstream strongly acidic cation exchange resin, such combinations would help reduce the production of waste regenerant.

Strong-base anion exchanger. It obtains its functionality from the quaternary ammonium exchange sites. This IXR can be operated at any pH, ranging from 0 to 14, and can split strong or weak salts. It requires high-grade NaOH for regeneration. The resin has a strong tendency to adsorb strong acids, such as nitric, sulfuric, and hydrochloric acids. Its affinity for metal ions is rather low, which enables the resin to separate acid from metal solutions. Typical IX reactions associated with such resins are given in Table 1. Regeneration with a strong base such as caustic soda can return the functional group from acid to its hydroxide form.

There are two general classes (Type I and Type II) of strong-base anion exchange resins as determined by the differences in their chemical nature (7,8,12). For instance, both types would remove silica, carbon dioxide, and other anions. However, their effectiveness can be quite different depending on the silica and CO_2 concentrations in the feed solution. The Type I resin is more effective at removing silica when the total silica and CO_2 content of the feed stream is above 25% of the total anions present. On the other hand, the Type II resin is more effective when the combined silica and CO_2 content in the feed is below 25% of the total anions. This is often the case when CO_2 has been removed with a degasifier ahead of the anion exchanger unit.

The behaviors for these two resins during application and regeneration are also different. Type I resins swell more than Type II during application and are also more difficult to regenerate. It is, however, more tolerant to elevated temperatures. Therefore, the resin is applied when the operating temperature is high and the feedwater has high silica content. It is also cheaper than Type II resins. On the other hand, Type II resins are more easily regenerated and are less susceptible to fouling.

Weak-base anion exchanger. This resin acts as adsorbers for acids (7,12). They can efficiently remove strong acids such as sulfuric and hydrochloric acids. The resin has tertiary amine functional groups, which are similar to ammonium hydroxide. The resin is, however, not able to remove CO_2 and silica. They are used in systems where strong acids predominate and where silica and/or CO_2 are of less concern. This resin is more economical than other types when used to remove chlorides and sulfates. It is often used prior to strong base resins in demineralization processes. The IX reactions are given in Table 1.

This resin is useful only in the acid pH region, where the amine functional groups can become protonated and can act as positively charged exchange sites for anions. The working pH range is rather narrow and the resins are not able to separate salts. They are used to treat strong acid waters containing chloride, sulfate, and nitrate. The alkalinity in such solutions would be low. The resin is not able to remove CO_2, silica, and other anions satisfactorily at pHs above 6. The resin is more tolerant to organic fouling and can be used to precede a strong-base anion resin to afford protection for the latter against organic fouling and to reduce regeneration costs. The resins are readily associated with the hydroxyl ion, making regeneration easy. Such resins can be regenerated by applying caustic soda, soda ash, or ammonia.

2.2.2. Capacity

The exchange capacity of an IXR is the most important parameter for both manufacturers and users. It is defined as the quantity of positively or negatively charged ions (i.e., cations or anions) that an IXR can accommodate on its charged surfaces. This capacity can be expressed as milliequivalents (meq) per 100 g IXR. The dry weight capacity is very often used. In addition to this, a resin's salt splitting capacity is sometimes used to describe the strongly functional component of a resin's total capacity. Determination of the total capacity can be made by direct titration on either a dried resin or on a swollen resin. The total capacity would then be expressed in terms of the total amount of exchangeable ions per unit weight of resin dried at 105°C or per unit volume of swollen resin settled in water (meq/g or meq/mL). Because many ion-exchange processes are operated in columns housed in cylindrical pressure vessels, total exchange capacity (or saturation) on a bulk volume basis may be more practical as a design parameter. Elution methods are used in volume exchange capacity determinations whereby the total number of equivalents of exchangeable ions per unit volume of the resin is measured.

Determination of a resin's total capacity can also be determined by an acid–base titration. The capacity of the resin is found from the points on the titration curve where the rate of change in pH with titrant addition is greatest. However, the value of the apparent capacity may differ markedly from the total capacity value when the ions examined cannot occupy every exchange site owing to their greater size compared to the pore sizes on the resin. While the total capacity is constant and a characteristic of a given ion-exchange resin, the value of the so-called break-through capacity measured on an ion-exchange column depends on the pH, grain size, column size, flow rate, and other factors. The total capacity values of both strong-acid and strong-base resins can be determined by a suitable analytical method after burning the resin to ash, and measuring the sulfur or nitrogen contents in the ash. The total capacity can be calculated from the sulfur or nitrogen content.

2.2.3. *Selectivity*

Just like metal adsorption onto activated carbons and biomaterials, different ions are absorbed on ion-exchange sites with different affinities. In other words, ion exchange resins are selective for ions. Multivalent ions normally are more strongly absorbed from dilute solutions than ions of lower valence (e.g., $\mathrm{Ca^{2+}}$ vs $\mathrm{Na^+}$).

The order of affinity between various ions and IX sites of strong acid cation exchange resins is as follows:

$$\mathrm{Li^+ < H^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+ < Ag^+ < Tl^+}$$

$$\mathrm{Mn^{2+} < Mg^{2+} < Zn^{2+} < Co^{2+} < Cu^{2+} < Cd^{2+} < Ni^{2+} < Ca^{2+} < Sr^{2+} < Pb^{2+} < Ba^{2+}}$$

$$\mathrm{Al^{3+} < Sc^{3+} < Y^{3+} < Eu^{3+} < Sm^{3+} < Nd^{3+} < Pr^{3+} < Ce^{3+} < La^{3+}}$$

In the case of ions carrying an identical charge, affinity increases with decreasing hydrated radius of the hydrated ion. Other factors such as complex formation, activity/reactivity of functional groups, and ionic strength of the solution can also play a role in the IX process (7,8,12). Complex formation is important in the uptake of copper, nickel, and cobalt ions by ion exchangers. The above order may vary according to the type of active groups on the resins.

Weak-acid ion exchange resins adsorb hydrogen ions most strongly. A slight excess of hydrogen ions in the solution can displace all other cations from the resin. Weak-acid resins are particularly selective for multivalent metal ions.

The order of uptake of ions by both strong- and weak-base resins is determined by the valence, the hydrated ion radius, the strength of acid corresponding to the anion, and the chemistry of the target ions. The last factor is especially important for removal of organic ions.

For a weak-base anion exchange resin, the order of uptake is as follows:

$$\begin{gathered}\mathrm{HCCl_3^- < Ac^- < F^- < Cl^- < Br^- < I^- < NO_3^- < H_2AsO_3^-} \\ \mathrm{< H_2PO_4^- < oxalate < HSO_4^- < citrate < OH^-}\end{gathered}$$

The general order of ion uptake by strong-base anion exchange resins is

$$\begin{gathered}\mathrm{F^- < OH^- < Ac^- < HCO_3^- < Cl^- < NO_2^- < HSO_3^- < CN^-} \\ \mathrm{< Br^- < NO_3^- < ClO_3^- < HSO_4^- < phenolate < I^-}\end{gathered}$$

2.2.4. *Degree of Cross-Linking*

Cross-linking provides the key chemical bonding between adjacent polymer chains, which provides the resin with good inherent physical strength (3–8,12). The degree of cross-linking has an obvious effect on the physical and mechanical properties of a resin. When a resin contains a high degree of cross-linking, it swells less in aqueous solutions and has a smaller loss of volume during drying. Its mechanical strength is of course higher. A higher degree of cross-linking can result in a more rigid matrix and reduce the number of larger pores. At the same time, it can cause higher porosity and a larger surface area within the resin particles, which leads to faster kinetics.

Divinylbenzene (DVB) is widely used as a cross-linking agent. During suspension polymerization, a three-dimensional network of IX resins start to form from a liquid state after a certain time, which is determined by the ratio of the amounts of the individual monomers used during its synthesis (4,7,8,12). When its content is higher in DVB, the number of functional groups that are attached to the matrix would become lower and the uptake kinetics would decrease (22). Resins with a low proportion of DVB swell strongly in aqueous solutions, leading to high uptake kinetics.

2.2.5. *Swelling*

Ion-exchange resins can swell or shrink during application. There are two types of swelling: reversible and irreversible. The former refers to the reversible volume changes that occur between one swollen ionic form and another for a given resin. The volume changes reflect the difference in magnitude of the degree of cross-linking, the interactions among the ions and the functional groups, and the degree of hydration of the ions. Irreversible swelling is mainly observed with acrylic strong-base anion exchange resins; an irreversible expansion of around 7–10% may occur.

The degree of swelling is affected by the following factors: (a) composition of ion exchanger, (b) physical strength of the resin matrix, and (c) chemistry of the solution. Silicate-based ion exchangers have a low swelling capacity, while the swelling capacity of synthetic resin-based ion exchangers is much higher and thus more important.

The charge density and swelling capacity increase with an increase in the amount of active groups on resin. The swelling decreases with increasing valence. For ions of the same charge, the volume of a swollen resin also depends on both resin and solution chemistry. The volume of a resin increases with increasing volume of hydrated ions. When the ionic groups of a resin are highly dissociated, the resin swells to a greater degree. In the case of ion pair formation and association, the degree of swelling decreases. It is often observed that hydrogen bonding in the weak acid or base ion-exchange resins can significantly decrease their swelling.

The degree of swelling is very much dependent on the chemical and physical properties of the resin matrix and on the degree of cross-linking. The more cross-linked the resin is, the smaller is the degree of the swelling. However, if cross-linking does not exist, the resin can swell without limit in aqueous solutions (e.g., non cross-linked sulfonic polystyrene resin).

Electrolyte concentration in solutions can affect the degree of swelling as the osmotic pressures between the external and internal solutions decrease with an increase of the electrolyte concentration (8,12,23,24). When the degree of cross-linking of the resin is lower, the effect of salt concentration variation is more considerable. Ion-exchange resins are generally more swollen by strongly polar solvents than by less polar ones.

3. ION-EXCHANGE CALCULATIONS

Four types of ion-exchange reactions are given in Table 1. The degree of target ion uptake is dependent on the chemical and physical properties of the resins and the solution chemistry. The calculations in relation to ion-exchange processes include determination of equilibrium state conditions and kinetics in batch reactors as well as transportation in fixed-bed and fluidized-bed reactors.

3.1. Equilibrium

The equilibrium aspect here is referred to as the sorption isotherm. The calculation can be conducted according to empirical expressions such as Langmuir and Freundlich equations and IX theories. The aim of the calculations is to determine the treatment results and the operational conditions (e.g., mass of IXR applied).

The Langmuir equation can be expressed as

$$q_e = \frac{q_{\max} bC_e}{1 + bC_e} \tag{2a}$$

where q_e is the amount of substance adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of substance in solution (mg/L), $q_{\max}$ is the maximum sorption capacity, and b is the Langmuir constant related to heat of adsorption.

The Freundlich equation is expressed as

$$q_e = K_f C_e^n \tag{2b}$$

where K_f is Freundlich sorption constant and n is a measure of sorption intensity.

The sorption constants can be obtained by linear or nonlinear regression. However, the later method provides a better description of the experimental data.

Empirical equations are simple and easy to use; however, they fail to describe the sorption mechanisms and are not able to provide the concentrations of ions released from the IXR to the solution. Therefore, IX theory has been used to overcome the problems.

In the following discussion, it is assumed that the solution chemistry is simple enough such that the target ions (to be removed) are the only species in the system. Competing effects due to the presence of other ions are assumed less important and ion-exchange reactions are the only reactions that remove the target ions. If the reader needs to consider a more-complicated system, computation programs such as MINEQL for the estimation of ion exchange processes would need to be used (17,19,20).

Assuming an IX resin initially contains only cations B and the solution has the cations A (target ions). The reversible ion exchange reaction can be represented by:

$$mA^{n+} + n\overline{B^{m+}} \Leftrightarrow m\overline{A^{n+}} + nB^{m+} \tag{3}$$

where the stoichiometric coefficients m and n are the valencies of ions B and A, and the overbars denote the ion exchanger (solid phase).

Thus, we have

$$K_{A\to B} = \frac{\{\overline{A^{n+}}\}^m \{B^{m+}\}^n}{\{A^{n+}\}^m \{\overline{B^{m+}}\}^n} \tag{4a}$$

$$K_{A\to B} = \left(\frac{\{\overline{A^{n+}}\}}{\{A^{n+}\}}\right)^m \left(\frac{\{B^{m+}\}}{\{\overline{B^{m+}}\}}\right)^n \tag{4b}$$

where the curly brackets denote activity or concentration of species, and $K_{A\to B}$ is the equilibrium constant or otherwise referred to as the selectivity coefficient.

Table 2
Selectivity Scale for Cations on 8% Cross-linked Strong-Acid Resin and for Anions on Strong-Base Resins

Cation	Selectivity	Anion	Selectivity
Li^+	1.0	HPO_4^{2-}	0.01
H^+	1.3	CO_3^{2-}	0.03
Na^+	2.0	OH^- (Type I)	0.06
UO^{2+}	2.5	F^-	0.1
NH_4^+	2.6	SO_4^{2-}	0.15
K^+	2.9	CH_3COO^-	0.2
Rb^+	3.2	HCO_3^-	0.4
Cs^+	3.3	OH^- (Type II)	0.65
Mg^{2+}	3.3	BrO_3^-	1.0
Zn^{2+}	3.5	Cl^-	1.0
Co^{2+}	3.7	CN^-	1.3
Cu^{2+}	3.8	NO_2^-	1.3
Cd^{2+}	3.9	HSO_4^-	1.6
Ni^{2+}	3.9	Br^-	3
Be^{2+}	4.0	NO_3^-	4
Mn^{2+}	4.1	I^-	8
Pb^{2+}	5.0	SO_4^{2-}	9.1
Ca^{2+}	5.2	SeO_4^{2-}	17
Sr^{2+}	6.5	CrO_4^{2-}	100
Ag^+	8.5		
Pb^{2+}	9.9		
Ba^{2+}	11.5		
Ra^{2+}	13.0		

The thermodynamic constant $K_{A \to B}$ is a function of temperature and is determined by the standard free energy of the ion-exchange reaction. Seasonal variations in temperature of up to 30°C are possible in practical ion-exchange processes. Therefore, the effect of temperature cannot be ignored. Thermal regeneration induced by such temperature changes can be possible for some resins and this causes redistribution of ions on the resins.

It is always preferable to obtain the constant through experimental measurement. However, if the measurement is not possible, one can use the following equation for a rough estimation of the constant:

$$K_{A \to B} = \frac{K_A}{K_B} \tag{5}$$

where K_A and K_B can be found from Table 2.

The distribution of species A and B in both the solid and solution phases can be determined by the above equations together with a mass-balance equation. When the calculation is conducted, the species can be treated as those in solution reactions with units of meq/L. If the ionic strength is not high, activity can be treated as concentration, which makes the calculation less complicated.

Anderson had developed a method to simplify the IX calculation, which has been widely used in the water industry. His method is described as follows (12):

Let q and c represent concentration of species in the IX resin (solid phase) and solution phases, and Eq. (4b) can then be written as:

$$K_{A\to B} = \left(\frac{q_A}{c_A}\right)^m \left(\frac{c_B}{q_B}\right)^n \tag{6}$$

Let Q be the total exchange capacity of the IX resin (eq/L) and C be the total ionic concentration in the solution (eq/L), and also let X and $\overline{X}$ represent the percentage of species in solution and solid phases. We then have

$$q_A = \overline{X_A} \times Q \tag{7a}$$

$$q_B = \overline{X_B} \times Q \tag{7b}$$

$$c_A = X_A \times C \tag{8a}$$

$$c_B = X_B \times C \tag{8b}$$

$$\overline{X_A} + \overline{X_B} = 1 \tag{9a}$$

$$X_A + X_B = 1 \tag{9b}$$

Thus, Eq. (6) can be rewritten as:

$$K_{A\to B} = \left(\frac{\overline{X_A}}{X_A}\right)^m \left(\frac{X_B}{\overline{X_B}}\right)^n \left(\frac{Q}{C}\right)^{m-n} \tag{10}$$

Combining Eqs. (9a), (9b), and (10) yields

$$K_{A\to B} = \left(\frac{\overline{X_A}}{X_A}\right)^m \left(\frac{1-X_A}{1-\overline{X_A}}\right)^n \left(\frac{Q}{C}\right)^{m-n} \tag{11}$$

$$\frac{\overline{X_A}^m}{(1-\overline{X_A})^n} = K_{A\to B} \frac{X_A{}^m}{(1-X_A)^n} \left(\frac{Q}{C}\right)^{m-n} \tag{12}$$

The above reaction and equations can be further simplified for some special cases. For the monovalent ion exchange process, $n = 1$ and $m = 1$:

$$A^+ + \overline{B^+} \Leftrightarrow \overline{A^+} + B^+ \tag{13}$$

Equation (10) can then be simplified and yields

$$\overline{X_A} = \frac{K_{A\to B} X_A}{1 + (K_{A\to B} - 1) X_A} \tag{14}$$

Figure 1 illustrates the distribution of species A in both resin and solution with a different selectivity values in a monovalent ion-exchange process. As shown, more species A are present in the solid phase when $K_{A\to B}$ value is higher. When $K_{A\to B}$ is equal to unity, 50% of A is in the solid while the remaining 50% is in the solution.

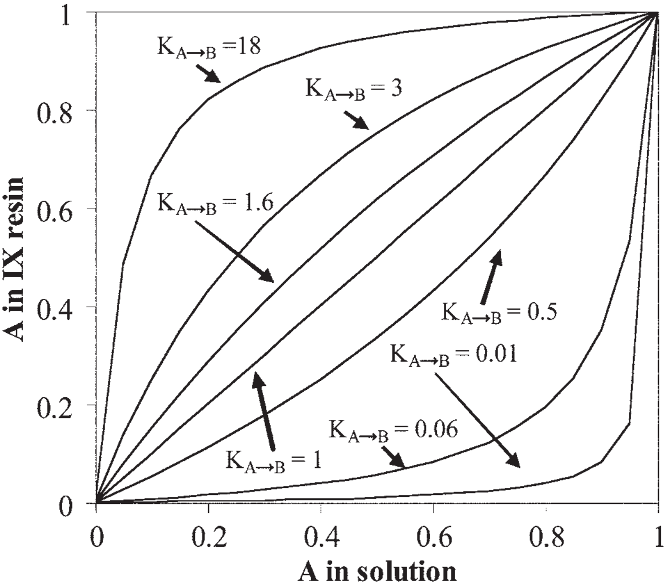

Fig. 1. Distribution of species *A* in both resin and solution with different selectivity values in a monovalent ion-exchange process.

In the exchange of calcium or magnesium ions for sodium or hydrogen ions in a water treatment process, $n = 2$, $m = 1$, then

$$mA^{n+} + n\overline{B^{m+}} \Leftrightarrow m\overline{A^{n+}} + nB^{m+}$$

$$K_{A\to B} = \left(\frac{\overline{X_A}}{X_A}\right)^m \left(\frac{1-X_A}{1-\overline{X_A}}\right)^n \left(\frac{\overline{Q}}{C}\right)^{m-n}$$

$$A^{2+} + 2\overline{B^{+}} \Leftrightarrow \overline{A^{2+}} + 2B^{+} \tag{15}$$

$$K_{A\to B} = \left(\frac{c_B}{q_B}\right)^2 \frac{q_A}{c_A} \tag{16}$$

or

$$K_{A\to B} = \left(\frac{\overline{X_A}}{X_A}\right)^2 \frac{1-X_A}{1-\overline{X_A}} \frac{C}{Q} \tag{17}$$

An alternative parameter to measure the preference of an ion exchanger for a particular ionic species is the separation factor (α_B^A), which is defined as

$$\alpha_B^A = \frac{\overline{X_A}/X_A}{\overline{X_B}/X_B} \tag{18}$$

Note that the equilibrium constant ($K_{A\to B}$) of the IX reaction is the same as the separation factor (α_B^A) when both m and n are equal to unity.

The separation factor ultimately reflects the likelihood of exchange occurring between particular ions. It provides information on the degree of interaction between the ions and the ion-exchange resin. If $\alpha_B^A = 1$, it indicates that the resin shows no preference for *A* over *B*. If it is above than unity, *A* interacts more strongly with the resin than *B*.

The separation factor relies on the design of the active sites on the resins and the solution chemistry. Mechanisms contributing to chemical selectivity reportedly include the hard–soft acid–base principle (HSAB), hydrophilicity/hydrophobicity selectivity, and pore size recognition. These mechanisms have common characteristics and their effects are thus not easy to distinguish.

Example 1

A strong-base anion exchange resin is used to remove nitrate ions from a groundwater with characteristics as given in the table below. The resin capacity is 2.5 eq/L. The selectivity for nitrate is 4.0. Determine the maximum volume of water that can be treated if 10 L of resins are used.

Cation	Concentration	mg/meq	meg/L	Anion	Concentration	mg/meq	meg/L
Ca^{2+}	30	20.04	1.5	Cl^-	106.5	35.5	3.0
Mg^{2+}	12.15	12.15	1.0	SO_4^{2-}	0	48.03	0
Na^+	57.5	23.00	2.5	NO_3^-	100	50	2.0
Total			5.0	Total			5.0

Solution

1. Determine the equivalent fraction of nitrate in solution:

$$X_{NO_3^-} = 2.0/5.0 = 0.4$$

2. Determine the equivalent fraction of nitrate on the resin:

$$NO_3^- + \overline{R - X^-} \Leftrightarrow \overline{R - NO_3^-} + X^-$$

$$K_{NO_3^- \to X^-} = 4$$

Given

$$\overline{X_A} = \frac{K_{A\to B} X_A}{1 + (K_{A\to B} - 1)X_A},$$

we have:

$$\overline{X_{NO_3^-}} = \frac{4 \times 0.4}{1 + (4-1) \times 0.4} = 72.7\%$$

This means 73% of resin sites are occupied by nitrate ions.

3. Compute the maximum useful capacity *Y*

$$Y = 2.5 \text{ eq/L} \times 72.7\% = 1.83 \text{ eq/L} = 1830 \text{ meq/L}$$

4. Compute the volume of water (V) that can be treated when 1 L of resin is used:

V = (1830 meq/L of resin)/(2.0 meq/L of water) = 915 L of water per liter of resin

5. Thus, the total volume of water which can be treated when 10 L of resins are used = 915 × 10 = 9150 L.

Example 2

A strong-acid cation exchanger is used to remove cadmium ions from a waste acidic solution. Cadmium ions *(A)* are exchanged with hydrogen ions *(B)* in the exchanger, which is similar to that in Table 2. The total exchange capacity of the cation exchange *(Q)* is 1.9 eq/L. At the total ionic concentration in the solution *(C)* of 0.1 eq/L, determine the equilibrium equivalents of cadmium ions in the exchanger when the cadmium concentration is 2.25 g/L.

Solution

$$A^{2+} + 2\overline{B^{+}} \Leftrightarrow \overline{A^{2+}} + 2B^{+}$$

$$K_{A\to B} = \frac{c_B^2 q_A}{c_A q_B^2}$$

From Table 2, we have $K_A = 3.9$ and $K_B = 1.3$, thus,

$$K_{A\to B} = \frac{K_A}{K_B} = \frac{3.9}{1.3} = 3$$

The copper concentration in the solution at equilibrium $(c_A) = 2.25/112.4 = 0.02\ M = 0.04\ N$

$$Q = q_A + q_B$$

Noted that c_A, c_B, q_A, and q_B have units of eq/L or N. Thus, we have

$$3 = \frac{(0.1 - 0.04)^2 \times q_A}{0.04 \times (1.9 - q_A)^2}$$

Solving the above equation gives:

$$q_A = 0.84\ N$$

3.2. Kinetics

Ion exchange takes place between liquid and solid phases. Ion-exchange kinetics is therefore governed by resistance in both phases. The liquid-phase resistance is often illustrated by the thin-film model, while the solid phase resistance is usually described by the pellet model. The ion-exchange process is considered to consist of the following steps:

1. Diffusion of ions from bulk solution to the edge of the static film around the IX resin.
2. Diffusion of ions through the static film.
3. Diffusion of ions through the matrix of the resin to the ion-exchange sites.
4. Ion exchange reactions at the ion exchange sites on the particle surface.
5. Diffusion of released ions through the matrix of the particles.
6. Diffusion of released ions through the static film.
7. Diffusion of released ions to the bulk solution.

Generally, the overall kinetics is primarily governed by the external and internal diffusion (also called the “two-step mass transport mechanism”; Steps 2 and 3 above). The intraparticle diffusion model described below can therefore be used for calculation of ion uptake by IX resins. When the mass transfer is due only to the diffusion of adsorbate molecules through the pore liquid, a “pore diffusion model” is often used. On the other hand, in the case where the intraparticle mass transfer is contributed by the diffusion of the adsorbed molecules, the “surface diffusion model” should be adopted (9). If the adsorbents are assumed spherical and homogeneous in terms of density, size, porosity and chemical properties, the control equation and its corresponding initial and boundary conditions are shown below:

Pore diffusion model:

$$\varepsilon_p \frac{\partial c}{\partial t} + \rho_p \frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial}\left(D_p r^2 \frac{\partial c}{\partial r} \right) \tag{19}$$

Surface diffusion model:

$$\frac{\varepsilon_p}{\rho_p}\frac{\partial c}{\partial t} + \frac{\partial q}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial}\left(D_s r^2 \frac{\partial c}{\partial r} \right) \tag{20}$$

$$q = f(c) \tag{21}$$

where c is concentration in particle (M), ε_p is porosity of the particle, ρ_p is particle density (kg/m^3), r is radial distance from center of particle (m), D_p is pore diffusivity (m^2/s), D_s is surface diffusivity (m^2/s).

It is assumed that the instant local equilibrium described by Eq. (21) is established. The Langmuir equation or other sorption isotherms can be utilized to represent the equilibrium relationship. The initial and boundary conditions are

$$c = 0, \qquad 0 \le r \le R,\ t = 0 \tag{22}$$

$$\frac{\partial c}{\partial r} = 0 \qquad r = 0,\ t > 0 \tag{23a}$$

$$\frac{\partial c}{\partial r} = \frac{k_f}{D_p}(C_b - c^*) \qquad r = R,\ t > 0 \tag{23b}$$

or

$$\frac{\partial c}{\partial r} = \frac{k_f}{D_s}(C_b - c^*) \qquad r = R,\ t > 0 \tag{23c}$$

where R is radius of particle (m) and k_f is external mass transfer coefficient, m/s.

The kinetic model can be solved by a finite-difference method available in the literature (9). By comparing the modeling results with the experimental observations, the kinetic parameters can be obtained. Readers may like to refer to Chen and Wang’s work (9) for detailed information.

3.3. *Fixed-Bed Operation*

In fixed-bed operation, in addition to the “two-step mass transport mechanism,” advection and dispersion play key roles in ion exchange. These factors must be considered. As influent concentration is assumed low, solution velocity can be considered constant. If pore diffusion is an important factor in the ion uptake, the following equations can be used. Similar expressions for surface diffusion can be obtained:

$$\frac{\partial C_b}{\partial t} + v\frac{\partial C_b}{\partial z} - D_L \frac{\partial^2 C_b}{\partial z^2} + \frac{1-\varepsilon_b}{\varepsilon_b}\frac{d}{dt}(\varepsilon_p \bar{c} + \rho_p \bar{q}) = 0 \tag{24}$$

Initial and boundary conditions can be described as,

$$C_b = 0 \qquad t = 0 \tag{25}$$

$$C_{\text{inf}} = C_b - \frac{D_L}{v}\frac{\partial C_b}{\partial z} \qquad z = 0 \tag{26a}$$

$$\frac{\partial C_b}{\partial z} = 0 \qquad z = L \tag{26b}$$

The intraparticle mass balance can be expressed as

$$\left[\varepsilon_p + \rho_p f'(c)\right]\frac{\partial c}{\partial t} = \frac{D_p}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right) \tag{27a}$$

$$\frac{d}{dt}\left[\varepsilon_p \bar{c} + \rho_p \bar{q}\right] = \frac{3k_f}{R}(C_b - c^*) \tag{27b}$$

$$\frac{\partial c}{\partial r} = 0 \qquad r = 0 \tag{28a}$$

$$\frac{\partial c}{\partial r} = \frac{k_f}{D_p}(C_b - c^*) \qquad r = R \tag{28b}$$

$$C_b = 0 \qquad t = 0 \tag{28c}$$

An orthogonal co-location method can be used to convert the above partial differential equations (PDE) into the ordinary differential equations (ODEs). An ODE solver, *EPISODE* can be used to solve the (ODEs) (25). In the model, the diffusivity is obtained from a batch kinetic study while the external mass transfer coefficient can be calculated from empirical equations or is available in the literature. The longitudinal dispersion coefficient (D_L) is determined by matching the model output with the experimental data. Readers may like to refer to Chen and Wang's work (9) for detailed information.

4. APPLICATIONS

So long as a target substance carries a charge or charges, it can usually be concentrated onto an ion-exchange resin, which can be natural or synthesized. As a result, the concentration of the substance in the solution phase decreases, while that on the solid phase (resin) increases. Deionization in industrial cooling water pretreatment, water softening, production of ultra-pure water for electronic and pharmaceutical industries are typical and among the largest ion-exchange applications. It can also be used for separation of rare elements and removal of organic matters (e.g., phenol and protein). Ion exchange is frequently more efficient when the pollutants are in low or trace concentrations. Operating costs depend mainly on the amount of pollutants to be removed, while capital cost is affected by hydraulic flow rates. If the appropriate resin is selected, it can effectively concentrate the target substance(s) from the aqueous solutions. However, the IX process has several disadvantages, such as regeneration, fouling of IX resin, and head loss. Ion-exchange systems can be operated in one of four models: batch, fixed-bed, fluidized-bed, and continuous.

Ion exchangers can be easily fouled by natural organic matters (NOMs) such as humic or fulvic acids and an irreversible decrease in the exchange capacity would occur. There are three methods for solving this problem. The first is to adopt a more effective pretreatment and cleaning process. The second is to synthesis ion exchangers with high porosity. These pores allow the humic acids to move in and out of the ion-exchanger beads, thereby increasing the diffusion of such large molecular weight substances. The third one is to replace aromatic polymer matrices within IX resins with aliphatic structures using acrylic acid as the starting monomer.

4.1. Water Softening

The concentration of calcium and magnesium ions in water is an indication of its hardness. If the hardness of water is high, a metal carbonate such as $CaCO_3$ can be formed on the heat-exchange equipment such boilers and pipelines. The scales (deposits) act as an insulating layer, which affects heat transfer efficiency. Hard water also creates problems for home laundry and washing purposes, requiring the use of more soap and synthetic detergents. Some vegetables cooked in hard water lose color and flavor. Beans and peas become tough and shriveled. General guidelines for classification of waters are: 0–60 mg/L $CaCO_3$ is classified as soft; 61–120 mg/L $CaCO_3$ as moderately hard; 121–180 mg/L $CaCO_3$ as hard; and more than 180 mg/L $CaCO_3$ as very hard.

In addition, the presence of alkalinity due to bicarbonate, carbonate, and hydroxide ions is often the predominant cause of foaming and carry over of solids with steam, resulting in corrosion of metal and damage to auxiliary equipment (24). Furthermore, the presence of other metal ions such as iron and manganese can discolor water and form deposits in water lines and boilers, and interfere with dying, tanning, and paper manufacture.

Water softening is the most important application for ion exchange. In the operation, sodium ions in the resins exchange with calcium, magnesium, and other polyvalent cations in the water. As a result, hardness (calcium and magnesium) is significantly reduced. The process scale can be small, such as home use and laboratory use, or large, such as water treatment plant use.

Water softening is usually conducted in a downward-flow mode in a fixed-bed column. The effectiveness and size of the operation is dependent on the incoming water hardness, the total dissolved solids, the flow rate, the presence of organic substances, the water temperature, and the resin particle size. Following use, the resin would eventually become “exhausted” and thus must be regenerated before it can remove hardness again. The water-softening operation must then be paused before the exhaustion occurs and the resin regenerated in order to ensure water quality can be maintained.

The regeneration cycle starts with backwash, an upward flow which loosens the resin bed and flushes out accumulated particulates. Regeneration occurs when a solution of sodium chloride (salt) brine is passed through the resin in an upward direction. Concentrated brine is drawn from a storage tank and diluted to the right concentration before use. The large excess of sodium ions causes the resin to release its hold on the hardness causing ions picked up during the preceding service cycle and returns the resin to its sodium state.

The brining step is followed by a slow downflow rinse to displace spent brine from the resin. It also carries the hardness removed from the resin to drain. The rinse rate is regulated to ensure the correct contact time between the salt and the resin is maintained.

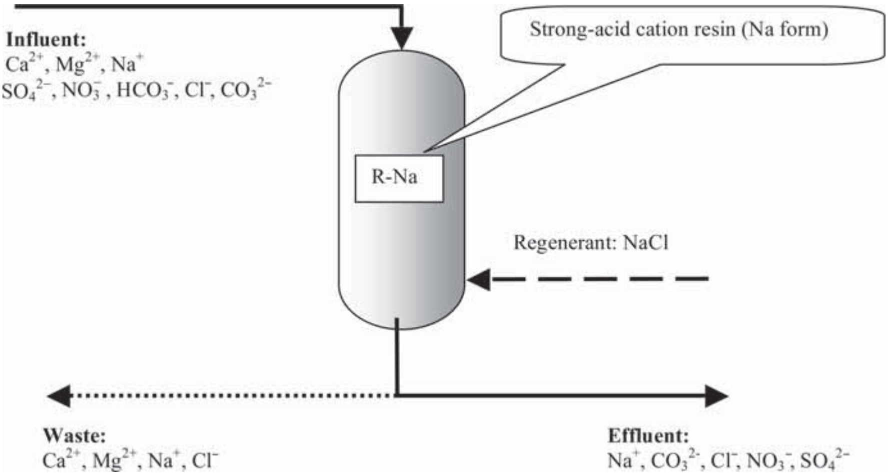

Fig. 2. Demonstration of typical columnar softening process.

This slow rinse usually lasts about 30 min. A final fast downflow rinse, or purge, flushes all remaining brine from the tank and this lasts about 5 min.

The most frequently used resin type for water softening is the Na type. A typical ion-exchange reaction is described by Eq. (29). Owing to the presence of $NaHCO_3$, treated effluent pH is always weakly caustic. The regeneration of resin performed with sodium chloride solution is described by Eq. (30):

$$R - \mathrm{Na} + \begin{Bmatrix} \mathrm{Ca(HCO_3)_2} \\ \mathrm{Mg(HCO_3)_2} \end{Bmatrix} \rightarrow R - \begin{Bmatrix} \mathrm{Ca} \\ \mathrm{Mg} \end{Bmatrix} + \mathrm{NaHCO_3} \tag{29}$$

$$R - \begin{Bmatrix} \mathrm{Ca} \\ \mathrm{Mg} \end{Bmatrix} + \mathrm{NaCl} \rightarrow R - \mathrm{Na} + \begin{Bmatrix} \mathrm{CaCl_2} \\ \mathrm{MgCl_2} \end{Bmatrix} \tag{30}$$

Figure 2 shows a typical column operation used to soften a hard water containing calcium magnesium and sodium salts.

4.2. Deionization and High-Quality Water Supply

Water softening is a well-documented ion-exchange process. It solves a very common form of water contamination, hardness. The disadvantages of water softening become apparent when high-quality water is required. Although softening removes the hardness-causing ions from the water, it replaces these with sodium ions. Therefore, the treated water now contains sodium instead of calcium or magnesium, which could make it unsuitable for many uses.

The most demanding requirements with respect to water quality are in the electronics industry and in power plants. Ion-exchange technology is capable of treating large volumes of water economically and is widely used in ultra-pure water production systems. Usually, such deionization systems consist of four stages (7,8,24):

- The first stage is a cationic exchanger, which reduces the concentrations of cations such as sodium ions to less than 0.1 mg/L in effluent.

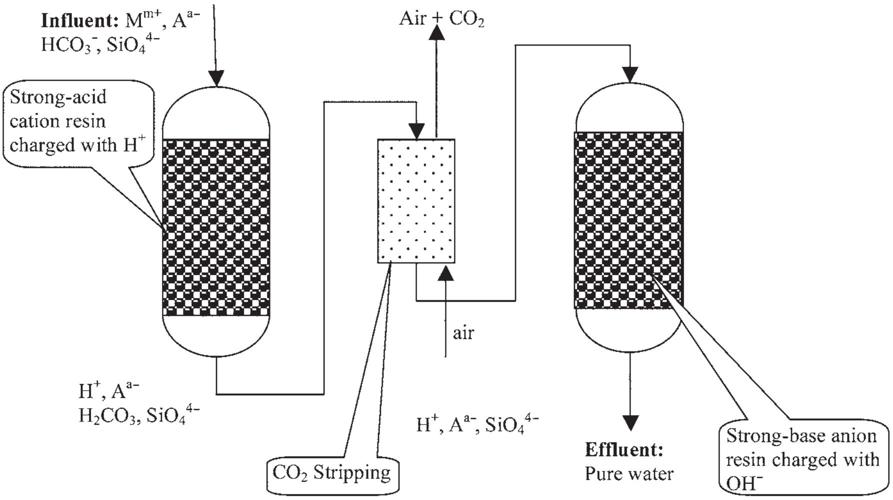

Fig. 3. Ion-exchange process for water demineralization.

- A degasifier (removal of dissolved gases) follows and this reduces the concentration of CO_2 to less than 5 mg/L.
- The third stage is an anion-exchange bed.
- The final stage is a mixed-bed, which ensures the conductivity of the product water is less than 0.3 µs/cm.

Ion-exchange deionizers use synthetic resins similar to those used in water softeners. The feed is typically prefiltered before entering the IX processes. Two types of synthetic resins are used: one to remove positively charged cations and another to remove negatively charged anions. Cation deionization resins exchange hydrogen ions for cations such as calcium, magnesium, and sodium. Anion deionization resins exchange hydroxide ions for anions such as chloride, sulfate, and bicarbonate. The displaced H^+ and OH^- combine to form H_2O. Deionization can produce extremely high-quality water in terms of dissolved minerals. However, they do not generally remove organics and can become a breeding ground for bacteria, and diminish water quality where organic and microbial contaminations are critical.

Cation resins are regenerated by treatment with acid, which replenishes the sites with hydrogen ions. Anion resins are regenerated with a strong base that replenishes hydroxide ions. Regeneration can take place off-site with regenerated “exchange-tank” deionizers brought in by a service company, or regeneration can be accomplished on-site by installing regenerable deionizers and regeneration equipment and chemicals. The scale of the operation would determine the option selected.

The two basic deionizer configurations are the two-bed and mixed-bed. Two-bed deionizers have separate vessels for the cation and anion resins. In mixed-bed deionizers, the anion and cation resins are blended in a single vessel. Generally, mixed-bed systems produce higher-quality water but have a lower total capacity compared with two-bed systems. Figures 3 and 4 are schematics of typical ion exchange demineralization processes.

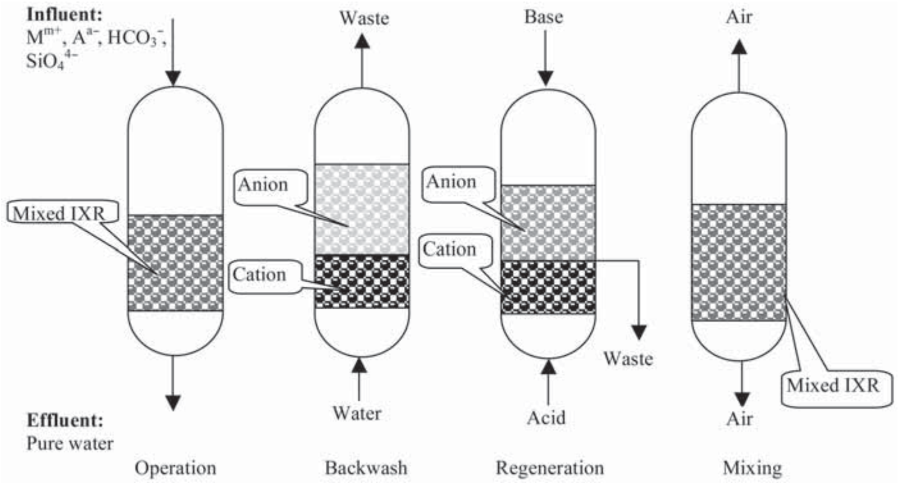

Fig. 4. Mixed-bed ion-exchange demineralization.

4.3. *Removal and Recovery of Heavy Metals*

The demands for heavy-metal removal or recovery come from heavy-metal contaminations in both surface and groundwaters due to industrial operations. Natural geochemical contamination through soil leaching can contribute dissolved metal ions (e.g., arsenic) in groundwaters. For example, over 70 million people in Bangladesh and in other regions of the Indian subcontinent are routinely exposed to arsenic poisoning through drinking groundwater. Arsenic, copper, lead, and mercury are important elements in metal contamination. The ion-exchange process is suitable for metals removal at low influent concentration levels. If the concentrations are high, chemical precipitation would usually be more cost-effective.

A complete treatment system for metal waste treatment includes removal of suspended and organic matters, and ion-exchange processes for removal of cations and anions. Dependent on the characteristics of the waste metal stream, the pretreatment of the waste stream involving, among other possible processes, pH adjustment, coagulation, and filtration may have to be considered.

For example, in chrome-plating wastewater treatment, the first step is the removal of suspended solids and organic matter, and the second one is removal of cations and anions. Because of the low pH (usually below 2) of the rinse water (i.e., the wastewater), a strong-acid cation ion exchanger must be used to remove the cations. Regeneration of the exhausted cation exchanger is performed by sulfuric acid or hydrochloric acid. Because of the strong bonding between polyvalent heavy metal cations and the resin, a high dose of acid is required for regeneration. Effluent from the regeneration process contains ferric, chromic, and sodium sulfates, and sulfuric acid. This spent regenerant stream does not have much value and hence is usually treated with lime and discharged. The anion exchange unit is more important in terms of chemical recovery. If the amount of rinse water is small, usually there is no recycling consideration. In such situations, regeneration of the anion exchanger is performed with NaOH. The spent regenerant is neutralized with acid and discharged to the sewer. However, if the volume of rinse water is large, it is more economical to recover the metal wastes. For the recovery of chromic acid, the spent regenerant is treated with a strong-acid cation exchanger to convert the chromates to chromic acid.

A new development in ion exchange for heavy and precious metal removal and recovery is the application of naturally occurring biomaterials and their derivatives. This process is very often termed biosorption. It should be noted that biosorption is different from bioaccumulation as there are no bioactivities involved. The biosorption process can be considered an ion-exchange process as its working mechanism is essentially ion exchange. Typical biosorbents used include seaweeds and alginate (a biopolymer from inactive organisms). These biosorbents are promising ion-exchange materials as they can concentrate heavy metal ions with very high efficiency in terms of both metal uptake capacity and kinetics. For example, a novel ion-exchange resin called CABIER developed by Chen and co-workers (17) can concentrate copper and lead with capacities of 2–3 mmol/g-CABIER. This is more than 10 times higher than most of conventional adsorbents. The biosorption process takes about 1 h to reach its completion. This is much shorter than other adsorbents, such as activated carbon. However, the weight loss during application can be a concern if they are used in industrial operations.

4.4. *Removal of Nitrogen*

Nitrogen is a key nutrient element for the growth of organisms. Nitrogen fertilizers are applied to crops in order to encourage healthier plant growth. Excess nitrate not consumed by plants can move easily through soil when carried by snowmelt, irrigation water, and rain, ultimately ending up in the surface water and groundwater. Besides fertilizers, other possible sources of nitrate in groundwater include waste dumps, animal feedlots, landfills, and defective septic tanks. Groundwater contamination is enhanced when the soil is sandy or gravely giving rise to a high hydraulic conductivity and hence greater contaminant mobility. The contamination is more likely in areas where the water table is close to the surface. In addition, ammonium ions from the secondary effluent of conventional biological wastewater treatment can enter surface and groundwaters and subsequently convert to nitrates. Even well-treated wastewater can carry nitrates unless denitrification is practiced at a treatment plant. This is because the activated sludge process operated with sludge aged more than 15 d can cause biological nitrification. Consequently, nitrate ions can also enter surface waters. Last, but not least, nitrate ions can be formed due to UV disinfection, which is discussed in another chapter in this handbook. Background nitrate concentration in surface water is usually below 5 mg/L of NO_3^-–N. However, the nitrate concentrations can exceed 20 mg/L NO_3^-–N in some wells.

Groundwater pollution by nitrates, which are perhaps the most ubiquitous of all groundwater contaminants, is a widespread problem in many locations in the world. High nitrate concentrations in drinking water present a potential health risk to the public (26). In the short-term effect, excessive levels of nitrate in drinking water have caused serious illness and sometimes death. The serious illness in infants is due to the conversion of nitrate to nitrite by the body, which can interfere with the oxygen-carrying capacity of the child's blood. This can be an acute condition in which health deteriorates rapidly over a period of days. Symptoms include shortness of breath and blueness of the skin.

In the long-term effect, nitrates and nitrites have the potential to cause the following effects from a lifetime exposure at levels above the Maximum Contaminant Level (MCL): diuresis, increased starchy deposits, and hemorrhaging of the spleen. As a result, the US EPA has set Maximum Contaminant Level Goal (MCLG) for nitrates at 10 ppm, and for nitrites at 1 ppm (14).

Removal of nitrates from drinking water is an important area of research. Although technology in this area is developing, there is still a need to further optimize the current treatment. Physicochemical methods allow effective removal of nitrate ions from nitrate contaminated waters. Among these methods, the capital and operating costs are the lowest for the ion-exchange process (7,8,12,27).

Anion-exchange resins with positively charged sites that are bonded to negatively charged chloride ions are often used to remove nitrate ions from water. Sodium chloride can be used to regenerate of the spent IX resins.

Competition is an important phenomenon in the process. If sulfate concentration is high, it can significantly reduce the nitrate removal efficiency. Similarly, the presence of bicarbonate, chloride, and other anions can affect the uptake of nitrate. Recent developments have been toward a nitrate-selective resin, which prefers to exchange chlorine with nitrate in normal drinking water concentrations. Resins with a higher preference for nitrate ions can be produced by increasing the amount of carbon atoms around ammonium nitrogen in the base structure. By making this change, selectivity increases from bicarbonate, chloride, sulfates to nitrates. In fact, the sulfate to nitrate selectivity increases from 100 to 1000. This increase in selectivity is attributed to steric strains in the resin that result from the higher steric requirements of alkyl groups, and the increased capability of nitrate to reduce the steric strains compared to sulfate. These nitrate selective resins have potential to reduce brine production, and improve treated water quality. A disadvantage associated with application of such IXRs is the production of nitric acid, which would require disposal.

4.5. Removal of Phosphorous

Phosphorous pollution comes from agricultural activities and domestic wastewater discharge. Because phosphorous is one of the limiting elements for plant growth, especially to the freshwater plants, excessive phosphorous in a water body is generally regarded as an important factor, which causes eutrophication. This results in the rapid propagation of aquatic plants such as algae. An algal bloom can thus lead to dissolved oxygen depletion, release of toxins, and large fish kills.

In many countries, municipal wastewater is treated biologically before discharge into nearby watercourses. However, traditional biological treatment methods only remove up to 50% phosphorous from sewage. Two important nutrient elements, nitrogen and phosphorous, still remain in the secondary effluent and have to be treated by other technologies if the eutrophication is concerned. Phosphate removal can be achieved through the use of chemical precipitation as well as by biological means (24). Phosphorus removal by means of chemical precipitation has declined in its popularity because of the associated sludge-disposal problems.

The use of ion exchange has been reported as an alternative to reduce phosphate concentration in the secondary effluent due to its operational simplicity and adaptability

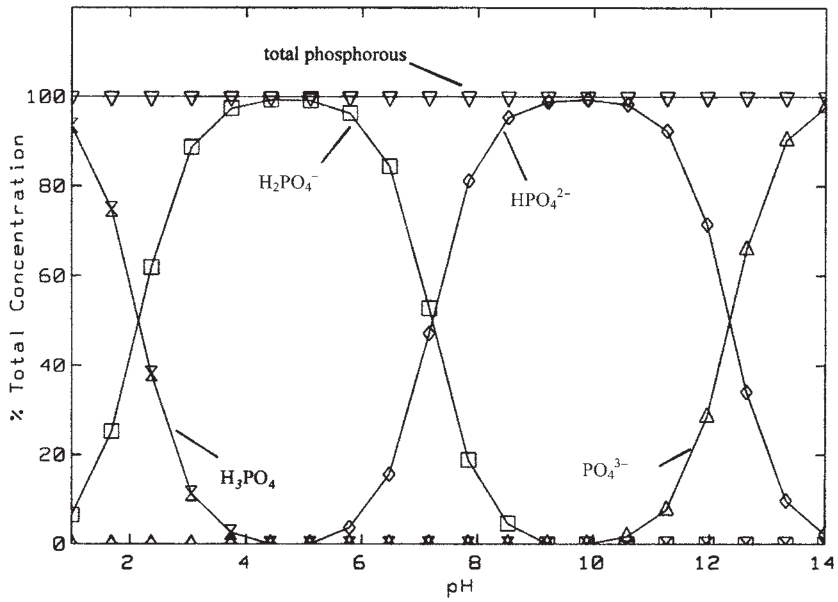

Fig. 5. Distribution of phosphorous species with pH variation.

to various flow rates and compositions. The possible ion exchange reaction can be described by the following equation (28):

$$n\overline{\mathrm{Cl}^-} + \mathrm{H}_i\mathrm{PO}_4^{(3-i)-} \rightarrow \overline{H_{i-j}\mathrm{PO}_4^{(3-i)-}} + n\mathrm{Cl}^- + j\mathrm{H}^+ \tag{31}$$

Phosphorous can exist as $H_iPO_4^{(3-i)}$ ($i = 0, 1, 2,$ and 3) at different pH values. As shown in the above equation, solution pH will decrease with the release of hydrogen ions. According to the pC–pH diagram illustrated in Fig. 5, the formation of $H_2PO_4^-$ and HPO_4^{2-} contributes to the uptake of phosphorous at pH 1 to 5 and 5 to 10, respectively. The pH dependency of phosphorous removal indicates that the amount of $\overline{HPO_4^{2-}}$ is higher than that of $\overline{H_2PO_4^-}$ as shown in Fig. 6.

Besides the variations in pH, the impurities in the water also affect the performance of such an ion exchanger. For example, when Cl^- is present, the above reaction would be shifted from the right to the left, leading to less removal of phosphorous. Meanwhile, CO_3^{2-}, SO_4^{2-}, and humic substances can be adsorbed by the resins, resulting in less available exchange sites for phosphorous and subsequently leading to lower removal (28).

4.6. Organic-Chemical Removal

Organic compounds are widely used, and many of these are potent contaminants when they are released into freshwater ecosystems. Industrial operations and human activities generate increasing amounts of wastewater contaminated with toxic and hazardous organic compounds and many of these are not amenable to biological treatment. These industrial wastewaters must nevertheless be treated, before discharge.

Because of their structural complexity, the organic materials present in wastewater may interact with ion exchangers in a variety of ways. Dependent on their chemical

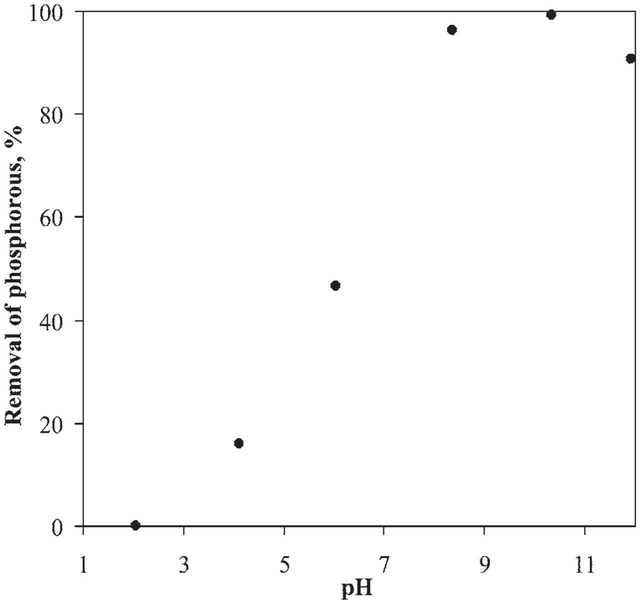

Fig. 6. Effect of solution pH on removal of phosphorous: $[P]_{initial}$ = 19.5 ppm, [IXR] = 1 g/L. Amberlite IRA910 Cl (strong basic macroreticular anion exchange resin) was used.

properties, industrial organic wastes can be removed by cation- or anion-exchange resins. However, anion resins are often used. Similar to removal of inorganic substances, the treatment of organic compounds is determined by chemical and physical properties of both the solution and resins. These properties would include initial concentrations, pH, and loading.

Phenol can be removed by weak-base resin (e.g., Ionac AFP-329). The capacity of this resin is not affected by the neutral salt. Regeneration of the resin is performed by methanol, isopropanol, or dilute alkali. The use of alcoholic solvents allows the recovery of phenol as the free acid, because the alcohol can be stripped from the regenerant effluent stream, leaving the phenolic concentrate. The recovered alcohol can then be reclaimed and used for subsequent regenerations, and the phenol can be recycled back to the process stream. The use of dilute alkali allows the recovery of the phenol as the sodium salt.

Wastewater from the meat, poultry, and fish industries contains large amounts of protein and fat. Proteins are amphoteric. They become predominantly cationic at pH levels below the isoelectric point of the protein because of the presence of $-NH_3$ groups, whereas at pH levels above the isoelectric point they have anionic characteristics because the presence of –COO groups. Below the isoelectric point, molecular association of the protein is a possibility and can result in increased adsorption. Cation exchangers exhibit considerably greater uptake capacities than anion-exchanger resins when both the protein and resin contain carboxylic acid groups in the uncharged form. With weak electrolyte ion-exchange resins, the pH of the system will also influence the degree of ionization of the resin and, consequently, the ion exchanger's capacity for the organic substance. The most unfavorable conditions for uptake of a protein by weak-electrolyte resins will be when the pH is in the vicinity of the dissociation constant of the resin and also close to the isoelectric point of the protein. Recovery of the protein from a resin can be affected by acid, alkali, or salt regenerant. Certain solvents such as alcohols may also be employed. In general, the regenerant must be able to alter the degree of ionization of the functional groups on the resin or must be capable of neutralizing the electrostatic forces binding the protein to the resin.

Organic chemicals such as NOM pose a problem in water treatment for a number of reasons. Apart from aesthetic issues such as color, taste, and odor (the latter two especially so after disinfection with chlorine which would also bring about the potential health hazard of disinfection by-products), NOMs cause fouling of membranes and ion-exchange resins, and the deterioration of water quality in distribution systems because of bacterial growth. NOM is composed of compounds formed by the biological degradation of organic substances. The compounds involved are amino acids, fatty acids, phenols, sterols, sugars, hydrocarbons, urea, porphyrins, and polymers.

The use of anion-exchange resins to remove some of NOMs from drinking water is well documented. Quaternary ammonium resins are normally used in the chloride form, with the chloride ions being replaced by the organic anions. Regeneration is achieved with brine or caustic brine. Trihalomethane (THM) precursors can be significantly removed.

Resins of open structure and high water content have been noted to be better performers, being very efficient at removal of any charged material, especially those of smaller molecular size (29). Quaternary ammonium resins containing polar groups are especially effective. The presence of a neighboring –OH group close to the quaternary nitrogen, heteroatoms in the bridge between the exchange site and the polymer backbone, a secondary amino group as the exchange site, or a low ratio of carbon to quaternary nitrogen is beneficial. A suitable balance of polar and nonpolar regions in the resin structure appears to be required. Weakly basic amino groups may have a greater affinity for hydrophilic counterions than quaternary ammonium groups, but generally there are fewer charged sites in the resin at neutral pH. Weak-base resins have NOM uptakes nearly as high as strong-base resins of similar water content. Water content is the most important parameter, the effect is less pronounced for strong base resins.

The patented magnetic ion-exchange (MIEX®) resin was reportedly used to specifically remove NOMs from drinking water, which are precursors to disinfection by-products (DBPs) (30). The resin has traditional anion-exchange properties, such as a polyacrylic matrix in the chloride form, a macroporous structure, and strong-base functional groups. In contrast to traditional anion-exchange resins, the resin has magnetized iron oxide incorporated into the polymer matrix. The magnetic component aids agglomeration and settling of the resin, allowing the resin beads to be smaller so that they can be applied to raw water in a slurry form. Its diameter is approx 180 μm, two to five times smaller than traditional IXRs, leading to higher mass transfer in completely mixed reactors operated in both continuous and batch modes (31–35). Treatment with MIEX® is more effective than coagulation at removing UV-absorbing substances and dissolved organic substances. Treatment with MIEX® and treatment with MIEX® followed by coagulation yielded similar results, suggesting that coagulation of MIEX®-treated water does not provide additional removal of organic carbon. The treatment reduces the trihalomethane formation potential and haloacetic acid formation potential. Treatment with the resin is most effective in raw waters having a high-specific UV absorbance and a low anionic strength. The resin also removes bromide to varying degrees, depending on the raw water alkalinity and initial bromide ion concentration.

5. OPERATIONS

There are several basic operating methods for ion exchangers. They consist of batch reactor, continuously stirred tank reactor, fixed-bed (column), and moving bed reactors.

Batch operation consists of dumping resin and solution into a tank, mixing and allowing for equilibrium. Resin is then regenerated for the next cycle. This process is limited by the selectivity of the resin under equilibrium. The total capacity used is due to selectivity. Column operation is like numerous batch reactors in series. It is carried out in a row of containers. The purpose of column operation is to work around the limitation of selectivity. It is realized that the improvement in each stage is less than that obtained in preceding one. It can be seen with an unfavorable selectivity there is a need for more stages.

Three types of column operations are downflow, upflow, and counterflow. Most beds operate with downflow operation. This is where feed and resin pass down through the resin bed. On the contrary, upflow operation is when the feed and resin are raised through a bed. The final flow is counterflow and it consists of the feed flowing down from the top and the regenerate flows up from the bottom.

In moving beds operation, the resin is contacted countercurrently with the exhausting stream and regenerated stream. The operation and result are similar to a fixed bed. The advantage of operation is that there is a continuous product of uniform quality at less space, capital, and labor. The problem is a complexity of the design problem for an operating system.

IX operation is very often affected by fouling due to the impurities in the feed solutions. Inorganic fouling is due to metal precipitation reaction. Calcium sulfate and calcium carbonate are the common problem. It can be resolved when acids such as hydrochloric acid are applied. Organic substances in the feed solution, such as humic and fulvic acids, are common in the surface waters. The IXR can be badly affected by the adsorption of the organic substances on its surface. The damage can be irreversible for some cases. The current solution is to clean up the IXR by alkaline solution, such as alkaline brine. It is therefore very important to set-up a pretreatment unit before the water enters the IXR system to minimize both organic and inorganic fouling. An alternative solution is to use IXR with large pore sizes, which may be able to tolerate the fouling.

NOMENCLATURE

b	The Langmuir constant related to heat of adsorption, L/mg
C_e	The equilibrium concentration of substance in solution, mg/L
C_A, C_B	Concentration of species A and B in the solution phases, meq/L
C^*	Aqueous phase concentration at the particle surface, in equilibrium with q^*, mole/L
C_b	Concentration in bulk solution, molar/L
c	Concentration in particle, mole/L
CABIER	Calcium alginate based ion exchange resin

DOC	Dissolved organic carbon
DVB	Divinylbenzene
D_s	Surface diffusivity within the particles, m^2/s
D_p	Pore diffusivity, m^2/s
D_L	Longitudinal dispersion coefficient, m^2/s
DBPs	Disinfection by-products
IX	Ion-exchange
IXR	Ion-exchange resin
K_f	Freundlich sorption constant
k_f	External mass transfer coefficient, m/s
$K_{A \to B}$	Equilibrium constant
K_A, K_B	Selectivity scale for component *A* and *B*
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
NOM	Natural organic matter
n	Freundlich sorption constant
q_e	The amount of substance adsorbed at equilibrium, mg/g
$q_{\max}$	The maximum sorption capacity, mg/g
q	Concentration of species in the IX resin (solid phase), meq/L
q_A, q_B	Concentration of species *A* and *B* in the IX resin (solid phase), meq/L
q^*	Aqueous phase concentration at the solid phase, mole/L
r	Radial distance from center of particle, *m*
R	Radius of particle, *m*
THM	Trihalomethane
X	Percentage of species in solution
$\bar{X}$	Percentage of species in solution and solid phases
$\overline{X_A}$	Percentage of specie *A* in solution and solid phases
$\overline{X_B}$	Percentage of specie *B* in solution and solid phases
X_A	Percentage of specie *A* in solution
X_B	Percentage of specie *B* in solution
α_B^A	Separation factor *A* to *B*
ε_p	Porosity of the particle
ρ_p	Particle density, kg/m^3

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9

Fluoridation and Defluoridation

Jerry R. Taricska, Lawrence K. Wang,
Yung-Tse Hung, and Kathleen Hung Li

CONTENTS

1. INTRODUCTION

Fluorine is the 13th most abundant element, and it is naturally introduced into the environment in both water and air (1). As a result, fluorine is present in small yet varying amounts in almost all soils, water supplies, plants, and animals. It is a normal constituent of our diets. The highest concentration of fluorine is found in our bones and teeth. The process of increasing or adding the trace element fluorine into drinking water in its ionic form as fluoride for the prevention of dental caries (tooth decay) is known as water fluoridation, whereas water defluoridation is the lowering of the naturally occurring fluoride level in drinking water to prevent dental fluorosis or the browning (mottling) of teeth (2). In 2001, US Surgeon General David Satcher stated: "Water fluoridation continues to be a highly cost-effective strategy, even in areas where the overall caries level has declined and the cost of implementing water fluoridation has increased" (3). It has been reported that the cost of fluoridation of public water systems averages $0.54 per person annually (4). In recent years, water consumption from bottle water has increased; some of the water used for bottling has a suboptimal level of fluoride. This consumption may reduce the effectiveness of a community fluoridation program.

Table 1 presents an overview of how fluoride was determined to be the cause of dental mottling. Physicians at the US Public Health Service and dentists can claim the credit for first ascribing dental mottling to some unknown constituent in drinking water; but water chemists were the first to implicate the element fluorine. It was initially thought

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Table 1
History of How Fluoride Was Determined to be the Cause of Dental Mottling (2,5–9)

Year	Who	Reported what
1901	U.S. Public Health Service (US PHS)	A physician stationed in Naples, Italy observed black teeth in emigrants from nearby region. The discoloring was believed to have been caused by water charged with volcanic fumes.
1916	Dr. Federick S. McKay (Dentist)	Observed the discoloring of teeth in his patients from Colorado Springs, CO, USA. Dr. McKay later concluded that a substance in the water supply was causing the discoloring.
1925	Colorando Spring, USA	Changed water source to a nearby spring that had been used by children whose teeth were not discolored.
1931	A. W. Petrey, Aluminum Company of America, Chemist	Reported the presence of calcium fluoride when examining for the presence of aluminum in water sample from Bauxite Arkansas, USA.
1931	H. V. Churchill, Aluminum Company of America, Chemist	Reported that areas with dental mottling had 2 mg/L or greater of fluoride in water supply samples and areas without dental mottling had less than 1.0 mg/L of fluoride.
1931	Drs. H. V. Smith, M. C. Smith, & E. M. Lantz, Researchers at University of Arizona	Reported that experimental results showed that dental mottling occurred in rats that were fed concentrated naturally fluoridated water and rats fed a diet high in fluorides.
1936	Dr. H. Trendley Dean, US PHS	Reported on his on observation of thousands of children in community with varying fluoride levels. His research established mottled enamel index, which measured the severity of the discoloring of the teeth enamel from fluoride.

that a deficiency of fluorine was the cause of tooth discoloration. As analytical techniques were refined and data began to accumulate, the true role of fluoride in water was revealed. It is now known that a deficiency of fluoride can lead to extensive tooth decay, but that an excess causes the mottling of teeth (2,5–9).

As a result of these initial discoveries, the first controlled fluoridation projects began in 1945 in the cities of Grand Rapids, Michigan; Newburgh, New York; and Brantford, Ontario; and in 1947, Evanston, Illinois. These controlled studies determined that fluoridation can safely reduce dental caries by 50–60% (2,5,6). During the second half of the 20th century, a major decline in the prevalence and severity of dental caries has occurred in the United States due to the fluoridation of public water systems. Table 2 lists the populations by state that were serviced by public water systems (PWSs) in 2000. Additionally, the table lists populations that were fluoridated by those PWSs. In 2000, fluoridation was provided to over 65% of the US population that were serviced by public water systems; this was approx 58% of the total population (10,11).

Fluoridation is based on the simple premise of adjusting the concentration of a mineral in which particular water is deficient. This premise is not new—waters that are deficient

Table 2
Number of Persons and Percentage of the Population Receiving Optimally Fluoridated Water Through Public Water Systems (PWS), by State–United States, 1992 and 2000 (10)

State	2000 Fluoridated population	2000 Total PWS population	2000 Percentage fluoridated	1992 Percentage fluoridated (9)	Change in percentage 1992–2000
Alabama*	3,967,059	4,447,100	89.2%	82.6%	6.6
Alaska	270,099	489,371	55.2%	61.2%	–6.0
Arizona	2,700,354	4,869,065	55.5%	49.9%	5.6
Arkansas[†]	1,455,767	2,431,477	59.9%	58.7%	1.2
California	9,551,961	33,238,057	28.7%	15.7%	13.0
Colorado[†]	2,852,386	3,708,061	76.9%	81.7%	–4.8
Connecticut	2,398,227	2,701,178	88.8%	85.9%	2.9
Delaware	505,747	624,923	80.9%	67.4%	13.5
District of Columbia	595,000	595,000	100.0%	100.0%	0.0
Florida	9,407,494	15,033,574	62.6%	58.3%	4.3
Georgia	6,161,139	6,634,635	92.9%	92.1%	0.8
Hawaii*	109,147	1,211,537	9.0%	13.0%	–4.0
Idaho	383,720	845,780	45.4%	48.3%	–2.9
Illinois	10,453,837	11,192,286	93.4%	95.2%	–1.8
Indiana	4,232,907	4,441,502	95.3%	98.6%	–3.3
Iowa	2,181,649	2,390,661	91.3%	91.4%	–0.1
Kansas	1,513,306	2,421,274	62.5%	58.4%	4.1
Kentucky	3,235,053	3,367,812	96.1%	100.0%	–3.9
Louisiana*	2,375,702	4,468,976	53.2%	55.7%	–2.5
Maine	466,208	618,033	75.4%	55.8%	19.6
Maryland[†]	4,124,953	4,547,908	90.7%	85.8%	4.9
Massachusetts[†,*]	3,546,099	6,349,097	55.8%	57.0%	–1.2
Michigan	6,568,151	7,242,531	90.7%	88.5%	2.2
Minnesota	3,714,465	3,780,942	98.2%	93.4%	4.8
Mississippi	1,227,268	2,665,075	46.0%	48.4%	–2.4
Missouri*	4,502,722	5,595,211	80.5%	71.4%	9.1
Montana	143,092	645,452	22.2%	25.9%	–3.7
Nebraska*	966,262	1,243,713	77.7%	62.1%	15.6
Nevada[†]	1,078,479	1,637,105	65.9%	2.1%	63.8
New Hampshire	347,007	807,438	43.0%	24.0%	19.0
New Jersey	1,120,410	7,208,514	15.5%	16.2%	–0.7
New Mexico	1,187,404	1,548,084	76.7%	66.2%	10.5
New York[†]	12,000,000	17,690,198	67.8%	69.7%	–1.9
North Carolina	4,862,220	5,837,936	83.3%	78.5%	4.8
North Dakota	531,738	557,595	95.4%	96.4%	–1.0
Ohio	8,355,002	9,535,188	87.6%	87.9%	–0.3
Oklahoma[†]	2,164,330	2,900,000	74.6%	58.0%	16.6
Oregon[†]	612,485	2,700,000	22.7%	24.8%	–2.1
Pennsylvania	5,825,328	10,750,095	54.2%	50.9%	3.3
Rhode Island	842,797	989,786	85.1%	100.0%	–14.9
South Carolina	3,086,974	3,383,434	91.2%	90.0%	1.2

(Continued)

Table 2 ***(Continued)***

State	2000 Fluoridated population	2000 Total PWS population	2000 Percentage fluoridated	1992 Percentage fluoridated (9)	Change in percentage 1992–2000
South Dakota†	553,503	626,221	88.4%	100.0%	–11.6
Tennessee	4,749,493	5,025,998	94.5%	92.0%	2.5
Texas	11,868,046	18,072,680	65.7%	64.0%	1.7
Utah†,*	43,816	2,233,169	2.0%	3.1%	–1.1
Vermont	240,579	443,901	54.2%	57.4%	–3.2
Virginia	5,677,551	6,085,436	93.3%	72.1%	21.2
Washington†	2,844,893	4,925,540	57.8%	53.2%	4.6
West Virginia*	1,207,000	1,387,000	87.0%	82.1%	4.9
Wisconsin	3,108,738	3,481,285	89.3%	93.0%	–3.7
Wyoming*	149,774	493,782	30.3%	35.7%	–5.4
Total	162,067,341	246,120,616	65.8%	62.1%	3.7

*Reported PWS population exceeded total state population; PWS population was set to the 2000 U.S. census of state populations.

†Complete data were not available from Water Fluoridation Reporting System; additional information was obtained from states.

in alkalinity or hardness are often supplemented with appropriate compounds at the water plant. However, the nature of the chemical and the purpose for which it is added are different, and therein lies the problem. Some citizens, however, are concerned by the word "fluoride." Fluoridation was originally termed "fluorination," and fluorine, of course, is a toxic and highly reactive gas. Controversy continues over the benefits of fluoridation. This opposition is based on faulty science, half truths, so-called experts and innuendo by antifluoridationists (7). Chlorination, the adding of chlorine to water for disinfection, received a similar negative reception that still exists today.

2. NATURAL FLUORIDATION

The dental examination of thousands of children and adults and the analysis of hundreds of water supply sources for fluoride have shown a remarkable relationship between the concentration of waterborne fluoride and the incidence of dental caries. As a result, the following general relationships between fluoride level and dental caries can be stated (1,5,9,12):

1. A fluoride level greater than about 1.5 ppm does not significantly decrease the incidence of tooth decay, but does increase the occurrence and severity of mottling.
2. A fluoride level of approx 1.0 ppm provides the optimum level by maximizing reduction in caries with no aesthetically significant mottling.
3. A fluoride level below 1.0 ppm results in some caries reduction, but as the fluoride levels decrease no caries reduction can be observed.

Because all water supplies contain measurable amounts of fluoride, it can be said that all water supplies are fluoridated. However, those water supplies containing naturally occurring fluoride concentrations greater than 0.7 ppm and less than 1.5 ppm have appreciable dental significance, and are the ones we refer to as being naturally fluoridated.

Table 3
Recommended Optimal Fluoride Levels for Community Public Water Supply Systems (2)

Annual average of maximum daily air temperatures*		Recommended fluoride concentrations	Recommended control range (mg/L) 0.1–0.5	
ºF	ºC	(mg/L)	Below	Above
50.0–53.7	10.0–12.0	1.2	1.1	1.7
53.8–58.3	12.1–14.6	1.1	1.0	1.6
58.4–63.8	14.7–17.7	1.0	0.9	1.5
63.9–70.6	17.8–21.4	0.9	0.8	1.4
70.7–79.2	21.5–26.2	0.8	0.7	1.3
79.3–90.5	26.3–32.5	0.7	0.6	1.2

*Based on temperature data obtained for a minimum of 5 yr.

Table 4
Recommended Optimal Fluoride Levels for School Public Water Supply Systems (2)

Annual average of maximum daily air temperatures*		Recommended fluoride concentrations†	Recommended control range (mg/L)	
ºF	ºC	(mg/L)	20% below	20% above
50.0–53.7	10.0–12.0	5.4	4.3	6.5
53.8–58.3	12.1–14.6	5.0	4.0	6.0
58.4–63.8	14.7–17.7	4.5	3.6	5.4
63.9–70.6	17.8–21.4	4.1	3.3	4.9
70.7–79.2	21.5–26.2	3.6	2.9	4.3
79.3–90.5	26.3–32.5	3.2	2.6	3.8

*Based on temperature data obtained for a minimum of 5 yr.
†Based on 4.5 times the optimal fluoride level for communities.

Water supplies with fluoride levels that are below this range must be fluoridated to achieve dental benefits (reduction in dental caries) and water supplies with fluoride levels that are above this range must be defluoridated to prevent mottling of teeth.

The Centers of Disease Control and Prevention (commonly referred to as the CDC) has recommended the optimal level for fluoride in drinking water (2), which is dependent on water temperature and population type. As water temperature increases, the optimal level decreases. For community water systems (serving both adult and children) with water temperatures ranging from 50 to 53.7°F, the optimal level is 1.2 mg/L; for community water systems with water temperature ranging from 79.3 to 90.5°F, the optimal level is 0.7 mg/L. Table 3 presents the optimal fluoride level for community water systems. As shown in Table 4, the optimal levels are significant higher for a school public water supply system. The optimal level for school children is 4.5 times the levels for the general population serviced by a community system.

The US EPA lists fluoride in the secondary drinking water standard at a maximum contaminant level (MCL) of 2.0 mg/L. This standard is intended as a guideline for an upper boundary level in areas that have high levels of naturally occurring fluoride. The standard also aims to balance the beneficial effects of protecting teeth from tooth decay and the undesired effects from excessive exposures leading to tooth discoloration (13).

3. CONTROLLED FLUORIDATION

Controlled fluoridation of a water supply can be accomplished by blending the water with a high level of fluoride with one with a low level of fluoride. The second type of controlled fluoridation, in addition to blending, is when the fluoride content of a water supply is adjusted by the deliberate addition of a chemical compound that provides fluorine ions in water solution. In 2000 controlled fluoridation, which began with the four cities previously mentioned, was practiced by US public water systems serving over 162 million persons out of US total population of 281 million (10,11).

The experimental procedures to establish water treatment plant operational practices have not been without problems. A few of these problems were engineering in nature, such as material compatibility, type of pumps, chemical phase (liquid or solid). Feeding fluoride is like feeding other chemicals; experience provides insight in determining the best type of equipment. The feed equipment is in general the same equipment used for feeding alum, soda ash, lime, sulfuric acid, or other chemicals.

Three most commonly used fluoride chemicals in the United States for fluoridation are sodium fluoride, sodium silicofluoride, and hydrofluosilicic acid. When applied to drinking water, they should meet the AWWA Standard B703-00 and B701-99 and should be NSF/ANSI Standard 60 certified. These standards ensure quality of the chemicals and limit the amount of impurities in the chemical, such as heavy metals (lead) (3,14,15).

Sodium fluoride (NaF) is available in powder or granular form in 98% purity. Typical screen analyses for both forms are present in Table 5 (15). The dissociation of sodium fluoride into sodium and fluoride ions when the chemical is added to water is shown in Eq. (1). A sodium fluoride solution can typically have a pH range from 7 to 7.6. Solubility of sodium fluoride is constant at 4 g/100 mL (3,15).

$$\mathrm{NaF} \leftrightarrow \mathrm{Na}^{+} + \mathrm{F}^{-} \tag{1}$$

Sodium silicofluoride (Na_2SiF_6) is available as crystalline material in 98% purity. It has a solubility that varies from 0.44 g/100 mL of water at 0°C to 0.76 g/100 mL at 25°C to 2.45 g/100 mL of water at 100°C. A solution of sodium silicofluoride will be acidic with a pH ranging from 3 to 4. Equations (2) and (3) show the dissociation of this chemical in water (5,16):

$$\mathrm{Na_2SiF_6} \leftrightarrow 2\mathrm{Na}^{+} + \mathrm{SiF}_6^{2-} \tag{2}$$

$$\mathrm{SiF}_6^{2-} + 2\mathrm{H_2O} \leftrightarrow 2\mathrm{H}^{+} + 6\mathrm{F}^{-} + \mathrm{SiO_2} \tag{3}$$

Equations (4)–(7) show the dissociation of hydrofluosilicic acid (H_2SiF_6), which is nearly 100% (5). This product is also identified as fluorosilicic acid, hexafluorosilicic, and silicofluoric. This acid is available as commercial water solutions having concentrations ranging from 20% to 25% H_2SiF_6. The weight of 23% hydrofluorosilicic acid–water solution is 10.2 pounds per gallon at 60°F and contains 17.41% fluorine. Additionally, the acid–water solution will freeze at 5°F for a 23% solution and at –4°F for a 25% solution. The boiling point for the acid–water solution (23%) is 221°F. This

Table 5
Typical Commercial Screen Analyses for Sodium Fluoride (15)

Mesh (opening mm)	Granular (range)		Powder (range)	
+20 (0.850)	2%	Trace		
+100 (0.150)	50%	80%	10%	1%
+200 (0.075)				35%
–325 (0.045)	5%	2%		35%

+ indicates retained on sieve.
– indicates passing through sieve.

Table 6
Characteristics of Commercially Available Fluoridation Chemicals (5,6,15,16)

Chemical name (matrix)	Formula	Specific gravity	Application rate to achieve 1 mg/L	Containers
Sodium Fluoride (granular or powder)	NaF	2.5–2.6	8.6 kg (19 lb)/MG	50 & 100 lb bags 125 & 400 lb drums 1300 & 2000 lb super sack
Sodium Silicofluoride (powder)	Na_2SiF_6	2.6–2.7	6.3 kg (14 lb)/MG	50 & 100 lb bags 125 & 400 lb drums 1300 & 2000 lb super sack
Hydrofluosilicic Acid (acid–water solution)	H_2SiF_6	1.23*	20.8 kg (46 lb)/MG	15 gal carboys 55 gal drums 40,000 lb tank truck 196,000 lb tank car

*At 60°F.

chemical has a low pH with a 1% solution having a pH of 1.2, making it very corrosive. The flumes from the acid are lighter than air. As a result of the low pH and lightweight flume, this chemical is very difficult to handle (5,6,15):

$$H_2SiF_6 \leftrightarrow 2HF + SiF_4\uparrow \tag{4}$$

$$SiF_4\uparrow + 2H_2O \leftrightarrow 4HF + SiO_2\downarrow \tag{5}$$

$$SiF_4\uparrow + 3H_2O \leftrightarrow 4HF + H_2SiO_3 \tag{6}$$

$$HF \leftrightarrow H^+ + F^- \tag{7}$$

Table 6 summarizes the characteristics of these three commercial available chemicals. Water fluoridation has also been accomplished with ammonium silicofluoride, calcium fluoride, hydrofluoric acid, magnesium silicofluoride and potassium fluoride (5).

4. DRY FEEDERS

Granular or powdered material can be fed by a dry feeder to a solution tank. The material is thoroughly mixed with water and then fed to a day tank, which then feeds the solution into the application point in the water treatment plant. All materials are not handled with equal ease. Materials that are too fine will flow like a liquid right through the measuring mechanism (“flooding”), while some materials will form an arch in the hopper that upon collapsing, emits a cloud of dust and floods the feeder. Additionally, some powdered materials, either hygroscopic by nature (water–attracters) or produced with a significant moisture content, tend to form lumps that will affect the feed rate or not be fed at all. To achieve a consistent feeding, which is required for a controlled dosage of fluoride, the graduation of material must meet a narrow size distribution and the material must have low moisture content. The feedability index *(F)* was developed from the feeding problems with sodium silicofluoride. Equation (8) presents the feedability index:

$$F = 100 - (A + B + 10C) \tag{8}$$

where A = percentage retained on a 100-mesh sieve (0.150 mm), B = percentage passing through a 325-mesh sieve (0.045 mm), and C = percentage of moisture. Because the values used in the equation are percentages, the feedability index is an abstract number. Generally, a feedability index below 80 proves to be unsatisfactory, 80–90 is good, and 90–100 is excellent.

4.1. Example of Dry Feeders

A water treatment plant is using silicofluoride for fluoridation. To prevent feeding problems, the operational staff requested all shipment be subject to the feedability index prior to shipment.

<u>Batch No.1</u>

The first batch of sodium silicofluoride was sampled and subjected to particle-size analysis (see Section 4.3) with the following results: 3% retained on 100-mesh sieve, 9% passes through the 325-mesh sieve. The moisture content was 0.05%. Applying the feedability formula yields:

$$F = 100 - (3 + 9 + [10][0.05]) = 87.5$$

This feedability value indicates that this material will have good feeding characteristics.

<u>Batch No.2</u>

The second batch of sodium silicofluoride, when sampled and tested as described above, gave the following results: 1% retained on 100-mesh sieve, 20% passes through the 325-mesh sieve. The moisture content again was 0.05%. Applying the feedability formula yields:

$$F = 100 - (1 + 20 + [10][0.05]) = 78.5$$

The feedability value indicated that this material would be troublesome, with the excess ultra-fine powder (the portion passing through the 325-mesh sieve) causing arching, flooding, and dust problems. Therefore, Batch 1 was ordered and shipped to the water treatment plant.

4.2. Checking Particle Size

To ensure good handling and feeding characteristics for dry chemicals, it is important that the dry chemical adhere to graduation specifications. The size gradation for crystalline (coarse) sodium fluoride for use in a downflow saturator (see the Section 5) should be in the 20–60-mesh range (0.85–0.25 mm), and powdered sodium silicofluoride

Table 7
Result of Sieve Analysis

Sieve	Sieve opening (mm)	Amount retained (g)	% of total
Retained by 100 Sieve	0.150	10	10
Retained by 140 Sieve	0.106	25	25
Retained by 200 Sieve	0.075	30	30
Retained by 325 Sieve	0.045	30	30
Retained by the pan (after passing through the 325 sieve)		5	5
Total		100	100

for use in a dry feeder should be relatively free from extremely coarse or extremely fine particles to ensure the best feeding characteristics.

The size of particles is usually determined with a set of standard sieves; the size designation referring to the range of sieve sizes which best describes those particles. For example, a 20–60 specification means that most particles pass through a size 20 sieve but are retained by a size 60 sieve (the larger the sieve number, the smaller the opening).

The testing procedure is determined somewhat by the apparatus used, but generally a set of standard testing sieves is stacked, coarsest on top and progressively finer toward the bottom, above a collecting pan. A weighed amount of material is placed in the uppermost sieve, the set of sieves shaken gently (mechanically) for about 5 min, and then the portion collected by each sieve and the pan are weighed separately.

4.3. *Example of Sieve Analysis*

A 100 g sample of sodium silicofluoride was used in a sieve analysis. Table 7 presents the amounts retained in the 100, 140, 200, and 325 sieve meshes and in the pan. Assuming the moisture content of this particular material was 0.05% or less, applying the feedability formula yields:

$$F = 100 - (10 + 5 + [10][0.05]) = 84.5$$

This value for feedability indicates that the material should feed satisfactorily through a dry feeder.

4.4. *Feeding System*

The simplest feeding system would involve a manually prepared fluoride solution and a flow-paced feed pump that introduces the fluoride solution into a water supply at a fixed rate. The requirements for auxiliary equipment are minimal. This system would include a platform scale, dissolving tank with a manual paddle or electric mixer for stirring, and a solution tank with a solution feed pump, this is all the equipment needed. Depending on the type of pumps (non-positive displacement) used to feed the fluoride solution, a vacuum breaker can be incorporated into the design of the pump feeding system to prevent pulling unmetered quantities of fluoride solution into the water system in the event of a low-pressure situation.

Extra equipment could include a volumetric or gravimetric feeder, an alarm system for detecting and reporting low solution levels, a softener for removing hardness constituents from the solution water, a small meter for measuring the amount of water used in solution preparation. As the size and complexity of the fluoridation system grows, the number and complexity of these pieces of auxiliary equipment increases, and they become necessary components.

Table 8 provides guidelines for preparing a fluoride–water solution using 98% NaF. Using the table, one can determine the fluoride concentration of the fluoride–water solution, when a certain amount of 98% NaF is added and mixed into a prescribed amount of water.

4.5. Meters

The water meter, often absent on the water line where the fluoride is injected, is one of the primary requisites for accurate fluoride feeding. Usually water treatment plants produce water at constant rate but, owing to seasonal demands and operational conditions, water product will vary. If the water line where the fluoride is injected is unmetered, calculation of the fluoride feed rate will have to be estimated, and even the selection of an appropriate feeder may be open to uncertainty.

The type of meter used for water flow depends on the flow rate and velocity. Meter types include Venturi, propeller, turbine, and magnetic. The manufacturer of each should be consulted for their limitations, which include pipe size, up- and downstream straight pipe available at flow meter installation, minimum and maximum velocity through meter, and calibration requirements. Unfortunately, meters are usually selected by pipe size, not flow rate, so the water meter is often grossly oversized for the flow rate through it. Because most meters are least accurate at the low velocity end of their measurement range, the result is that water flow is not accurately measured.

The remedy is to select a meter no larger than necessary to handle the minimum flow rates expected, even if the pipe and meter sizes do not match. The velocity through the meter at minimum flow should have range between 2 and 5 fps and at maximum flow have a range of 8–12 fps (1 fps = 1 ft/s = 0.3048 m/s). In some cases, this may involve the use of pipe reducers to adapt the water line to the meter size; a practice which is acceptable provided that the resulting pressure loss is not excessive. Manometers (measuring pressure differential) can be used to calibrate Venturi type meters, whereas only controlled water tests can be used to accurately calibrate propeller, turbine, and magnetic type meters.

Other applications for water meters, besides the water line where the fluoride is injected as discussed above, are on supply lines for solution makeup water. Additionally, a flow meter is a necessity when a sodium fluoride saturator is used to prepare the fluoride solution. (see Section 5.) Because the water usage rate in a saturator installation is minimal, the meter must be the smallest available (usually 1/2 in; 1 in. = 2.54 cm). A propeller type is commonly used here.

4.6. Auxiliary Equipment

In all fluoridation installations except ones based on a sodium fluoride saturator, scales are a necessity for either weighing the quantity of dry material to be used in solution preparation, weighing the quantity of solution fed, or weighing the quantity of dry

Table 8
Preparation of Solution of Sodium Fluoride

Pounds of NaF	Gallons of water									
(98% pure)	10	20	30	40	50	60	70	80	90	100
1	1.2	0.6	0.4	0.3						
	5200	2600	1750	1300						
2	2.3	1.2	0.8	0.6	0.5	0.4	0.3			
	10300	5200	3500	2600	2100	1750	1500			
3		1.75	1.2	0.9	0.7	0.6	0.5	0.45	0.4	0.4
		7750	5200	3900	3100	2600	2250	1950	1750	1600
4		2.3	1.55	1.2	1.0	0.8	0.7	0.6	0.5	0.5
		10300	7000	5200	4200	3500	3000	2000	2300	2100
5			2.0	1.5	1.2	1.0	0.85	0.75	0.7	0.6
			8600	6500	5200	4350	3700	3300	2900	2600
6				1.8	1.4	1.2	1.0	0.9	0.8	0.7
				7800	6200	5200	4300	3900	3500	3150
7				2.0	1.65	1.4	1.2	1.0	0.9	0.8
				9000	7300	6000	5200	4600	4000	3650
8					1.9	1.6	1.35	1.15	1.05	0.95
					8300	6900	6000	5100	4650	4200
9					2.1	1.75	1.5	1.3	1.2	1.1
					9300	7800	6700	5850	5200	4700
10						1.95	1.7	1.5	1.3	1.2
						8600	7400	6500	5800	5200
11						2.15	1.85	1.6	1.45	1.3
						9450	8200	7200	6400	5750
12							2.0	1.8	1.6	1.4
							8900	7800	6900	6250
13								1.9	1.7	1.5
								8400	7500	6750
14								2.1	1.8	1.65
								9100	8100	7300
15									1.95	1.8
									8600	7800
16									2.0	1.9
									9000	8300
17										2.0
										8800

The above table gives strengths of solutions prepared by dissolving the given weights of sodium fluoride in various volumes of water. The upper figures represent approximate solution strength in percent *sodium* fluoride, while the lower figures represent approximate solution concentration in ppm F. Example: If 2 lb of NaF are dissolved in 50 gallons of water, what is the solution strength? Reading across (horizontally) from 2 lb to the 50 gal column gives 0.5% NaF and 2100 ppm F.

The absence of figures in a column indicates that the preparation of the particular solution would be impractical or impossible (1 lb = 454 g; 1 gal = 3.785 L; 1 ppm = 1 mg/L).

fluoride compound or fluosilicic acid delivered by the appropriate feeder. Softeners are required depending the hardness of the water used to prepare solution sodium fluoride (include saturator) and sodium silicofluoride solutions. Mixers are required for the preparation of sodium fluoride solutions, dilution of fluosilicic acid, or the dissolution of the output of dry feeder.

4.6.1. Scales

The type of scale can vary from a small household-type used for weighing pounds of sodium fluoride to be used in solution preparation to the complex built-in mechanism of a gravimetric dry feeder. The most generally applicable type is the platform scale, on which can be placed an acid day tank, a carboy of acid, or an entire volumetric dry feeder. Although the scales may be specifically designed for the application, as are those supplied by manufacturers with volumetric dry feeders, in many cases an industrial platform type of scale will be perfectly satisfactory for applications. Minor modifications may be necessary on this type of scale, such as removing the wheels or rotating the beam. This type of scale will be sufficient as long as it has adequate capacity and sensitivity. It is important to remember that the scale must be capable of weighing the tank and its contents when full or the volumetric feeder and its hopper when full, with measurements to the nearest pound or better. When measuring sodium fluoride to be used in manual solution preparation, the sensitivity of the scale should be to the nearest ounce.

When mounting volumetric dry feeder with solution tank on industrial-type platform scales, the solution tank's fixed connections to a water line and the discharge line must be modified. These fix connections can be modified by using flexible connections that permit the scale to operate properly.

4.6.2. Softeners

When sodium fluoride is used for a fluoridation system, it should be remembered that, while sodium fluoride is quite soluble, the fluorides of calcium and magnesium are not. Thus, the fluoride ions in solution will combine with available calcium and magnesium ions in the makeup water and form a precipitate that can clog the feeder, the injection port, the feeder suction line, the saturator bed, etc. Therefore, water used for sodium fluoride dissolution should be softened whenever the hardness exceeds 75 ppm, or even if the hardness is less than this value (17). Only the water used for solution preparation must be softened.

A household type of ion-exchange water softener is usually adequate for this application because the volume of water to be softened is usually quite small. This type of softener is available from manufacturers like Calgon or MacClean. The softener can be installed inline on the water supply line to the solution tank. When resins (zeolite or synthetic resin) become saturated with calcium (exhausted), the resin (zeolite or synthetic resin) can be regenerated with brine solution made from common salt.

For high magnesium levels, the sequestering process (keeping in solution) may be used. This is accomplished by adding polyphosphates to the water. Usually 7–15 mg/L of polyphosphates is required. The polyphosphates may be added directly into the solution tank. When an eductor is used for addition of the fluoride solution, both the eductor water and the fluoride solution water should be softened. A chemical pump must be used to introduce the polyphosphates into the eductor water.

4.6.3. Mixers

In the prepared solutions, whether it is manual preparation of sodium fluoride solutions, dilution of fluosilicic acid, or the dissolution of the output of dry feeder, it is very important that the solution be kept homogeneous without suspended solids. Solutions with suspended solids or settled solids (undissolved sodium fluoride or sodium silicofluoride) cannot be tolerated in the feeding of fluorides, because undissolved fluoride compounds can go into solution subsequently, causing a higher-than-optimum situation to result. Additionally, these solids can also clog chemical feed pumps and other devices having small openings, and if allowed to accumulate, can result in considerable waste.

Solutions should be thoroughly mixed when preparing a dilution solution, as in the preparation of fluosilicic acid dilutions. Because these two liquids (water and fluosilicic acid) have differing specific gravities, they tend to stratify, which could result in feeding a solution too concentrated or, at the other extreme, plain water. Even though sodium fluoride is highly soluble in water, the preparation of sodium fluoride solution requires continuous and sufficient agitation to ensure all solids are dissolved. If not, the undissolved material will settle to the bottom of the solution tank. As the diluted solution is being pumped, the settled solids will gradually dissolve, which will result in a stronger solution forming at the bottom of the tank. This stronger solution will tend to remain in its own stratum.

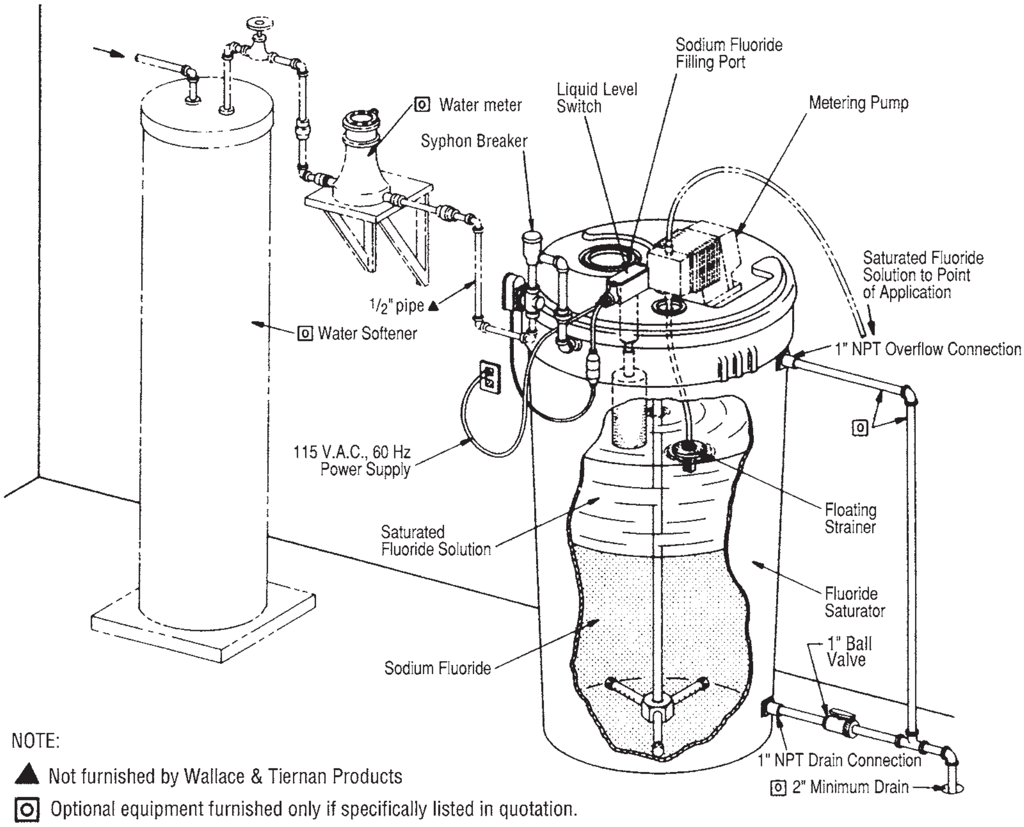
Using a paddle with sufficient manual mixing will suffice for the initial preparation of a dilute solution, although it will not be sufficient to prevent stratification. Therefore, a mechanical mixer is preferred. Mixers are available in various sizes, with shafts and propellers made of various materials to meet chemical-resistant requirements for different fluoride chemicals. Depending on the size of the mixing tank, a fractional horsepower mixer with a stainless-steel shaft and propeller will be satisfactory for sodium fluoride solution, and a similar mixer with a corrosion-resistant alloy or plastic-coated shaft and propeller will handle fluosilicic acid (15).

The dissolution of sodium silicofluoride in the solution tank of a dry feeder package unit can be accomplished by a jet mixer, but again a mechanical mixer is preferred. Because of the low solubility of sodium silicofluoride, particularly in cold-water applications, and the limited retention time available for dissolution, violent agitation is needed to prevent the slurry discharge. The preferred construction materials for a mechanical mixer are 316 stainless steel, plastic-coated steel, and Hastelloy-C® (15).

5. SATURATORS

Regardless of whether there are substantial variations in solution water temperature and the uses of automated devices for preparing saturated solutions, the solubility of sodium will remain around 4% (approximately 18,000 ppm as F). A saturator is a device that eliminates the need for weighing sodium fluoride, measuring solution water volume, and stirring to ensure dissolution.

A saturator produces a saturated solution by allowing water to trickle through a bed of coarse granular sodium fluoride solids in excess of the amount required for saturating the water solution. Two types of saturators are available: upflow and downflow. In a downflow saturator, the sodium fluoride solids are isolated from the saturated solution by a plastic cone or a pipe manifold and a filtration barrier composed of layers of sand and gravel. The barrier prevents particles of undissolved sodium fluoride solids from infiltrating the solution area under the cone or within the pipe manifold. With the upflow type, no barrier is used, because the water comes up through the bed of sodium fluoride



NOTE:
▲ Not furnished by Wallace & Tiernan Products
⊡ Optional equipment furnished only if specifically listed in quotation.

Fig. 1. Upflow saturator.

solids and the specific gravity of the solids keeps it from rising into the area of clear solution above. Figure 1 presents commercially available upflow saturators and higher capacity units can be ordered (large sizes are also available). In the downflow type, the fluoride–water solution feed pump takes suction from within the cone or manifold, while in the upflow type, the fluoride–water feed pump uses floating suction intake on the solution in order to avoid withdrawal of undissolved sodium fluoride. Downflow saturators are not commercially available but can be specially made.

5.1. Downflow Saturators

In the operation of a downflow-type saturator, water is introduced at the top of the saturator tank (there is an air gap to avoid the possibility of a cross-connection) and the level is regulated with a float-operated controller valve on the water supply line. The water then trickles down through the bed of sodium fluoride solids; the solution is clarified in the sand and gravel filter bed and ends up as a clear, saturated solution at the bottom of the tank where it is withdrawn by the feeder. The fluoride–water solution pump withdraws the solution and delivers it into the water system at a desired dosage rate. Operator attention is required only to ensure that an adequate quantity of sodium fluoride solids is kept in the saturator and that the saturator is kept in a reasonably clean condition.

Table 9
Recommended Maximum Feed Rates for Downflow Sodium Fluoride Saturator (2)

	Water temperature (°F)		
Bed depth (in.)	60	50	40
6	950 gpm 200 mL/min	859 gpm 175 mL/min	710 gpm 150 mL/min
6½	1065 gpm 225 mL/min	950 gpm 200 mL/min	830 gpm 175 mL/min
7	1190 gpm 250 mL/min	1065 gpm 225 mL/min	950 gpm 200 mL/min
7½	1300 gpm 275 mL/min	1190 gpm 250 mL/min	1065 gpm 200 mL/min
8	1425 gpm 300 mL/min	1300 gpm 275 mL/min	1190 gpm 250 mL/min
8½	1550 gpm 325 mL/min	1425 gpm 300 mL/min	1300 gpm 275 mL/min
9	1660 gpm 350 mL/min	1550 gpm 325 mL/min	1425 gpm 300 mL/min
9½	1780 gpm 375 mL/min	1660 gpm 350 mL/min	1550 gpm 325 mL/min
10	1900 gpm 400 mL/min	1780 gpm 375 mL/min	1660 gpm 350 mL/min

The recommended maximum feed rates for downflow saturator at various water temperatures and sodium fluoride bed depths are listed in Table 9. At a given water temperature and bed depth, the water flow and solution feed rates are listed. The lower figures represent the maximum feed rate (or withdrawal rate) of saturated sodium fluoride solution and the upper figures represent the water flow rate which can be fluoridated to a level of 1.0 ppm of fluoride. These rates assume that there is less than 0.1 ppm natural fluoride content in the water. These flow rates can be used for higher water flow rates if there is a higher natural fluoride content or if the desired level is less than 1.0 ppm of F. The following are the current procedures for setup and operating downflow saturator:

Saturator Setup

1. For either the manifold or cone inlet, carefully place by hand a 2–3 in. layer of coarse, clean gravel (1–2 in. size) in the 50-gal saturator tank around the manifold or cone and over the manifold or over the lower edge of the cone. Cover the coarse layer with a 2–3 in. layer of finer gravel (1/2–1 in. size). Then add 4–6 in. layer of clean, sharp filter sand over the gravel. (Do not use beach sand, clay sand, or ordinary soil.) Level the surface of the sand layer. (The aforementioned layers can be replaced with one 12 in. layer of 1/8 to 1/4 in. filter gravel.)
2. Add 200–300 lb of coarse crystalline sodium fluoride (20–60 mesh coarse crystal). (Do not use powdered NaF or fine crystal.) Make sure the sodium fluoride surface does not interfere with float and float rod of the level indicator. Add water to keep down the dust and to assist in leveling the fluoride surface.
3. If the sodium fluoride surface interferes with operation of level float, make a depression in the surface of the sodium fluoride in order to provide clearance for the float and float rod.

4. Connect the cold-water supply line to the water intake connection of the saturator. Upstream of this connection, the water line should have a small water meter (1/2 in.) for use in calculating the feed rate, and there should be a shut-off valve between the meter and the saturator. To lower the amount of dirt to the saturator, a sediment filter (20 mesh) should be installed upstream of the saturator between the softener and water flow meter.
5. Turn on the water supply and adjust the level control float with the low-water level no less than 2 in. above the sodium fluoride surface and the high-water level just below the overflow outlet.
6. The suction line from solution feed pump can now be inserted into the pipe leading to the inner cone or manifold as the case may be. The foot valve and strainer on the suction line should be 2–3 in. above the bottom of the saturator tank. Make sure the feed pump has an anti-siphon valve, which will prevent overdosing. The saturator can now be placed into service.

Saturator Operation

1. The translucent wall of the saturator tank will allow you to distinguish the layers of sodium fluoride, sand, and gravel. Monitor the thickness of the sodium fluoride layer. When this layer decreases to 6 in., add another 100 lb quantity of sodium fluoride. Note that the water level in the tank should be allowed to reach its lowest level, or if necessary, shut off the water supply temporarily until water level is low enough so that the addition of sodium fluoride will not cause water to come out of the overflow opening.
2. When operating the saturator at a high rate, i.e., if more than 1000 gpm of water is being treated, sodium fluoride should be added daily in sufficient amounts to keep the fluoride layer at a thickness of at least 10 in. This procedure should also be used when the makeup water temperature is below 60°F, even if less than 1000 gpm of water is being treated.
3. Prior to adding sodium fluoride to the saturator, the surface of the sodium fluoride layer in the saturator should be scraped free of accumulated dirt, insoluble material, or the slimy film of fine particles that sometimes forms.
4. At a 3-mo cycle or a shorter cycle depending on usage (treating 100 gpm or greater) and the accumulation of dirt, the saturator will have to be cleaned out. To minimize wastage of chemicals and decrease the amount of material that has to be removed, follow these steps:
    a. Continue operating the saturator until the level of sodium fluoride is as low as practical. Shut off the makeup water supply; this will cause the level of water to drop down to the fluoride layer.
    b. Remove each layer and place in separate containers. A scoop could be used to accomplish this task. Properly dispose of old material or save the gravel and sand for cleaning and reuse.
    c. Remove and clean the inner cone or manifold assembly. Clean the inside of the saturator tank and then reinstall the cleaned cone or manifold.
    d. When the old sand and gravel are to be reused, wash them repeatedly with water until all traces of sodium fluoride and dirt are removed. The filter bed of sand and gravel is then reinstalled with either the cleaned or new material.
    e. Add sodium fluoride as outlined startup procedures. Remember to turn on the water supply.
5. If the water supplied to the saturator exceeds 50 ppm hardness, a household-type water softener should be installed on the water supply line to the saturator. The softener will minimize the amount of insoluble material accumulating in the saturator and thus increase the interval between cleanings.
6. Use the readings of the water meter on the saturator supply line to calculate the amount of fluoride fed. Because the solubility of 98% sodium fluoride is approximately 4% and 45.2% available fluorine in sodium fluoride, then water–fluoride solution in the saturator

will be equivalent to approximately 18,000 ppm of F (4% × 10,000 ppm/% × 0.98 × 0.452). Using the following equation, the ppm of fluoride in the water system (water pumped) can be determined:

$$R1 \times C1 = R2 \times C2 \tag{9}$$

where $R1$ = water system flow rate (where the sodium fluoride is being added), $C1$ = fluoride level desired, $R2$ = solution feed rate, and $C2$ = fluoride concentration of the solution. Therefore,

$$\text{ppm of F fed } (C1) = \left[\frac{\text{gallons of water supplied to the saturator } (R2)}{\text{gallons of water pumped } (R1)}\right] \times \left[\text{ppm F of solution concentration } (C2)\right]$$

$$\text{ppm of F fed } (C1) = \left[\frac{\text{gallons of water supplied to the saturator } (R2)}{\text{gallons of water pumped } (R1)}\right] \times \left[18{,}000 \text{ ppm of F}\right]$$

5.2. *Upflow Saturators*

Upflow saturators use a bed of undissolved sodium fluoride as a bed in which water is forced through upward. Water under pressure is distributed through a spider-type distributor head located at the bottom of the tank. This head contains hundreds of tiny slits in which water is forced under pressure through these slits and flows upward through the sodium fluoride bed at a controlled rate to ensure the desired 18,000 ppm of fluoride solution. An upflow saturator requires water pressure at a minimum of 20 psi to a maximum of 100 psi, and the flow into the saturator is regulated at 2 gpm. Because the introduction of water to the bottom of the saturator constitutes a definite cross-connection, a certified backflow preventer must be installed on the water supply line to the saturator along with anti-siphon valve on the solution feed pump (2).

Saturator Setup

1. Install the feedwater distribution tube with distribution header and remove the floating suction device. Add 200–300 lb of sodium fluoride directly to the tank. (Various graduations of sodium fluoride can be used, from coarse crystal to fine crystal to powder, but fine crystals will produce less dust than powder and dissolve better than coarse crystal.)
2. Connect the cold-water supply line with a solenoid valve to the distribution tube. Make sure the float system used to control the water level in the tank is operating freely and connected to the solenoid valve. Check if the solenoid valve is connected to an electrical supply. Turn on the water supply. Observe the water level. It should be slightly below the overflow; if it is not, adjust the level float system. A water flow rate of 2 gpm should be sufficient and should register satisfactorily on a $^1/_2$ in. meter.
3. Reinstall the floating intake and suction line for chemical feed pump. The saturator is now ready for use.

Saturator Operation

1. The translucent wall of the saturator tank will allow you to see the undissolved level of sodium fluoride. When this layer decreases to 12 in., add another 100 lb quantity of sodium fluoride. Note that the water level in the tank should be allowed to reach its lowest level, or if necessary, shut off the water supply temporarily until the water level is lower

enough so that the addition of sodium fluoride will not cause water to come out of the overflow opening.
2. The slits in the distribution header are designed to be essentially self-cleaning, and the accumulation of insolubles and precipitates does not constitute as serious a problem as it does in a downflow saturator. Cleaning frequency of the distribution header will depend on the usage and amount debris accumulated in the saturator.
3. The upflow saturator provides a thicker bed of sodium fluoride and more fluoride–water solution, allowing for higher withdrawal rates than a downflow saturator. A maximum of 1000 mL/min saturated fluoride–water solution can be withdrawn from an upflow saturator; this is a rate sufficient to treat about 5000 gpm of water to a fluoride level of 1.0 ppm.
4. As with a downflow saturator, the hardness of the water supplied to the saturator should be examined, and if necessary, a softener should be installed to reduce the accumulation of solids. (hardness should not exceed 50 ppm).
5. The calculation to determine the amount of fluoride–water solution fed is the same for both types of saturators. Use Eq. (9).

6. COMMON OPERATIONAL PROBLEMS IN PREPARATION OF FLUORIDE SOLUTION

Care should be taken when preparing of solutions of fluoride compounds, whether performed manually or automatically.

Common errors in the manual dilution of hydrofluorosilicic acid-water solutions include:

1. Inaccurate volume or weight of acid.
2. Inaccurate volume or weight of water.
3. Incomplete mixing.
4. Miscalculation of acid strength as received.
5. Miscalculation of fluoride concentration in dilution.

Common errors in the manual preparation of sodium fluoride-water solutions include:

1. Inaccurate weight of sodium fluoride.
2. Inaccurate weight or volume of water.
3. Incomplete dissolution.
4. Incomplete mixing.
5. Attempting concentration greater than 2%.
6. Miscalculation of fluoride concentration in the sodium fluoride.
7. Miscalculation of fluoride concentration of the sodium fluoride-water solution.

Several factors can adversely affect the proper functioning of devices (saturators) that automatically prepare sodium fluoride–water solutions. These factors are as follows:

1. The amount of sodium fluoride is insufficient.
2. Sodium fluoride–water solution feed rate was not adjusted for temperature.
3. Sodium fluoride–water solution feed rate was too high.
4. Sifting of sodium fluoride down through sand and gravel (downflow type).
5. Water supply rate is too high, causing lifting of sodium fluoride (upflow type).
6. Improper size gradation for sodium fluoride crystal (too fine for the downflow type).
7. Short-circuiting through the sodium fluoride layer (downflow type).
8. Insufficient water supply flow rate (stoppage or valve closing, malfunctioning level float).

7. CALCULATIONS INVOLVING SOLUTIONS

Equation (9) determines the theoretical feed rate of various fluoride feed solutions to obtain a desired level of fluoride in a water supply system. It is important to note that accurate values for weights or volumes of materials used are necessary for accurate calculations. Additionally, the use of appropriate units (which can be cancelled arithmetically) will produce a calculated result in the desired units and verify the proper insertion of figures into the equation. Case in point, all flow rate ($R1$ and $R2$) units must be the same (gal/min) and all concentration levels ($C1$ and $C2$) must be the same (ppm or mg/L). Without consistency of units, calculation errors will result. Typical calculations are presented below.

7.1. Example 1

During the winter months, a water treatment plant produced 350,000 gal of water in one day. The plant operator prepares a sodium fluoride solution by dissolving 9 lb of 98% NaF in 50 gal of water. The solution tank is mounted on a scale. After one day of operation, the scale indicates that 300 lb of solution was fed. What is the theoretical fluoride level in the treated water?

Solution

$$R1 \times C1 = R2 \times C2$$
$$C1 = \frac{R2 \times C2}{R1}$$

Because the feed rate ($R2$) is in lb/d and the concentration of the feed solution is ppm, the flow rate ($R1$) of the water being treated must be lb/d and the concentration of fluoride ($C1$) in the treated water will be in ppm. Table 8 indicates that when 9 lb of 98% pure NaF is dissolved into 50 gal of water, the fluoride–water solution will have a fluoride concentration of 9300 ppm:

$$C1 = \frac{(300\ \text{lb/d})\,(9300\ \text{ppm})}{(350{,}000\ \text{gal/d})\,(8.34\ \text{lb/gal})} = 0.96\ \text{ppm}$$

7.2. Example 2

If 350,000 gal of water are pumped, and 150 lb of a hydrofluosilicic acid solution containing 25% acid diluted at the rate of 1 gal acid to 9 gal of water are fed, what is the theoretical fluoride level? Note that the only 79% fluorine is available in hydrofluosilicic acid.

Solution

$$R1 \times C1 = R2 \times C2$$
$$C1 = \frac{R2 \times C2}{R1}$$

With $R2$ being defined in pounds, then $R1$ must be defined in pounds. Because we want know what is the level of fluoride ($C2$) in water in ppm, then the concentration in the solution feed ($C1$) will be converted to ppm.

$$C2 = \frac{\%\text{ of fluosilicic acid}}{100}\left(\frac{\text{gallons of fluosilicic acid}}{(\text{gallons of fluosilicic acid} + \text{gallons of dilution water})}\right) \times \left(\frac{\%\text{ available F}}{100}\right)$$

$$C2 = \frac{25\%}{100}\left(\frac{1\text{ gallon}}{1\text{ gallon } + 9\text{ gallons}}\right)\left(\frac{79\%\text{ F}}{100}\right) = 0.25(0.1)(0.79) = 0.01975$$

$$C2 = 0.01975(100\%)\left(\frac{10{,}000\text{ ppm}}{\%}\right) = 19{,}750\text{ ppm}$$

$$C1 = \frac{(150\text{ lb})(19750)}{(350{,}000\text{ gal})(8.34\text{ lb/gal})} = 1.01\text{ ppm}$$

7.3. Example 3

In a saturator installation, after each of day of operation total water usage was 16 gal (42 mL/min) as indicated by the water supply meter. The flow meter for the water being treated with sodium fluoride measured 300,000 gal daily. The analysis provided by the manufacturer indicates that the product contains 98.2% of sodium fluoride and the solubility is 4.0 % at 60°F. What is the calculated fluoride concentration?

Solution

$$\text{MW Na} = 23 \text{ and MW F} = 19$$

Fractional part of fluorine in NaF is

$$\text{Fractional part fluorine} = \frac{19}{23+19} = 0.45$$

Because we want the fluoride concentration ($C1$) in the water in ppm, then concentration of fluoride in the solution ($C2$) will be determined in ppm.

$$C2 = \left(4\%\frac{10{,}000\text{ ppm}}{\%}\right)(0.98)(0.45) = 17{,}640\text{ ppm}$$

$C1$ is determined as follows:

$$C1 = \left[\frac{\text{gallons of water supplied to the saturator }(R2)}{\text{gallons of water pumped }(R1)}\right] \times [\text{ppm F of solution concentration }(C2)]$$

$$C1 = \left[\frac{16\text{ gal}}{300{,}000\text{ gal}}\right][17{,}640\text{ ppm F}]$$

$$C1 = 0.94\text{ ppm}$$

Examination of Table 9 indicates that the feed rate of 42 mL/min is well within the maximum feed rate of 400 mL/min for a downflow saturator. Since an upflow saturator eliminates gravel beds, their capacities are equal to or greater than those of downflow saturators.

Therefore, an upflow saturator could also be utilized in this application. If there is an appreciable natural fluoride level in the untreated water, that amount should be added to the calculated level based on fluoride added. Similarly, when calculating feed rates, the natural fluoride concentration should be subtracted from the desired level in order to determine the quantity to be added.

7.4. Example 4

A small community in the Midwestern US wants to fluoridate their potable water system. The community has a population of approximately 1700 and serves a large rural school with an equivalent school population of 2667. The community has two wells that are located 2 miles apart and are automatically controlled with pressure switches. Each well has a well house that contains bleach, polyphosphate, and soda ash storage and feed systems. Average daily production from both wells is 0.210 MGD. The water has natural fluoride level of 0.13 mg/L. The optimal fluoride level for this community system is 0.8 mg/L. Determine: (a) the feed rate and annual amount of sodium fluoride; and (b) the feed rate and annual amount of fluorosilicic acid solution. (c) Provide the advantages and disadvantage of each chemical feed system.

Solution

(a) Sodium fluoride (98% pure) feed rate

Concentration of fluoride required = 0.8 mg/L – 0.15 mg/L = 0.65 mg/L

$$\text{fluorine concentration in NaF} = \frac{\text{atomic weight of fluorine}}{\text{atomic weight of NaF}}$$

$$\text{fluorine concentration in NaF} = \frac{19}{42} = 0.45$$

Fluoride concentration in NaF chemical feed rate

$$= \frac{(\text{fluorine concentration required, mg/L})(\text{average water flow rate, MGD})(8.34)}{(\text{fluorine concentration})(\text{chemical purity})}$$

$$\text{NaF feed rate} = \frac{(0.65\ \text{mg/L})(0.21\ \text{MGD})(8.34)}{(0.45)(0.98)} = 2.58\ \text{lb/d}$$

$$\text{Annual amount of NaF} = (2.58\ \text{lb/d})(365\ \text{d/yr}) = 941.7\ \text{lb/yr}$$

(b) Fluorosilicic acid (23%) solution rate

$$\text{fluorine concentration in } H_2SiF_6 = \frac{\text{atomic weight of fluorine}}{\text{atomic weight of NaF}}$$

$$\text{fluorine concentration in } H_2SiF_6 = \frac{114}{144.1} = 0.79$$

$$H_2SiF_6 \text{ feed rate} = \frac{(0.65\ \text{mg/L})(0.21\ \text{MGD})(8.34)}{(0.79)(0.23)} = 6.27\ \text{lb/d}$$

$$\text{Annual amount of } H_2SiF_6 = (6.27\ \text{lb/d})(365\ \text{d/yr}) = 2288.6\ \text{lb/yr}$$

(c) Approximately 2.4 times more fluorosilicic acid (hydrofluorosilicic acid) is required than sodium fluoride. Owing the corrosiveness of the fluorosilicic acid, specialized equipment is necessary to handle and deliver this chemical. When comparing both chemicals, the chemical cost and capital cost for the equipment must be considered.

Additionally, fluorosilicic acid's extreme corrosiveness presents a high health risk to water treatment plant personnel.

8. DEFLUORIDATION

Although moderate amounts of fluoride are beneficial in the prevention of dental caries, excessive concentrations of fluoride cause permanent mottling of tooth enamel and, in severe instances, pitting of the enamel and loss of teeth. Water defluoridation is the lowering of the naturally occurring fluoride level in drinking water to prevent these dental effects. Defluoridation can be accomplished by blending water with a high level of fluoride with water with very lower level of fluoride or by percolating the water with high levels of fluoride through granular beds of activated alumina, bone meal, bone char, or tri-calcium phosphate or using coagulation and precipitation.

In the case of activated alumina beds, the optimal removal of fluoride occurs in the pH range from 5 to 8. The activated alumina beds can be regenerated by treatment with a caustic soda (NaOH) solution when they become saturated with fluoride and the excess caustic soda is removed by rinsing and neutralization with an acid (H_2SO_4 or HCl).

Mixed-bed demineralizers can also be used to reduce the fluoride concentration. A mixed-bed demineralizer will remove other minerals along with the fluoride. Additional methods of fluoride removal include coagulation with alum and precipitation with lime. Alum coagulation requires high alum dosage in the range of 250 mg/L or greater at pH ranging from 5.5 to 7.0 lower fluoride level 1 to 2 mg/L. A lime softening process can also be used to lower levels of fluoride. In this process, the fluoride is removed from the water by forming an insoluble precipitate and co-precipitator magnesium hydroxide. Precipitation of substantial concentrations of aluminum or magnesium is required for fluoride lowering to be effective (18).

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Ultraviolet Radiation for Disinfection

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CONTENTS

1. INTRODUCTION

1.1. Historical Background and Technology Development

Natural water, such as surface water and groundwater, exists as an open system. Natural and/or synthesized organic substances, oxygen, nutrients are thus able to enter various waters. Owing to the presence of these key elements, microbial growth eventually becomes possible. Different microorganisms can therefore exist and grow in the waters. Similarly, domestic and industrial wastewater and treated wastewater contain significantly high amounts of microorganisms.

Because most of the microorganisms in the waters are pathogenic, they must be disinfected before use. The concept of disinfection is different from that of sterilization. Disinfection refers to killing of most of pathogens, while sterilization addresses a complete killing of pathogens. Thus, the cost of disinfection is lower than sterilization. There are several measures for disinfection. As long as pathogens can be removed or killed, the process can then be considered as a disinfection process. For example, gravity filtration can be one of processes because it can remove the pathogenic microorganisms.

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However, to effectively control the waterborne diseases, a combination of various chemical and physical processes is often adopted in typical water and wastewater disinfection processes.

An ideal disinfection technology should be cost-effective without significantly negative environmental impacts such as producing disinfection by-products (DBPs) in significantly high levels. Disinfection discussed in this chapter refers to the killing, removal, and inactivation of pathogens in water, wastewater, and air. The commonly used disinfection alternatives include chemical methods (e.g., chlorine, chlorine dioxide, hydrogen peroxide, and ozone), physical methods (e.g., heat and sunlight), mechanical methods (e.g., microfiltration), and radiation methods (e.g., ultraviolet light and gamma rays). Nevertheless, none of these methods are universally applicable.

The germicidal properties of ultraviolet (UV) radiation have been recognized for more than 100 yr. UV radiation, in cost-effective doses, effectively inactivates common pathogens such as *Cryptosporidium* and *Giardia*; UV treatment does not create significant levels of DBPs. These factors have led to UV disinfection gaining increased acceptance and use as an attractive cost-effective control for pathogens in many applications, such as ground and surface waters. The UV radiation currently finds its widest application for small water systems for homes, commercial establishments, aboard ship, and in some industrial water-purification systems. It has been used for wastewater disinfection for the past 20 yr, which have recently triggered a series of serious studies. UV radiation also sees its increasing applications in air disinfection in buildings and industrial manufacturing processes. This technology is simple, reliable, and economical and is employed either as a stand alone solution or in combination with other methods such as membrane filtration and carbon adsorption.

UV radiation virtually exists everywhere in our life. It is part of the electromagnetic spectrum with a wavelength ranging from 10 to 400 nm. The sun is an excellent provider of the UV light. People like sunshine; however, too much exposure to sunlight could be dangerous. Overexposure to the sun's UV radiation can cause immediate effects such as sunburn and long-term problems such as skin cancer and cataracts. Developed by the US National Weather Service (US NWS) and the US Environmental Protection Agency (US EPA), the UV Index with a scale of 0 to 10+ provides a daily prediction of UV intensity. It takes account of wavelengths of 290–400 nm, latitude, elevation, and clouds. The Index of 0–2 represents minimal radiation; while that of 10+ indicates very high radiation. With the UV Index, outdoor activities can be properly planned to prevent overexposure to the sun's rays. Clouds, time, seasonal weather variation, and other local conditions affect the amount of UV radiation reaching the ground in different areas. With the rapid development of industrialization over the last 50 yr, UV radiation has become worse. Because the ozone layer shields the Earth from harmful UV radiation, ozone depletion as well as weather variations cause different amounts of UV radiation to reach the Earth at any given time.

UV radiation has been used widely in water and air disinfection, as well as organic pollutant oxidation. The germicidal properties of UV radiation were first discovered in 1801. In 1877, the bactericidal effect of sun light (containing UV light with a wavelength more than 290 nm) was reported by Downes and Blunt. In 1901, the first mercury vapor lamp was commercialized as a method of UV generation (1). Nine years later, the first large industrial application for drinking water disinfection with a capacity of 200 m^3/d appeared in Marseille, France (2). The disinfection system was unreliable and also complicated to use because of the poor state of the UV technology at that time. Compared with low-cost chlorine and its family, the UV radiation was considered as less cost-effective at that time. In addition, people did not realize the serious health impact from the DBPs from the chlorine disinfection. As a result, the UV technology in terms of its development, its reorganization, and its use had lagged behind for several decades after it was first introduced.

Since 1950s, the interest in the UV technology had been renewed because of advances in the technology, the DBPs were better understood, and there were growing taste and odor concerns with using chlorine (1). Presently, almost all the full-scale UV installations for public water supplies are in Europe. Its application includes inactivation of *Escherichia coli* and *Aeromonas* bacteria in the treatment of groundwater, reduction of colony counts after activated carbon filtration, and replacement for post-chlorination. Today, there are over 2000 UV disinfection systems treating drinking water in Europe (3,4). Switzerland, Austria, and Norway have more than 500, 600, and 400 UV disinfection installations with water treatment capacity of 2.5, 3.2, and 6.3 million gallons per day (MGD), respectively. On the other hand, its application in the United States has been limited to small point of entry or point of use systems for treatment of groundwater supplies. Presently, there are more than 2000 installations where UV radiation is used to disinfect primary, second, and filtered tertiary effluents. This is mainly due to three reasons (1–3):

1. UV disinfectant is not able to stay in the water for a long period, which acts as a prevention for the pathogens in the distribution network system.
2. It is not effective for disinfection of *G. lamblia* cysts and *Cryptosporidium parvum* oocysts.
3. The groundwater systems have not been required to provide primary disinfection for bacteria and viruses.

UV can cause permanent inactivation of virus, bacteria, spores, fungi and other pathogens. UV irradiation disinfection requires no additional chemicals. Unlike chlorination disinfection, it does not produce odor; it is usually deemed as the best choice with very low or no DBPs and no residual toxicity. In addition, it is able to kill some chlorine-resistant pathogens such as *Cryptosporidium* and *Giardia.* Compared with other disinfection alternatives, UV is a cost-effective, clean, and simple approach. UV disinfection system does not require the transportation, storage, and handling of regulated chemicals such as chlorine.

UV technology has been widely used in disinfection in various areas, such as air emission sanitation control and disinfection of drinking water, groundwater, industrial process water, and wastewater. UV disinfection has its limitations. One disadvantage is that it is not suitable for high turbidity and high absorbance water. Unlike chlorine, UV does not provide residual dosage when used in disinfection because the UV light is a physical means and cannot stay in water and air. When the UV is used as the primary disinfection method, it is often supplemented by other chemical disinfectants.

UV light can be absorbed by most organics. It contains higher energy, which can break down complex organic compounds. As an alternative pollutant treatment approach, UV oxidation sees its wide applications in many areas, such as treatment of contaminated groundwater and wastewater. Detailed description of UV oxidation is given in Chapter 14.

In this chapter, the mechanisms of UV disinfection will be presented. A mathematical description of microorganism killing by UV radiation is given. Design approaches of disinfection systems are demonstrated. Case studies will also be presented at the end of this chapter.

1.2. UV Radiation Process Description

UV radiation disinfection uses a special lamp to transfer electromagnetic energy to the target organism cells. The most efficient and widely used device is the mercury arc lamp. It is popular because approx 85% of its energy output is of the 253.7 nm wavelength, within the optimum germicidal range of 250–270 nm. The lamps are long thin tubes. When an electric arc is struck through mercury vapor, the energy discharge generated by the mercury excitation results in the emission of UV radiation. This radiation then destroys the cell's genetic material and the cell dies.

The effectiveness of radiation is a direct function of the energy dose absorbed by the organism, measured as the product of the lamp's intensity and the time of exposure. Intensity is the rate at which photons are delivered to the target. The intensity in a reactor is governed not only by the power of the lamp, but also by the placement of the lamps relative to the water, and by the presence of energy sinks that consume UV radiation. Water with suspended solids, color, turbidity, and soluble organic matter can react with or absorb the UV radiation, reducing the disinfection performance. Therefore, water with high concentrations of these substances may receive inadequate disinfection.

The radiation dose absorbed by the water is the water's UV demand, which is analogous to chlorine demand and is quantified as the absorption of UV energy (at a wavelength of 253.7 nm) in a given depth of water. The measurement is most commonly expressed by the UV absorbance coefficient alpha:

$$\text{alpha} = 2.3 \text{ absorbance units (a.u.)/cm}$$

In addition to intensity and UV demand of the water, the exposure time also affects the energy dosage that the target organisms absorb. Exposure time is controlled by the residence time of the water in the reactor. Continually maintaining the required residence time is not always possible, but the system design should maximize plug-flow operation.

If the energy dosage is not sufficient to destroy the target organisms' DNA macromolecules, disinfection is not effective. Photoenzymatic repair occurs if the genetic material is only damaged during irradiation. This repair mechanism, called photoreactivation, occurs with exposure to light from the sun or most incandescent and fluorescent lights (at wavelengths between 300 and 500 nm). Photoreactivation does not occur with all bacterial species and is therefore difficult to predict.

To prevent photoreactivation, the rule of thumb is to increase the dosage necessary to meet a required reduction in organism numbers. For example, if the disinfection criteria require a 3-log reduction of microorganism concentrations, the UV radiation system should be designed to provide a 4-log reduction.

In this chapter, UV radiation for both disinfection and oxidation of organic contaminants is addressed. In the UV disinfection, common pathogens in the environment and

UV germicide mechanisms are introduced. Basic principles of UV disinfection system design, installation, and operation considerations are presented. The concern about UV disinfection by-products is also discussed. In addition, the mechanisms of UV oxidation are addressed. Its applications on organic pollutants decomposing as an emerging water and wastewater treatment technology are discussed.

2. PATHOGENS IN THE ENVIRONMENT

Pathogens are usually termed as a group of microorganisms that can cause various human diseases. Four categories of pathogens are usually of concern in water and wastewater pollution, namely, bacteria, viruses, parasites, and fungi. When the pathogens are contacted or ingested, one may catch different diseases such as cholera, typhoid, and hepatitis. These diseases can be greatly harmful to our health. The pathogen contaminants in water and wastewater come from many different sources, such as human or animal fecal waste, discarded food waste from industrial processing, and waste from hospitals. When these wastes are discharged into surface water, groundwater, or sewer systems, pathogens are brought into these waterbodies. Thus, the removal of these pathogens to a safe level is the main task of disinfection in water and wastewater.

In addition to the waters, pathogens can also be found in air emissions in many locations, such as long operated ventilation and air-condition systems of hospitals, shopping centers, offices, and residential areas (5,6). The severe acute respiratory syndrome (SARS), the most severe epidemic in 2003 in Asia, is suspected to spread out through airborne particles or droplets (7,8).

Viruses are usually not considered as "living" entities because they are not able to replace their parts or carry out metabolism on their own. They are very small in size, ranging from tens to hundreds of nanometers. They can be replicated only when they are in association with a living cell (host). The host translates the genetic information present in the virus, which lead to its replication. The consequence of this replication to the living host is either disease or death. The viruses have very simple genetic elements that consist of nucleic acid surrounded by protein and other substances (3,9).

Untreated wastewaters can contain virus with an amount of 10^3–10^4 plaque-forming units (PFU) per 100 mL. Generally, viruses are the most hazardous among the pathogens. They exist widely in human and animal fecal waste and can cause different diseases. For example, they can cause gastrointestinal illness such as diarrhea, vomiting, and cramps. Hepatitis A virus present in contaminated seafood such as oysters can lead to infectious hepatitis and liver inflammation. Two major outbreak of the infectious hepatitis that infected more than 20,000 people occurred in Delhi, India and Shanghai, China, in 1950s and 1980s, respectively. The former case was caused by the sewage discharged to the river whose water was used as a source for a watertreatment plant; while the later was due to the contaminated oysters, which concentrated virus particles in the water contaminated with human feces.

Viruses can attach onto particles in water and survive under extreme conditions. For example, enteric viruses tolerate acid and hepatitis B virus can survive in hot water with a temperature of over 100°C for more than 10 min. The regulations of the US EPA prescribe that in drinking water disinfection, more than 99.99% virus must be removed/inactivated according to maximum contaminant level (MCL) and the maximum contaminant level goal (MCLG) is no virus detected in water.

Bacteria are single-cell organisms with a size ranging from 1 to 10 μm. Unlike viruses, they can be replicated without a host. Bacteria are ubiquitous; the same species can generally be found in every part of the world. They are able to survive in water, soil, and air. Water movement as well as air current helps them travel throughout the world. Numerous kinds of bacteria exist in the environment. Bacteria are extremely important to the water environment, as they are able to transform a great variety of organic wastes into harmless minerals. Activated sludge processes for municipal wastewater treatment is an excellent example. It is hard to imagine our Earth if these processes were not invented and applied.

The functions of bacteria are not all beneficial to humans. Their great importance to human health is without question, as they cause various diseases and death. For example, *Campylobacter jejuni* can cause gastroenteritis, diarrhea, fever, and abdominal pain. *Legionella pneumophilia* can lead to legionellosis, fever, headache, and respiratory illness.

In the US EPA's regulations, the restriction of total coliforms, heterotrophic plate count (HPC), and legionella are defined for drinking water (3,4,10). The number of total coliforms should be zero in at least 95% of the samples collected in 1 mo. The HPC should not exceed 500 bacterial colonies per milliliter. There is no limit on legionella because it is not able to survive with the effective removal of virus and *Giardia* (parasite).

Parasites include protozoa and helminths. Protozoa means "first animal" and refers to simple eukaryotic organisms composed of a single cell such as amebae. The size of protozoa ranges from several to tens of micrometers. Their reproduction can be through simple cell division, such as the ameboflagellates, or sexual involving the fusion of gametes in part of the life cycle, such as the apicomplexa. Some protozoa can form a protective cyst stage capable of withstanding harsh environmental conditions. Some kinds of protozoa, such as *Cryptosporidium* and *G. lamblia*, can cause gastrointestinal diseases. These protozoa come from human fecal or animal waste and are transmitted by cysts. In the US EPA's regulations, at least 99% removal must be attained for cryptosporidium and 99.99% removal for *G. lamblia*.

In contrast to the protozoa, helminths are multicellular with complex reproductive systems and life cycles involving intermediate hosts for the development of larval stages and a definitive host for the adult form. Adults may be dioecious with separate sexes or hermaphroditic. Helminths are flatworms and flukes such as nematodes and tapeworms. They are common enteric pathogens and can be transferred by directly eating or drinking parasite eggs, which may exist in polluted meat or water.

Like bacteria, fungi are the primary decomposer responsible for dead organic matters. Their metabolic properties are simple and unique: almost all of them are organolithotrophic and none are phototrophic. There are more than 50,000 different species of fungi in the world. Typical names are yeast, mushrooms, molds, mildews, and puffballs. Fungi are composed of masses of filaments. They can be classified into three major groups: *Eumycota, Mycophycomycota,* and *Myxophycomycota*. They are comparatively less abundant in wastewater; however, they can produce a large number of colonies at weaker acid conditions (pH 5–7).

3. DISINFECTION MECHANISMS

Disinfection of pathogens by UV radiation differs from that by chemical disinfectants such as chlorine (Cl_2), calcium hypochlorite [$Ca(OCl)_2$], sodium hypochlorite ($NaOCl$)

and ozone (O_3). Chemical approaches inactivate microorganisms (germs) by destroying or damaging the cellular structures, thereby interfering with the metabolism, the synthesis, and the growth. In UV radiation, a series of photochemical reactions is initiated, which can effectively damage and/or alter deoxyribonucleic acid (DNA) or ribonucleic acid (RNA) molecules in the cell wall and/or protoplasm of the pathogens. The damage to their nucleic acid is so serious that they can no longer reproduce. The cell division and the subsequent multiplication can no longer occur. As a result, the pathogens are inactivated. In this section, we will look at nucleic acid (DNA and RNA) structure, the damage leading to microbial inactivation, the ability of pathogens to repair the damage, and factors that affect inactivation (3,9).

3.1. *Chemistry of DNA and RNA*

In order to understand the mechanisms of pathogen disinfection by UV light, it is necessary first to be familiar with the structure of DNA and RNA, as they play key roles in two important aspects of reproduction of microorganisms: protein synthesis and the replication of chromosomes.

DNA and RNA are both nucleic acids; they are fundamental building blocks of life and are responsible for reproduction and for defining the nature of life (3,9). They are made up of subunits, called nucleotides. Nucleotides are made up of three different chemical groups: a phosphate group, a five-carbon sugar, and an organic base. The sugar molecular is always ribose in RNA and deoxyribose in DNA. Both DNA and RNA are long polymers comprised of combinations of four organic bases (called nucleotides in some textbooks). In DNA, the organic bases are adenine (A), guanine (G), cytosine (C) and thymine (T), while in RNA, thymine is replaced by uracil (U). A and G are purine bases with a double-ring structure, while C, T, and U are pyrimidine bases with a single-ring structure. Both purines and pyrimidines contain nitrogen and carbon atoms (9).

The subunits of nucleotides are linked together to form a long polymer chain in nucleic acids. The linkages are formed between the phosphate group of one subunit and the sugar group of the next. This matrix forms a sugar–phosphate backbone to the molecule of nucleic acid.

RNA is normally composed of a single strand of nucleic acid. It occurs in all cells in the form of messenger RNA (mRNA), transfer RNA (tRNA), and ribosomal RNA (rRNA). Their major functions are the synthesis of proteins. mRNA has 75–3000 subunits (nucleotides); it is not folded in any special way. It is produced in nucleus by DNA. It carries coded instructions from DNA in the nucleus to ribosomes in the cytoplasm where it initiates the process of protein synthesis. Compared to mRNA, tRNA is much smaller; it has only 75–90 nucleotides. In some 20 different types of tRNA, each corresponds to one of the 20 amino acids and forms a clover-leaf shape due to DNA. tRNA transports acids from "pool" to mRNA in ribosomes; it assembles amino acids in a sequence specified by the original DNA instruction. rRNA, on the other hand, is a very large molecule with thousands of nucleotides; it can fold back on itself to form regions of base-pairing; it is the major component of ribosomes. rRNA is made in the nucleus by DNA; its main function is to correct functioning of ribosomes during protein synthesis.

The structure of DNA is much more complex than that of RNA. It is enormously long and composed of millions of nucleotides. Unlike RNA, DNA is always double-stranded and consists of two parallel strands of nucleic acid whose sugar–phosphate backbones run in opposite directions. These two strands are held together by hydrogen-bonding between pairs of organic bases. This base paring can only occur between certain bases, A and T (with two hydrogen bonds) and G and C (with three hydrogen bonds). In DNA; all the nucleotides are held together by base-paring and the resultant three-dimensional structure is very stable. The two strands of nucleic acid are twisted to form a double helix.

The gully complementary nature of the base pairs in DNA means that each strand can act as a blueprint for the other. Assisted by the enzyme DNA polymerase, the DNA molecule can be "unzipped" and replicate itself exactly by the assemblage of new nucleotides from the cell's pool. This process is known as semiconservative replication because the two identical DNA molecules produced consist of one original and one new strand of DNA. DNA is able to replicate itself, which is essential to the process of cell division. As a result, an exact copy of the cell's genetic instructions can be handed on to the next generation of cells.

The long molecules of DNA occur within the nucleus of individual cells. It is thought that each DNA molecule corresponds to a single chromosome. There are a characteristic number of chromosomes for individual species. These carry the hereditary information of the individual on a series of shorter sections of the nucleic acid known as genes. The nucleic acid within the nucleus of most cells, such as bacteria and protozoa, is composed of double-stranded DNA. DNA contains the information necessary for the synthesis of ribosomal, transfer, and messenger RNA, which are responsible for synthesis of enzymes, which drive metabolic processes within the cell. The genetic material of viruses may either be DNA or RNA and can be single- or double-stranded (3).

3.2. Physical Properties of UV Light

UV light is part of electromagnetic radiation, the relationship between frequency, wavelength, and light speed can be expressed as:

$$C = \nu \times \lambda \tag{1}$$

where ν = frequency, Hz, λ = wavelength, m, and C = light speed, 3.0×10^{10} cm/s.

The photon energy E is given as

$$E = h \times \nu = h \times C/\lambda \tag{2}$$

where λ = wavelength, m, h = Planck's constant, 6.626176×10^{-34} J·s, and E = photon energy, J. Equation (2) can be simplified to

$$E = 1.9865 \times 10^{-15}/\lambda \tag{3}$$

As one can see from the above equation, the photon energy is higher as the wavelength is decreased. In the electromagnetic spectrum, UV lies between the visible light and the X-rays with the wavelength range from 100 to 400 nm as shown in Fig. 1 (3,10). This can be subdivided into vacuum UV (100–200 nm); UV-C (200–280 nm); UV-B (280–315 nm), and UV-A (315–400 nm). The most important range of UV in water disinfection is UV-C with a wavelength of 220–280 nm. Bacteria have the highest absorbance of light from 255 to 265 nm. Thus, the practical germicidal UV must be in a range of 200–300 nm. The low-pressure (LP) mercury-lamp (radiation wavelength at

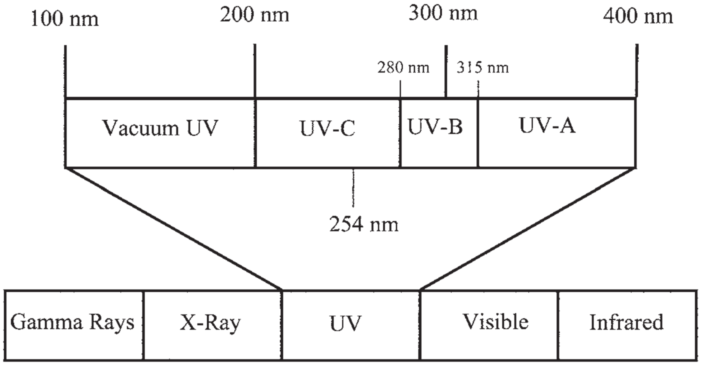

Fig. 1. Electromagnetic spectrum.

254 nm), low-pressure high-output (LPHO) mercury lamp, and medium-pressure (MP) mercury lamp are the most frequently used in water disinfection owing to their high radiation absorbance by pathogens.

Emission of UV light is a generally regarded as physical process. UV light is generated when the atoms return from a high-energy state to a lower-energy state. The energy change in this process is described by

$$E_1 - E_0 = h\nu \tag{4}$$

where E_1 = higher energy status, J and E_0 = lower energy status, J. According to the Stefan–Boltzman law, total radiation power (P) depends on the temperature of radiation source matter (3,11):

$$P = s \times T^4 \tag{5}$$

where T = temperature, K, P = total energy emitted by source matter, W·cm^{-2}, and S = Stefan–Boltzmann constant, 5.6703×10^{-12} W·cm^{-2}·K^{-4}.

3.3. Inactivation of Pathogens

It has been recognized that the inactivation of microorganisms by UV radiation is mainly due to the UV-induced damage of their DNA and/or RNA, which leads to a series of changes in the biological growth of the microorganism. Light must first be absorbed by reactants before chemical reaction(s) can be initiated. UV light can be absorbed by DNA and RNA, or their subunits, nucleotides, in a wavelength ranging from 200 to 300 nm; the absorption can thus enable the photoinduced biological damage of DNA and RNA. The absorption varies as the wavelength is changed as demonstrated in Fig. 2. It decreases from the wavelength of 220 nm to that of 230 nm; it then increases and reaches an absorption peak at the wavelength of near 260 nm. Once it reaches its peak, it decreases to its local minimum at the wavelength of near 300 nm.

As discussed previously, DNA and RNA have their basic elements of adenine, guanine, cytosine, thymine, and uracil. They can strongly absorb UV light; however, the damage with pyrimidines (C, T and U) is more serious. Absorbed UV light induces several types of damage and alteration in the DNA and RNA with varying levels of effectiveness dependent on UV dose (12).

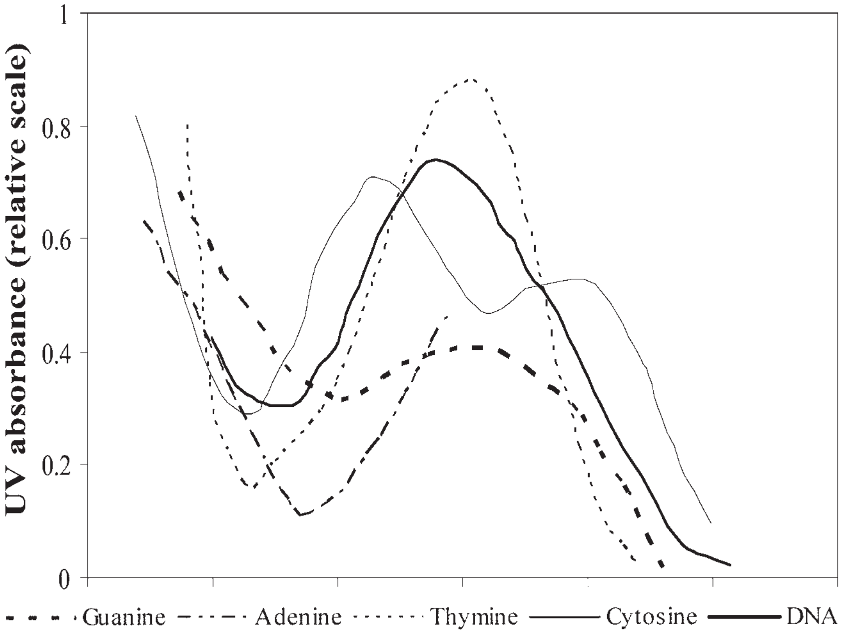

Fig. 2. Absorbance spectra for DNA and its basic elements.

When the UV dose is several orders higher than that used in the conventional UV disinfection, the DNA and RNA can be broken. At the same time, the DNA–DNA cross-linkage is formed between two different strands of DNA. For some germs, protein–DNA cross-linkage can be established between a protein and a DNA strand, which eventually changes the DNA structure.

The major UV damage is due to the pyrimidine–pyrimidine photoproducts. Pyrimidine dimers are formed by the formation of covalent bonds between two pyrimidines on the same DNA strand. They are the most common damage caused by the UV disinfection. While it is possible for T–T, C–C, and T–C dimers to form within DNA, T–T dimers are the most common. The pathogens with DNA rich in thymine tend to be more sensitive to disinfection. In RNA, U–U and C–C dimers are formed because thymine is not present. All these can destroy the cell's reproductive ability. Dimers cause faults in the transcription of information from DNA to RNA, leading to the disruption of cell metabolism and other biological functions. The damage to DNA and/or RNA, however, does not always prevent the cell from undergoing metabolism and other cell functions as discussed in the next section. There are some mechanisms present to cause repair the damage to the pathogens; as a result, the pathogens can be reactivated. For example, if the UV dosing is insufficient, the germs may react through a photoenzymatic repair action. Thus, the UV dosing must be high enough to completely damage the internal structure of the germs. However, if the UV dosage is too high, the temperature of the water is increased, which will cause unnecessary heat lost. In addition, the by-products due to the chemical oxidation reactions can be produced by high-dosage UV light.

In addition to the alteration in the DNA or RNA structures, photochemical oxidation is another mechanism that must be taken into consideration in the disinfection process.

When the UV light is in contact with the water, a series of powerful oxidizing radicals such as hydroxyl radicals can be formed, which act as good disinfection agents due to their strong oxidation ability. Besides, there may be hydrogen peroxide formed during the aqueous reactions, which can kill the germs.

The disinfection efficiency is dependent on the UV dosage as well as the physical and chemical conditions of the water and air to be disinfected. It is found that an UV irradiation dose of 8–14 mJ/cm^2 is required to meet the 3-log inactivation of *Cryptosporidium* spp. oocysts (i.e., 99.9% killing) and 12–20 mJ/cm^2 is necessary to achieve at least 3-log inactivation of *Giardia* spp. cysts in drinking water disinfection (13). The UV can also be used in seawater disinfection. A filter system combined with a series of 0.45-µm filters can reduce by as much as 60% of the bacteria in raw seawater. An UV dose 63.6 mJ/cm^2 is enough to achieve 4-log *Vibrio* and *Pseudomonas* bacteria reduction (14).

3.4. Reactivation of Pathogens

Unlike the chlorine and its compounds for water disinfection, UV is not able to stay for a long period. Once the radiation is stopped, the water has very minimum disinfection effect. Thus, the inactivated germs may be reactivated at certain conditions. The reactivation process is called "repair." The pathogens exposed to the UV radiation can still retain metabolic functions; some of them are able to repair the damage and regain infectivity. Photoreactivation (or called as photorepair) and dark repair are two main mechanisms for the reactivation of UV light-induced damaged germs.

Photoreactivation. The pathogens are inactivated when exposed in an UV light with a wavelength ranging from 200 to 300 nm; however, when the enzyme either from the pathogens or from their host germs is exposed to light with a wavelength of 310–490 nm, it will receive sufficient energy that can split the paired pyrimidine dimers. Because the cleaving of pyrimidine dimers is initiated by light, the reactivation process of the germs is therefore termed as photoreactivation. It depends on microorganism types, species, strains of a given species, and presence of host cells. The working conditions such as degree of inactivation, time between exposure to UV light and photoreactivating light, and the nutrient state of the microorganism are also important factors.

The photorepair of inactivated germs includes the following two steps. First, the pyrimidine dimer combines with a photoreactivating enzyme (PRE) to form PRE–dimer complex. Under a favorable light wavelength range from 310 to 490 nm, the complex releases PRE and the repaired monomerized dimer. Second, the PRE is free again to combine with another pyrimidine dimer. It has to be pointed out that this photorepair process can be significantly inhibited by increasing the UV dosage.

The effect of photoreactivation can be quite important in terms of operational cost (i.e., UV dosage) and disinfection efficiency. Knudson reported that the UV dose was 10 mJ/cm^2 for a 3-log inactivated *E. coli* in the absence of photorepair; however, the dose significantly increased to 25 mJ/cm^2 in the presence of photorepair (15). The photoreactivation increased the UV dose necessary to achieve 3-log inactivation of seven *Legionella* species between 1.1- and 6.3-fold. However, certain germs such as *C. parvum* cannot be reactivated through the photorepair mechanism (16). RNA viruses lack the ability to photorepair in a host cell.

Dark repair. Unlike the previously discussed photorepair, dark repair can reactivate the inactivated pathogens without a reactivating light. This process can occur in the presence or absence of light. It does not require a dark condition. In contrast to photoreactivation, dark repair experiences much more complex pathways and does not reverse DNA damage but replaces the damaged DNA with new and undamaged nucleotides. Excision repair is the most common in the dark repair and undergoes the following two major categories of pathways: base excision repair (BER) and nucleotide excision repair (NER). Recombinational repair and inducible error prone repair also contribute certain types of repair.

In the BER, the base excision pathway has evolved to protect cells from the deleterious effects of endogenous DNA damage. BER is important for withstanding lesions produced by ionizing radiation and strong alkylating agents, which are similar to those induced by endogenous factors. In NER removes a wide range of DNA distorting lesions such as cyclobutane pyrimidine dimers (CPDs) and 6–4PPs (photoproducts). It is highly conserved in eukaryotes and present in most organisms. NER uses the product of around 30 genes to remove a damage-containing oligonucleotide from cellular DNA.

Based on the difference in UV sensitivity of repair proficient and deficient bacteria, Jagger discovered that roughly 99% of repair is due to the dark repair (17). Unlike bacteria, viruses do not have the enzymes necessary for dark repair. However, virus can repair in the host cell using the host cell's enzymes (18).

4. MATHEMATICAL DESCRIPTION OF UV DISINFECTION PROCESS

4.1. UV Dose

UV dose is the most important operational parameter in the UV disinfection. It can be calculated by the UV intensity multiplied by the exposure time (3,11,19). If the UV intensity is independent of time, the UV dose can be calculated by the following equation:

$$D = I \times t \tag{6}$$

where D = UV dose, mJ/cm^2 or mW·s/cm^2, I = UV light intensity in the bulk solution, mW/cm^2, and t = exposure time, s. However, if the UV is dependent of time, the UV dose can then be determined by integration of the UV light intensity (I) over the exposure time (t):

$$D = \int_0^t I \times dt \tag{7}$$

The UV intensity measured by a radiometer, however, does not precisely represent the UV intensity received by the target pathogens, because several factors such as turbidity can hinder the transparency of the aqueous. Bolton and Linden developed an equation to calculate the UV light intensity when using low-pressure UV lamp (20). It takes account of the following important factors: (a) water factor, (b) divergence factor, (c) reflection factor, and (d) Petri factor.

Reflection factor. When a beam of UV light passes from the UV lamp to water solution, a small fraction of the beam is reflected off the interface between air and water. Therefore, reflection factor of $(1 - R)$, where R is fraction of light reflected at the surface of suspension based on the Fresnel's Law must be included.

Petri factor. The UV intensity or irradiance may be different over the surface area of the targets (pathogens) to be irradiated. The Petri factor (P_f) is then defined as the ratio of the average of the UV intensity (or incident irradiance) over the area of the Petri dish to the UV intensity (or irradiance) at the center of the dish. It is used to correct the intensity (irradiance) reading at the center of the Petri dish to more accurately reflect the average UV intensity (incident fluence) over the surface area. A well-designed collimated beam apparatus should be able to deliver a Petri factor ranging from 0.9 to 0.95.

Water factor. The water containing pathogens, colors, organic compounds, and suspended solids normally can absorb the UV light. Thus, it is necessary to take account of the light loss (or energy loss) arising from the absorption. The water factor can be determined, which was derived from integrating the Beer–Lambert Law over the sample depth, as follows:

$$\text{Water factor} = \frac{1-10^{-a_{10}\times d}}{a_{10}\times d\times \ln 10} \tag{8}$$

where a_{10} = decadic (base 10) absorption coefficient of the suspension or absorbance for a 1-cm path length, cm^{-1} and d = thickness of water layer or vertical path length of the water in the Petri dish, cm.

Divergence factor. Because there is a distance between the suspension and the UV lamp, the UV light may not be perfectly collimated and diverges. The divergence factor can be determined by the following equation:

$$\text{Divergence factor} = \frac{L}{L+d} \tag{9}$$

where L = distance from the UV lamp to the surface of the cell suspension. Thus, the resulting average intensity of UV light within the suspension can be determined by

$$\begin{aligned} I_{\text{ave}} = I_0 &\times \text{Petri factor} \times \text{reflection factor} \\ &\times \text{water factor} \times \text{divergence factor} \end{aligned} \tag{10}$$

$$I_{\text{ave}} = \frac{I_0 \times P_f \times (1-R) \times (1-10^{-a_{10}\times d})}{a_{10}\times d\times \ln 10} \times \frac{L}{L+d} \tag{11}$$

where I_{ave} = average intensity within the suspension, mW/cm^2 and I_0 = UV intensity measured at the surface of suspension, mW/cm^2. Therefore, the UV dose can be determined by Eq. (12):

$$D = I_{\text{ave}} \times t = \frac{I_0 \times P_f \times (1-R) \times (1-10^{-a_{10}\times d})}{a_{10}\times d\times \ln 10} \times \frac{L}{L+d} \times t \tag{12}$$

If the Petri factor, reflection factor, and divergence factor are considered, Eq. (11) can be further simplified and yield the following equation (11,21):

$$I_{\text{ave}} = I_0 \times \frac{\left(1-10^{-a_{10}\times d}\right)}{a_{10}\times d\times \ln 10} \tag{13}$$

4.2. Effect of UV Dose on Pathogen Inactivation

If the pathogens exist in a disperse form, the UV light can directly reach them and hence a complete disinfection can occur. The disinfection rate can then be described by first-order reaction kinetics, which is also called as Chick–Watson model (11):

$$\frac{dN_t}{dt} = -k_d N_t \tag{14}$$

where N_t = total number (or density) of pathogens at time t, t = time, s, k_d = disinfection rate constant, s^{-1}.

When a batch reactor is used in the disinfection, Eq. (14) can be integrated to

$$N_t = N_0 \times e^{-k_d \times t} \tag{15}$$

where N_0 = total number (or density) of pathogens prior to UV disinfection (i.e., $t = 0$).

Note that k_d depends on operational parameters. The important parameter is the UV intensity (I). Thus, we have,

$$k_d = k \times I \tag{16}$$

where k = UV inactivation rate coefficient, cm^2/mJ.

The log-linear inactivation of pathogens in a batch reactor is determined as

$$N_t = N_0 \times e^{-k \times I \times t} \tag{17}$$

Equations (6) and (17) can be combined, yielding the following equation:

$$N_t = N_0 \times e^{-k \times D} \tag{18}$$

The above equations can be applied to disperse pathogens exposed to UV disinfection. If the pathogens are embedded within particles, the UV light cannot be completely reached and thus the disinfection efficiency can be decreased. The number or density of surviving pathogens (e.g., coliform bacteria) as a function of applied UV dose (D) follows two phases in disinfection of water containing a certain amount of particles (or suspended solids) such as secondary or tertiary biological-treated effluent. The inactivation can be described by first-order kinetics shown in Eq. (17) at low doses ranging from 0 to 30 $mW{\cdot}s/cm^2$ according to a study by Loge and co-workers (22). A tailing region then occurs when the UV doses are further increased. This second phase is characterized by a reduced inactivation rate of pathogens. Figure 3 illustrates these two phases observed in disinfection of a secondary effluent from a biological wastewater treatment. Equation (17), therefore, must be revised with this consideration, which yields to the following equation for the disinfection of particle-associated coliform bacteria:

$$N_t = N_0 \times e^{-k \times D} + \frac{N_0^p}{k \times D}(1 - e^{-k \times D}) \tag{19}$$

where N_0^p = total number (or density) of particles (greater than 10 μm), enumerated prior to UV disinfection (i.e., $t = 0$), which contain at least one coliform bacteria.

As shown in Eq. (19), lower density of particles (N_0^p) present in the bulk liquid medium would lead to higher inactivation of pathogens. In the operation, either size

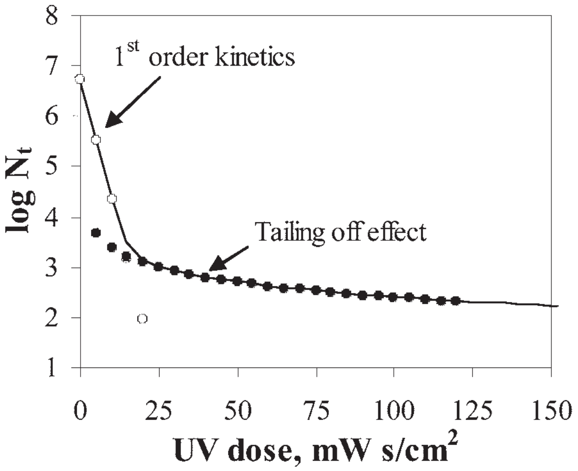

Fig. 3. Typical response of coliform bacteria to UV radiation in the secondary effluent from the biological treatment. Parameters are quoted from Table 1 of Loge et al. (22): N_0 = 5,180,000 MPN/100 mL, k = 0.546 cm^2/mW, and N_p = 13,500 MPN/100 mL.

Table 1
Typical UV-VIS Absorbance of Various Waters

Type of waters	Absorbance (cm^{-1})	Type of waters	Absorbance (cm^{-1})
Primary effluent	0.5–0.8[a]	Suprapure distilled water	10^{-6} [b]
Secondary effluent	0.17–0.5[a,b]	Good quality groundwater	0.005–0.01[b]
Nitrified secondary effluent	0.25–0.45[a]	Good quality distribution water	0.01–0.11[b]
Filtered secondary effluent	0.20–0.40[a]	Carbonate ion (50 mg/L)	4×10^{-6}[b]
Microfiltered secondary effluent	0.158–0.3[a]	Natural humic acids in water	0.07–0.16[b]
Reverse osmosis effluent	0.05–0.2[a]	Groundwater with high concentration humic acids	0.11–0.5[b]

[a] Ref. 11.
[b] Ref. 41.

exclusion, such as a disk filter, or granular medium filter, such as a sand filter, may be adequate at water and wastewater treatment plants for effective disinfection.

Harmful substances may be present in water in either undissolved or dissolved form. Some organic compounds in water can absorb the UV light in a wavelength range of 254–280 nm. Just as turbidity detection is used to measure the total solids content, UV absorption detection at a wavelength of 254 nm can be employed to measure the total content of dissolved organic matter. The typical absorbance values at 254 nm for some important types of waters are listed in Table 1.

The resulting UV intensity can then be used to determine the UV dose. A pathogen inactivation experiment result is related to the UV dose. The typical experiment will consist of most probable number (MPN) procedure for bacteria, a plaque count procedure for viruses, or an animal infectivity procedure for protozoans. UV light absorbance (A) can also be derived from UV transmittance (UVT) measurements using the following relationship:

$$\text{UVT}\ (\%) = 10^{-A} \times 100 \tag{20a}$$

or

$$A = \log_{10} \frac{1}{\text{UVT}} \tag{20b}$$

Note that the UV light absorbance is defined as

$$A = \log_{10} \frac{I_0}{I_t} \tag{21a}$$

$$\text{UVT}\ (\%) = \frac{I_t}{I_0} \times 100 \tag{21b}$$

where I_t = UV intensity transmitted by the sample at the desired UV wavelength (e.g., 254 nm), mW/cm^2.

UV attenuation through water is often measured in terms of absorbance for a fixed path length at a certain wavelength such as 254 nm. Using the above equations, we can easily calculate either absorbance or transmittance. For example, if water has a UV absorbance of 0.022 cm^{-1}, the transmittance is 95%. A water with transmittance of 95%, 85%, 75%, and 65% is respectively considered as excellent, good, fair, and pretreatment needed for UV disinfection (1).

5. COLLIMATED BEAM TEST

As demonstrated in Eq. (19), the UV disinfection efficiency depends on the number (density) of particles containing pathogens (N_0^p), the UV dose (D), and the exposure time (t). It has been found that it is more convenient to design a disinfection system based on the collimated beam inactivation data. From the above equations and the data obtained, one can determine the critical UV dose for the disinfection. Bioassay is the most widely used method. It requires a collimated beam from an UV lamp and a small batch reactor, to which a known UV dosage is discharged. The test is commonly used as a basis for determining the necessary delivered UV dose for full-scale UV systems as measured by UV intensity and exposure time. By measuring microbial inactivation in the suspension as a function of UV dose, the microorganism's dose–response is determined (see Fig. 3 for example). A typical collimated beam apparatus is shown in Fig. 4.

The UV dose data from bench-scale collimated beam tests for UV disinfection was first reported by Qualls and Johnson (23). Their original apparatus consisted of low-pressure UV lamps housed in a cardboard box with a 5.08 cm diameter, 72 cm long tube extending from a cut-out hole in the middle of the lamp arc length (20).

The UV design has been somewhat of an art form based on utility and budget. While the germicidal UV dose can be estimated in a collimated beam system, the reported dose–response relationships, however, vary considerably. Therefore, a careful design of the system and analysis of data for full-scale UV disinfection become essential.

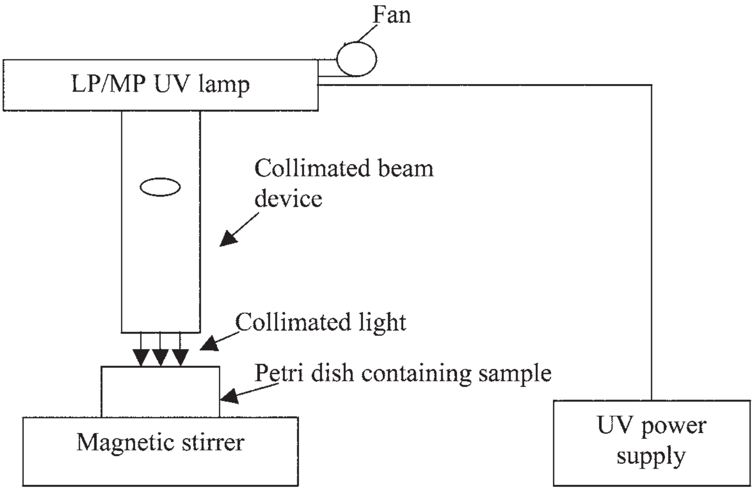

Fig. 4. Typical collimated beam apparatus.

As one can find from Eqs. (12) and (19), the collimated beam test is to measure I_{ave}, t, and number of pathogens left in the suspensions. Thus, a proper experimental determination of these parameters is very important. According to Eq. (12), the measurable items in the test include exposure time, distance from lamp centerline to suspension surface, depth of the suspension, and number of pathogens. The main procedure sequence is (3):

1. Determine the UV absorption coefficient of the water sample.
2. Place a known volume from the sample in a container and stir it by using magnetic stirrer.
3. Measure the water depth in the above container so that the depth of the Petri dish can be determined.
4. Measure the UV intensity (I_0) by a radiometer.
5. Block the light from the collimating tube using a shutter or equivalent.
6. Unblock the light from the collimating tube and start the timer at the same time.
7. When the target exposure time has elapsed, block the light from the collimating tube.
8. Remove the container and collect the sample for determination of the water sample (N_t). Store the samples in the dark at 4°C if the samples are not assayed immediately.
9. Calculate the UV dose and plot the UV dose–response curve (pathogen concentration as a function of the applied UV dose; see Fig. 3 for example).

As one can see from the above, many factors can affect the results. These factors include apparatus setup, collimated beam column, UV lamp, intensity measurement, shutter type and operation, Petri dish specifications, sample volume and depth of the liquid, mixing condition, pathogen testing, and water quality (24). In order to obtain consistent results, the recommendations below should be followed.

Lamps may be either LP mercury vapor (monochromatic at 253.7 nm) or MP mercury vapor (polychromatic UV light). A constant power source and a constant working temperature must be maintained in order to keep a stable UV light output from the lamp (i.e., a the variation less than 5%) (3). To prevent ozone formation, the lamp that emits 185 nm light must not be used. Most lamp sleeves will be "doped" to prevent emission of ozone-forming wavelengths. The emission spectra for LP and MP lamps are shown in Fig. 5.

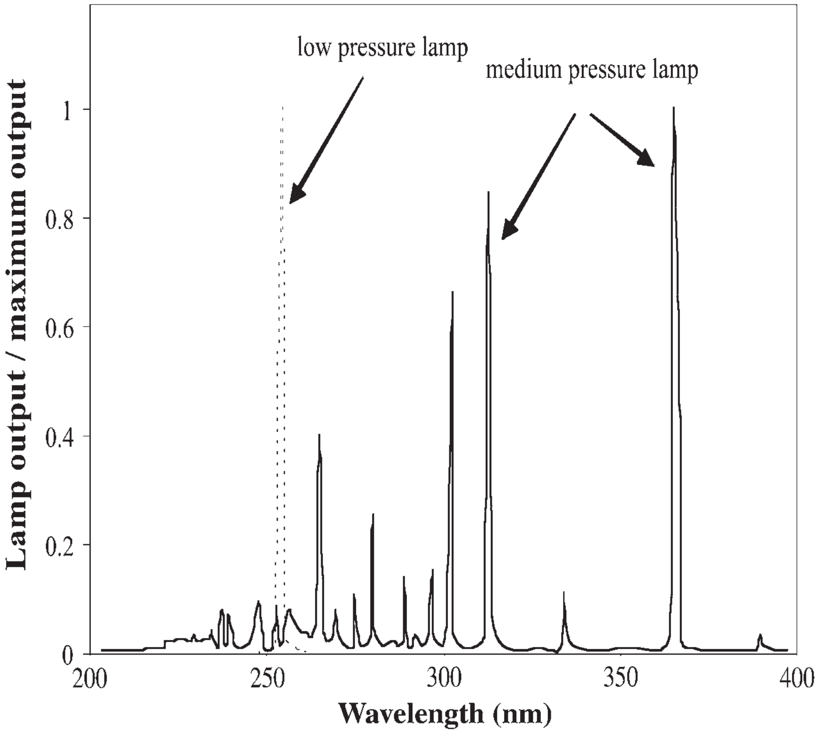

Fig. 5. UV output of LP and MP mercury vapor lamps.

Wavelengths between 240 and 280 nm are the most effective for pathogen killing. Modern LP mercury lamps can emit a wavelength of 253.7 nm with a power conversion efficiency of 80–90%. MP mercury lamps have a much higher intensity with a wavelength of 240 to 600 nm and lower power conversion efficiency. MP lamps can sustain a higher load with a compact lamp installation space. Because the wavelength of 400–600 nm is in the range of visible light, which is favorable to organism growth, as a result, microorganism fouling and photorepair are worth considering in the MP lamp disinfection.

The UV lamp should be located far enough above the surface of the microbial suspension so that uniform UV radiation is obtained across the sample's surface and UV light enters the suspension with a near zero degree angle of incidence. The distance from the lamp to the suspension must be at least six times the longest distance across the suspension's surface. In general, the collimated beam apparatus should have a Petri factor greater than 0.9. A box-like enclosure made of aluminum is recommended to use so as to protect the user from exposure to UV light. Exposure times more than 20 s are recommended. Shutters are used to regulate the exposure time in the UV dose determination. Shutter design has ranged from manually using a piece of cardboard to a pneumatically or electronically driven mechanism to block or allow passage of UV energy to a stage. During short irradiation times, the accuracy of a shutter system becomes important for delivering a repeatable dose.

The diameter of the open cylindrical container (Petri dish) should be smaller than the diameter of the light beam incident on the container; the depth of the sample should range from 0.5 to 2 cm. Like many other experiments, the container must not contain any physical and chemical agents that can affect the pathogens. The pathogen sample should be well mixed by a magnetic stirrer.

The optimal length-to-diameter ratio of the collimating column should be established in order to avoid waste of materials as well as to achieve the desired uniformity of UV rays. A warm-up period and stabilization of ultraviolet lamp are important to allow the lamp to reach its optimal temperature for each start-up. The operating temperatures of a MP UV lamp and a LP UV lamp are typically 600°C or higher and the neighborhood of 50–60°C, respectively. Distance between collimating column and surface of liquid should be less than 2.5 cm (24). The depth of microbial suspension should be on the order of 1 cm.

After the above experimental measurement, the UV dose can then be determined by using Eq. (12). The reflectance at the air–water interface estimated using Fresnel's law is 0.025 given an index of refraction of 1.000 and 1.372 for air and water, respectively. The calculation can be illustrated by using an example demonstrated in the literature with some simplifications (3).

MS 2 is commonly chosen for UV inactivation studies for the following reasons (1,3,25,26):

(a) The structure and size of MS 2 is similar to that of human enteroviruses;
(b) MS 2 is a RNA virus and its dose–response curve of UV inactivation follows first-order kinetics;
(c) MS 2 has a relatively high UV resistance, comparable to that of bacterial spores;
(d) MS 2 is not pathogenic to man, so it can be used for calibration of full-scale reactors without additional safety measures.

When MS 2 is used as a bioassay, the data are organized by plotting the dose–response data on a graph of the log inactivation versus the UV dose (mJ/cm^2). According to a report on ultraviolet disinfection released by the National Water Research Institute (NWRI), the data must fall in the area bounded by the following equations when using a collimated beam apparatus:

$$\log_{10}\left(\frac{N}{N_0}\right) = -0.040 \times \text{UV dose} - 0.64 \tag{22a}$$

$$\log_{10}\left(\frac{N}{N_0}\right) = -0.033 \times \text{UV dose} - 0.20 \tag{22b}$$

Example 1

A collimated beam test is carried out to determine the UV microorganism's dose–response. The UV intensity (incident irradiance) of 1.00 mW/cm^2 is measured using a radiometer. A 25-mL microbial suspension is irradiated for 60 s in a Petri dish. The irradiation time is monitored using a stopwatch. The Petri dish radius, measured using a ruler with 1 mm graduations, is 2.5 cm. The stir bar volume is 1 mL. The UV decadic absorption coefficient (a_{10}) of the microbial suspension for a 1-cm path length at 254 nm is 0.050 cm^{-1}. The Petri factor of 0.90 is calculated for the collimated beam apparatus. The distance from the lamp to the surface of the suspension is 25 cm. Determine the UV dose based on the above data given.

Solution:

The depth in the Petri dish (*d*) is calculated as the sum of the suspension and stir bar volumes divided by the area of the Petri dish.

$$d = \frac{\text{volume of sample}}{\text{area of Petri dish}} = \frac{25+1}{\pi \times 2.5^2} = 1.32 \text{ cm}$$

Note that $t = 60$ s, $I_0 = 1$ 1.00 mW/cm^2, $a_{10} = 0.05$ cm^{-1}, $P_f = 0.9$, $R = 0.025$, $L = 25$ cm. Using Eq. (12), we can have

$$\begin{aligned} D &= \frac{I_0 \times P_f \times (1-R) \times (1-10^{-a_{10} \times d})}{a_{10} \times d \times \ln 10} \times \frac{L}{L+d} \times t \\ &= \frac{1 \times 0.9 \times (1-0.025) \times (1-10^{-0.05 \times 1.32})}{0.05 \times 1.32 \times \ln 10} \times \frac{25}{25+1.32} \times 60 \\ &= 46 \text{ mJ/cm}^2 \end{aligned}$$

6. DESIGN OF UV UNIT FOR AQUEOUS-PHASE DISINFECTION

Similar to the design approaches employed in most water and wastewater treatment processes such as biological wastewater treatment, there are empirical (also called irrational) and model-based (rational) methodologies used for design of UV unit for aqueous-phase disinfection. The first one is based on empirical experience and has traditionally been used in the water industry, while the second one is based on a series of detailed mathematical analyses and experimental measurements and is still in the research phase. In the design, one will determine the requirement of UV lamps applied to the water based on the characteristics of water such as flow rate and the size of the disinfection unit.

6.1. *Empirical Design Approach*

This approach is essentially an enlargement of the reactor used in the bench-scale collimated beam test discussed previously. In the test, a small reactor is used. Based on the experimental data, one can plot the disinfection efficiency or killing as a function of the UV dose (see Fig. 3). The disinfection efficiency can be expressed in terms of numbers of pathogens remaining in the suspension or logarithm of the ratio of the pathogens remaining in the suspension after a certain amount of UV dose is applied to those initially present. The design can be followed by the below steps (19).

1. Determination of the UV dose for the lowest discharge limit required. It can be obtained through a collimated beam test or from published data. Table 2 gives UV dose corresponding to 1–4-log disinfection. Figure 6 demonstrates the effect of UV radiation on three major pathogens. For drinking water treatment applications, the UV dose ranges from 30 to 80 mJ/cm2.
2. Determination of safety factors for the required UV dose due to lamp aging and fouling.
3. Determination of UV intensity as a function of the transmittance or absorbance of filtered water samples by the point-source summation method or equivalent. The presence of suspended solids and colors can reduce the intensity of UV light in the waters.
4. Calculation of the exposure time.

Table 2
UV Dose–Response of Different Microorganisms in Drinking Water

		UV inactivation dose, mJ/cm^2[a]			
Microorganism	Type	1-log	2-log	3-log	4-log
Aeromonas hydrophila	Bacteria	1.1	2.6	3.9	5
Campylobacter jejuni	Bacteria	1.6	3.4	4	4.6
Escherichia coli O157:H7	Bacteria	1.5	2.8	4.1	5.6
Legionella pneumophila	Bacteria	3.1	5	6.9	9.4
Salmonella anatum	Bacteria	7.5	12	15	
Salmonella enteritidis	Bacteria	5	7	9	10
Salmonella typhi	Bacteria	1.8	4.8	6.4	8.2
Salmonella typhimurium	Bacteria	2	3.5	5	9
Shigella dysenteriae	Bacteria	0.5	1.2	2	3
Shigella sonnei	Bacteria	3.2	4.9	6.5	8.2
Staphylococcus aureus	Bacteria	3.9	5.4	6.5	10.4
Vibrio cholerae	Bacteria	0.8	1.4	2.2	2.9
Yersinia enterocolitica	Bacteria	1.7	2.8	3.7	4.6
Adenovirus type 40	Virus	30	59	90	120
Adenovirus type 41	Virus	22	50	80	
Coxsackievirus B5	Virus	6.9	14	21	
Hepatitis A HM175	Virus	5.1	14	22	30
Hepatitis A	Virus	5.5	9.8	15	21
Hepatitis A HM175	Virus	4.1	8.2	12	16
Poliovirus type 1	Virus	4–6	8.7–14	14–23	13–21
Rotavirus SA11	Virus	7.1–9.1	15–19	23–26	36
Cryptosporidium parvum	Protozoa	<2	<3	<6	
Giardia lamblia	Protozoa	<1	<3	<6	<2
Giardia lamblia[b]	Protozoa				<1
Giardia muris[c]	Protozoa		5		
Escherichia coli	Bacteria	2.5–4.4	3–6.2	3.5–7.3	5–8.4
Streptococcus faecalis	Bacteria	5.5–6.6	6.5–8.8	8–9.9	9–11
MS-2	Phage	4–21	16–40	38–61	62–71
ϕX174	Phage	2.1–4	4.2–8	6.4–12	8.5–10
PRD-1	Phage	9.9	17	24	30
B-40	Phage	12	18	23	28
Bacillus subtilis spores	Spores	29–36	40–49	51–61	78
G. muris cysts			5		
Oocyst				19	25

[a] Ref. 3.
[b] Ref. 49, buffered saline.
[c] Ref. 50, filtered surface water.

5. Determination of volume of water to be disinfected based on the exposure time and flow rate.
6. Determination of number of lamps required for the UV disinfection.

The empirical design approach can be illustrated by a following example.

Example 2

A wastewater is treated by a conventional biological treatment and subsequently disinfected by a UV unit such that the pathogenic content is reduced to 170 MPN/100 mL.

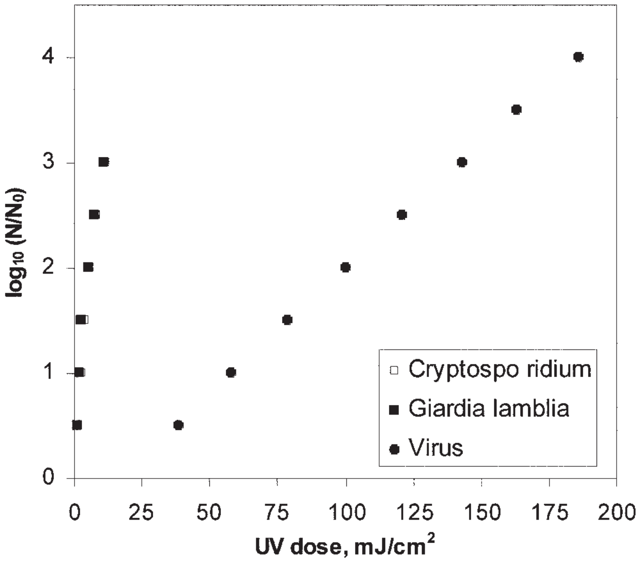

Fig. 6. Effect of UV dose on major pathogens.

The UV dose can be determined by a collimated beam test with a result illustrated in Fig. 3. The lamp aging and fouling can contribute 25% and 35% of reduction in the UV disinfection, respectively. The water has a filtered absorbance of 0.2 cm^{-1}, which corresponds to an intensity of 6 mW/cm^2. The design water flow rate is 500 L/s and the volume treated per UV lamp is 8 L. Determine the number of UV lamps required for the disinfection.

Solution:

From Fig. 3, one can find that the UV dose is 145 $\text{mW}\cdot\text{s/cm}^2$ in order to achieve a final effluent pathogenic content of 170 MPN/100 mL. However, the aging and the fouling of the UV lamps must be taken into consideration. A safety factor of 1.2 is included in the calculation. Thus, the UV dose applied in the UV disinfection is

$$\text{Requirement of UV dose} = \frac{145\ \text{mW}\cdot\text{s/cm}^2}{(1-0.25)\times(1-0.35)}\times 1.2 = 356.9\ \text{mW}\cdot\text{s}/\text{cm}^2$$

The absorbance of the water sample is 0.2 cm^{-1}, giving a transmittance of 63%. The UV light in such a water has an intensity of 6 mW/cm^2. Based on Eq. (6), the UV exposure time is

$$\text{Exposure time} = \frac{356.9\ \text{mW}\cdot\text{s/cm}^2}{6\ \text{mW/cm}^2} = 59.5\ \text{s}$$

The total volume of water to be disinfected is then calculated:

$$\text{Total volume of water} = \text{flow rate} \times \text{exposure time} = 500 \times 59.5 = 29.74 \times 10^3\ \text{L}$$

Because the volume treated per UV lamp is 8 L, the number of UV lamps is therefore

$$\text{Number of UV lamps} = \frac{29.74\times 10^3}{8} = 3718\ \ (\text{Lamps})$$

6.2. *Probabilistic Design Approach*

In this approach, an expression is first developed to relate total number (or density) of pathogens (N_t) at time t with the characteristics of the pathogenic suspension and operational parameters such as the UV exposure time (t). One typical expression is as follows:

$$N_t = \alpha \times \text{SS}^{\beta} \times N_0^{\gamma} \times \text{UFT}^{\lambda} \times I_{\text{ave}}^{\pi} \times t^{\eta} \tag{23}$$

where N_t = total number (or density) of pathogens at time t, MPN/100 mL, N_0 = total number (or density) of pathogens prior to UV disinfection (i.e., $t = 0$), MPN/100 mL, SS = suspended solids in the pathogen suspension, mg/L, UFT = unfiltered transmittance at 254 nm, I_{ave} = average intensity of UV light, mW/cm^2, t = exposure time, s, and α, β, γ, λ, π, and η = empirical coefficients.

Equation (23) is then calibrated with experimental data obtained from pilot-scale field tests. A secondary effluent has $\alpha = 10^{2.919}$, $\beta = 1.947$, $\gamma = 0.3233$, $\lambda = 0$, and $\pi = \eta = -2.484$ (19). Owing to the variability in the experimental data as well as the influent characteristics and operational parameters, statistical analysis such as Monte Carlo technique can subsequently be combined with the calibrated model for the design of the UV disinfection unit. This approach was developed by Loge and co-workers; interested readers may refer to their original manuscripts for more detailed information (19,22,27,28).

Chiu et al. developed a general probabilistic particle-centered model that combines kinetic information from a well-mixed batch reactor with a dose-distribution function to predict disinfection efficacy in practical UV systems (29). The particular case of disinfection using vertical (perpendicular to the direction of the open-channel flow) UV lamps in a staggered configuration was studied. A dose-distribution function that incorporates the effects of spatial nonuniformities in both hydrodynamics (a random-walk model) and UV intensity (a point-source summation model) was estimated. The flow-field information necessary for the random-walk model was obtained from laboratory measurements of the turbulent flow, while the dose–response function for microorganisms was obtained from completely mixed batch reactor experiments with a collimated beam test. Predictions of disinfection efficacy based on the developed dose-distribution function and the laboratory kinetic data compared well with measurements from a pilot-scale vertical UV system. The results suggest that the regions near the channel sidewalls where UV intensity is low represent a limiting factor in the process performance of continuous-flow UV disinfection systems.

6.3. *Model-Based Design Approach*

The UV radiation disinfects germs in an aqueous system, which can be operated as plug flow, continuous flow, or other modes. The killing efficiency is controlled by many factors, which can be classified into two aspects: disinfection kinetics and flow dynamics. Like many other processes in both chemical and environmental engineering, the mathematical modeling of the UV disinfection can be started from simulation of distribution of flow velocity together with definition of suitable kinetic model(s). The disinfection effect in terms of survival of pathogens as a function of operational conditions such as time and dose can then be estimated. Since the mathematical models involve many unknown parameters that must be experimentally determined, they are mainly used by researchers rather than applied in the UV disinfection design. In addition, there are very few successful models available in the literature.

Lyn et al. studied the UV disinfection in an open channel. The UV lamps are arranged with their length perpendicular to the water flow (30). A new disinfection model for illustration of pathogenic survival was developed. The flow dynamics model is based on the Reynolds-averaged Navier–Stokes equations and incorporates the *k*-*ε* turbulence model. A continuum approach to disinfection modeling is developed by combining a model of the spatial distribution of UV intensity with a model of disinfection kinetics that is assumed first order in the local UV intensity and the local concentration of viable microorganisms. Good agreement was found between flow predictions and measurements in the flow. Predictions of disinfection performance were satisfactory at high-throughput rates but deteriorate at low throughput rates.

A computational fluid dynamics (CFD) model coupled with irradiance modeling was developed to calculate UV energy used by various water qualities and disinfection efficiencies (31–33). By using the model, the movement of microorganisms through the disinfection system can be simulated and their exposure time to UV light can be determined. The discrete ordinates radiation model is used to describe the UV irradiance, which incorporates important operational parameters such as reflection and shading effects. The model can track trajectories of thousands of individual microorganisms and calculate their detailed motions and resultant UV dose. It can provide more detailed information such as flow patterns through the disinfection system and UV dose received by various pathogens.

The model can evaluate alternative designs so that an optimal UV system with much less time and a lower cost can be designed without building a physical prototype. With the model, the design can avoid short-circuiting and dead zones that can cause inefficient use of power and reduced contact time. The model can quickly determine effectiveness of any proposed design and to scale-up existing technology to large-scale systems that has a capacity of above 50 MGD. The model developers claimed that over-design can be effectively avoided, which normally occurs in design. Thus, both capital and operational costs can be reduced.

A computational model for wastewater disinfection was developed by Emerick et al. (28). The user can define multiple equations for UV disinfection reactions. The reaction vessel is simulated as a plug flow reactor. A similar model called *BioSys* was developed by Zeidan (34).

6.4. Professional Engineering Design Approach

In this section, the practical design approach used by professional engineers in the USA is introduced. The design approach is adopted from the US Environmental Protection Agency, Washington, DC. According to the US EPA, the basic design considerations for a UV process system are (a) satisfying the UV demand of the water; (b) maximizing the use of UV energy delivered by the lamps; and (c) maintaining conditions that encourage plug flow.

UV lamps are usually submerged in the water, perpendicular or parallel to the water flow. Submerged lamps are inserted into a quartz sleeve to minimize the water's fouling effects. The greater the distance between the water and the lamp, the weaker the radiation dosage delivered, because the energy dissipates or becomes dilute as the space it occupies increases in volume. The UV demand of other contaminants in water also consumes radiation.

Specific engineering design parameters to consider are:

(a) *Residence time distribution (RTD)*: This describes the detention time of the water in the reactor and should be determined for several flow conditions.

(b) *Plug flow*: The ability to maintain plug flow in the reactor is influenced by the inlet and exit designs. Disturbances at the inlet and exit planes of the lamp battery should be minimized and necessary changes in the flow direction should be made outside the lamp battery.

(c) *Dispersion number*: A key goal is to minimize the dispersion number, d (cm^2/s). As a design goal, d should be between 0.02 and 0.05. This number represents a plug flow reactor with low to moderate dispersion. This value is attained by increasing the product of the velocity (cm/s) and distance traveled (cm) by the water as it flows through the reactor while under direct exposure to UV radiation. However, extended lengths and higher velocities cause higher head losses; therefore, adjusting the dispersion number may be necessary to meet specific criteria for both full-scale modules or pilot units. Head loss is determined over a wide velocity range and excludes entrance and exit losses.

(d) *Effective volume*: The inlet and outlet designs should achieve equivalent water velocities at all points entering and exiting the lamp battery. This maximizes the lamp battery use and improves cost effectiveness. Stilling walls (i.e., perforated baffles) and weirs in the reactor design assist in controlling water velocities.

(e) *UV lamp designs*: Lamps used in UV disinfection systems typically have arc lengths of approx 0.8 and 1.5 m (2.5 and 4.9 ft) and full lengths of 0.9 and 1.6 m (3 and 5.3 ft), respectively. The arc length describes the active, light-emitting portion of the lamp. Lamp diameters typically are 1.52 and 2.0 cm (0.6 and 0.8 in.). A sleeve made of fused quartz or another material that is highly transparent to UV light, such as Vycor, protects lamps that are submerged. Non-submerged lamps are placed near the wall of the water conduit, which is made of a UV light-translucent material.

(f) *Water quality*: Initial microorganism density, suspended solids (or turbidity), UV demand of the water at the disinfection point, and water flow rate all affect the size and performance of the UV disinfection system. The performance of a UV disinfection unit relates directly to the initial density of the indicator organisms. The higher the initial density, the greater the dosage of radiation required. For this reason, microorganism density should be continually monitored. Turbidity directly affects the performance of the UV disinfection system as well. Particulates suspended in water block the UV radiation, thereby protecting bacteria and hindering disinfection. The UV demand of the water affects the radiation intensity in the reactor and, thus, affects the system size and the lamp placement that achieves the desired performance.

(g) *Water flow rate*: Flow rate is another key factor in determining system size. Both the hydraulic load to the plant and the design of the processes preceding disinfection affect flow. The size of the UV system, however, should be based on peak flow rates and projected flows for the plant's design year rather than on average flows, which are used to predict operating and maintenance requirements.

7. APPLICATIONS OF UV UNIT FOR AQUEOUS-PHASE DISINFECTION

Any ideal UV disinfection system should provide sufficient dose to kill pathogens in water and wastewater. Both closed and open UV systems can be used as shown in Figs. 7 and 8. Closed channel UV system is often used in drinking water disinfection, while open channel UV system is always adopted for wastewater disinfection. No matter

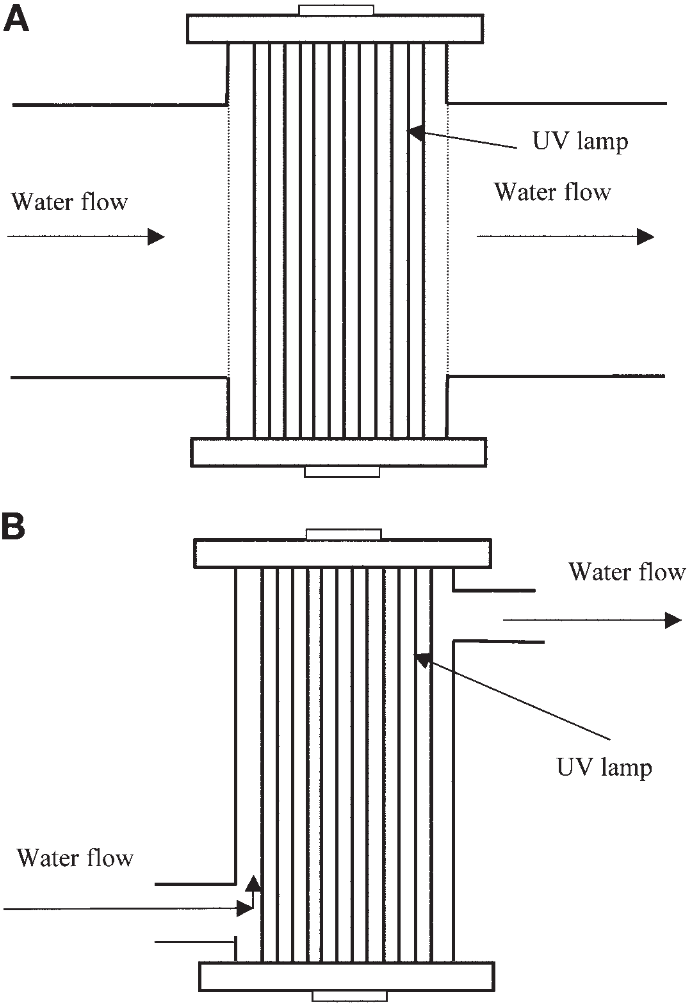

Fig. 7. Typical UV disinfection systems: **(A)** closed channel system (UV lamp perpendicular to flow); **(B)** closed channel system (UV lamp parallel to flow).

what type of system is used, the core component is the UV lamp. Other components include lamp sleeves, UV intensity sensors, cleaning devices and temperature sensors, ballasts, power supply, and supporting structures. Hydrodynamics in the UV system play important roles. Lamp placement, inlet and outlet conditions, and baffles all affect mixing in the reactor. Improvements to the hydraulic behavior can often be obtained at the expense of a headloss. Optimal dose delivery is dependent on lamp output and hydrodynamics.

The advantages of UV disinfection over chemical disinfectants include:

1. Much fewer disinfection by-products.
2. Effective toward viruses and bacteria.
3. More effective on some pathogens such as *Cryptosporidium* than chlorine.
4. Economical and easy installation and operation.

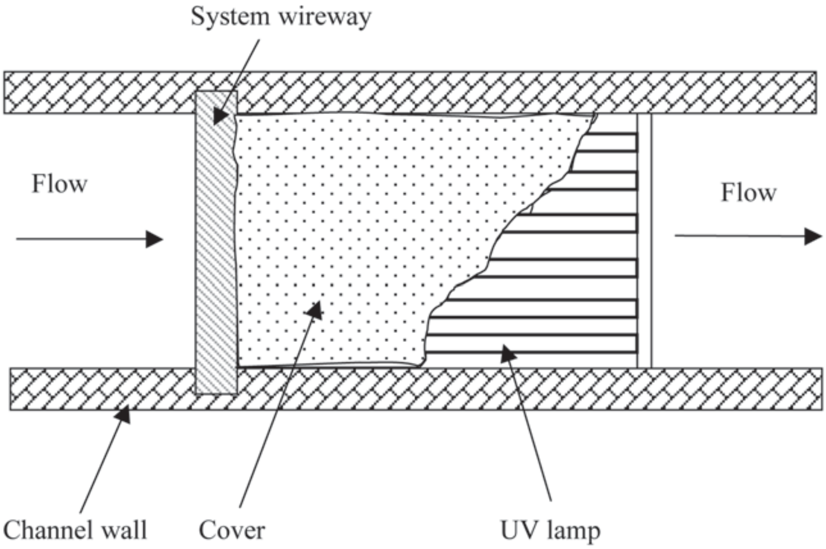

Fig. 8. Typical UV open channel disinfection system.

5. Shorter contact time.
6. No toxic chemical handling.
7. No requirements of manufacture, storage, and transport of disinfectants.

7.1. *Water Treatment*

As the UV light can cause serious damage on genetic substances in microorganisms, its radiation is widely used in drinking water treatment, high-quality industry process water treatment, and water reclamation. It is a mature technology in drinking water treatment, and has been applied as a separate operation unit for decades. It can be applied on a various scales from home units to large-scale systems up to 100 MGD.

Unlike chlorination, the main problem in UV disinfection is the lack of residual germicide effect. This problem can be solved by combining with other disinfection methods when the UV radiation is used as the primary choice. Another disadvantage is that it is less effective in inactivation of *Giardia* and some protozoan pathogens. However, with a recent increasing concern on disinfection products such as trihalomethanes (THMs), the number of UV disinfection operations has been increasing. When an exposure to *Giardia* and other protozoan pathogens is not of concern, the UV radiation is competitive among primary disinfection choices.

In the chlorine disinfection, reducing agents like sulfur dioxide must be used to eliminate the discharged toxic chlorine. Besides, special considerations must be applied to control natural organic matter (NOM) in water source or to reduce the potential by-product precursors after the disinfection unit. These concerns however become less obvious when UV radiation is used for disinfection of water.

The geometry of UV lamp arrangement, the water absorbance, the characteristics of the lamp, and the turbulence of water flow can influence the disinfection efficiency. Consequently, the elimination of dead area and the maintenance of uniform flow should be considered in the design.

Three types of UV system configurations are usually applied in drinking water disinfection: unsubmerged, closed channel submerged, and open channel submerged operations. In unsubmerged operation, the water flows inside of a transparent tube, while the UV lamp is outside of the tube. Special design must be applied to remove excess heat accumulated in the system.

When designing a UV disinfection system, the important issue is an effective contact of UV light and water flow. Supplemental cleaning, pretreatment, monitoring, safety protecting systems must be included. The required UV dose is based on a bioassay test, which is adequate to inactivate of target pathogens. A pilot test is often required to test preliminary design, including optimum UV dose, the arrangement of lamps, hydraulics, and the validation of manufacture specific lamp performance.

If disinfection is the first priority, the UV disinfection unit can be installed anywhere along the treatment train from the raw water source. However, because of concerns about the UV operational cost (mainly the UV dose) and the potential for formation of DBPs, it is strongly recommended that the UV disinfection process be placed after most of SS, particles, turbidity, organic compounds, and color are removed, which normally occurs after filtration. As discussed previously, the presence of SS would require a higher UV dose as shown in Fig. 3. On the other hand, the colors due to the presence of organic compounds and some metal ions can significantly change the UV absorbance, which essentially reduce the UV transmittance as demonstrated in Eqs. (20) and (21). If the organic concentrations in the water source are too high, which is normally observed in the poorly treated secondary effluent, a series of DBPs can be formed (35). In the water treatment, SS, turbidity, organic compounds, and colors are mainly removed by coagulation and filtration. Carbon adsorption sometimes can be used after filtration. The UV radiation unit must be applied after the filtration; otherwise, the UV disinfection can be badly influenced since the water after coagulation and sedimentation still contains high turbidity. In the post-filtration use of UV disinfection design, hydraulic profiles of each treatment unit must be carefully taken into consideration. Three configurations are used in the water treatment (3).

The post-filtration UV disinfection can be installed before the water storage (upstream of clearwells). There are two configurations as illustrated in Fig. 9:

1. Combined Filter Effluent Installation. The effluents from filtration units are combined and sent to the UV disinfection unit(s). The disinfected water is then pumped to the water storage. Of the three options described here, this installation is generally preferred when conditions permit. The UV operation is independent of the operation of individual filtration units, leading to great flexibility for design and operation. If the entire UV installation failed, a chemical disinfectant such as chlorine can be directly added to the water storage.

2. Individual Filter Effluent Piping Installation. Opposed to the first configuration, the effluent from individual filter is disinfected by the UV radiation and subsequently pumped to the water storage. If a water treatment plant changes its disinfection approach such as chlorination to UV radiation, this installation is more economical as lower construction costs are involved. However, there are several disadvantages to this installation location. Many filter galleries do not have sufficient space within existing effluent piping to accommodate a UV disinfection unit.

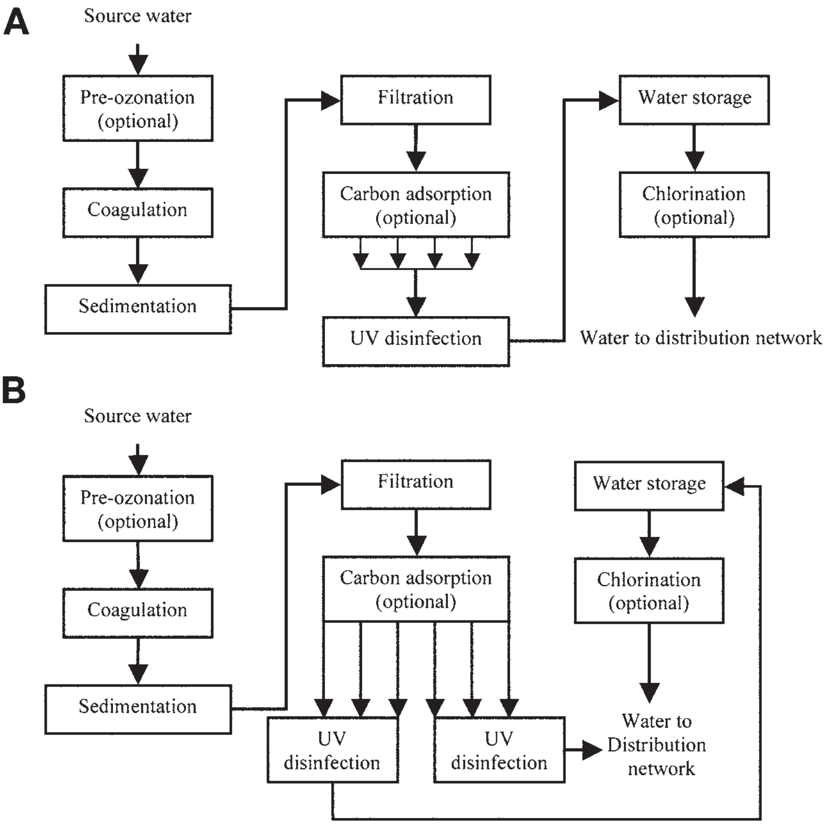

Fig. 9. Schematic for installation of post-filtration pre-water storage UV disinfection in water treatment: **(A)** combined filter effluent installation; **(B)** individual filter effluent piping installation.

UV disinfection can also be applied after water storage (downstream of Clearwell) as illustrated in Fig. 10. Unlike the above two installations, the effluent from filtration is first stored in the water storage and then disinfected by the disinfection unit(s). This configuration may cause greater fluctuations in flow rate and thus increase the size of UV system for accommodation of the flow fluctuations.

Compared with conventional chlorination, the UV disinfection has the following advantages (1,3):

1. It uses a shorter contact time (less than 10 s).
2. It has relatively lower capital and operational costs. No transportation, storage, handling, or dosing are required.
3. It can extremely effectively disinfect bacteria and virus and may hold promise for (oo)cysts.
4. DBPs and their precursors are not main concerns. Production of tastes and odors is neglectable.
5. The technology may be more accepted by the public because disinfectant chemicals are not heavily involved.
6. Because no chlorine or very low amounts of chlorine are used in the water treatment, the free chlorine in the product water is very low; thus, the corrosion problem in the water distribution network is not obvious.

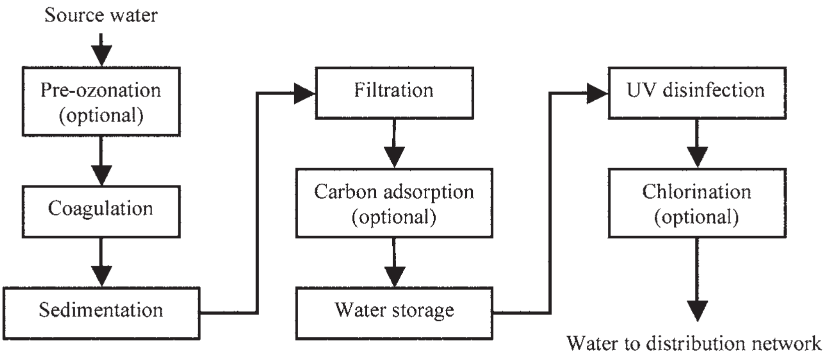

Fig. 10. Schematic for installation of post-filtration post-water storage UV disinfection in water treatment.

However, the technology has several disadvantages:

1. It does not provide residual protection for the distribution network, while chlorination does.
2. It is difficult to monitor disinfection effectiveness due to limitations of existing sensor technologies.
3. Presence of UV absorbing materials and particles can reduce its effectiveness.
4. Presence of organic compounds in the water may cause the extensive fouling of UV lamps, thus leading to lower efficiency and operational costs.
5. The effectiveness against cysts has not been verified.
6. Large systems have many electronic components such as ballasts, transformers, and switches, which can require extensive cooling and maintenance.

For some industries such as pharmaceuticals, electronics, and toiletries, ultra-pure water is always demanded. Pathogens, organic substances, and inorganic substances must be effectively removed to a very low level (e.g., less than 1 ppb TOC in semiconductor fabrication manufacturing). The source water is first filtered by multimedia filters and disinfected by UV light. The water is then treated by membrane units (usually reverse osmosis) and stored. Later on, UV photolysis, ion exchange resin and micro-filters are used alternatively to produce the high pure process water.

UV can also be used in water reclamation and reuse. An example is the reclamation of swimming pool water. Usually, the swimming pool water reuse process includes coagulation, filtration, clarifier, disinfection, and pH adjustment. The conventional swimming pool disinfection chemical is chlorine; however, high concentrations of residual chlorine can be harmful to human health. The UV technology can be placed between the filters and chlorine disinfection unit as a pre-disinfection unit and remove pathogens. Hence, much less amount of chlorine (compared with the process without UV unit) is needed for residue disinfectant level.

Another good example is the NEWater project in Singapore shown in Fig. 11 (36). The advanced water reclamation demonstration plant has been operated for 4 yr to produce 10,000 m^3/d of high-grade water. The source water (feed), which is the effluent from a conventional biological treatment plant, is first treated by microfiltration (MF) and reverse osmosis (RO), and then disinfected by UV radiation, and subsequently adjusted by acid, base, and carbonate in order to have a sufficient alkalinity. The source

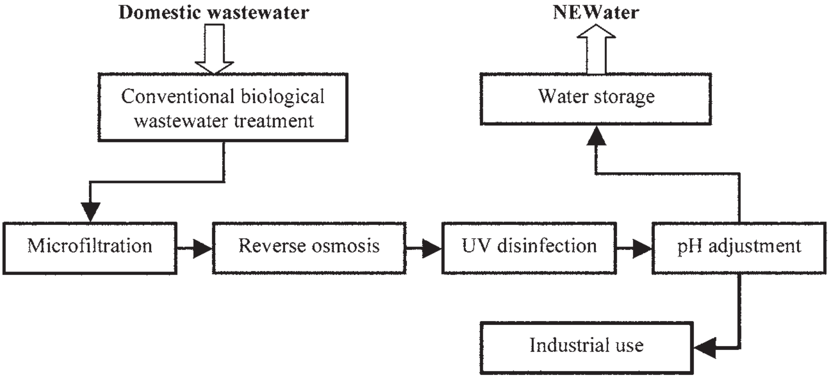

Fig. 11. Schematic of water reclamation process in the NEWater project.

water from a secondary clarifier of a conventional activated sludge treatment typically contains 5-d biochemical oxygen demand (BOD_5) of 10 mg/L, SS of 10 mg/L, ammonia–nitrogen of 6 mg/L, and total dissolved solids (TDS) of 400–1600 mg/L and total organic carbon (TOC) of 12 mg/L. It is first microscreened (0.3 mm), followed by the MF to 0.2 μm to remove fine particles and then demineralized by two parallel 5000 m^3/d RO trains equipped with thin-film aromatic polyamide composite membranes. UV 254 absorbance in 96 samples obtained in 2002 ranged from a minimum of not detectable concentration to a maximum of 0.011 cm^{-1}. Three UV units in series equipped with broad-spectrum medium pressure UV lamps delivering a UV dose of 60 mJ/cm^2 are applied. Because the water after MF and RO has no suspended solids, and very low levels of both organic compounds and metals, the possibility of microbial presence is very low (36–39). It is found that viruses, bacteria, and parasites are removed by the RO process. The UV disinfection here is used for prevention of any pathogens entering the water due to operational accidents such as leaking in pipelines. The UV disinfection is to provide an added safeguard again the microbial contaminants. The UV system was designed for a 4-log inactivation of microbes; however, the testing shows that better than 7-log is actually achieved. Measurement of microbial parameters of fecal coliforms, total coliforms, coliphage somatic, coliphage male–specific, *Enterococcus*, *Clostridium perfringens*, *Giardia*, *Cryptosporidium*, and *Enterovirus* shows that all these are not detectable; HPC has a mean of 5.2 with a maximum of 80 and a minimum of 1.1 CFU/mL. It is shown that the pathogenic content is far below the limits regulated by the US EPA and the WHO.

In food and soft drink industry processes, direct UV radiation on product solution is necessary to prevent micrograms from growing. UV disinfection as a cleaning method is used in bottle, tank, and plate disinfection. Other applications include oil industry consumption on drinking and water injection into rocks.

7.2. *Wastewater Treatment*

Disinfection of treated wastewater is necessary when the water is used for irrigation or possible downstream pollution is concerned. UV disinfection is competitive in the disinfection of treated wastewater due to its low operational cost and lower formation of disinfection by-products. Its application in wastewater treatment is slightly different to that in water treatment, even though the mechanisms are similar. The number of pathogens attached to particles in wastewater will impact greatly on UV disinfection performance as illustrated in Fig. 3. The elimination of microbes in treated wastewater is often necessary. It is strongly recommended that a filtration system be installed prior to an UV disinfection system. A filter itself can lower turbidity and a fraction of the pathogens. As a result, UV disinfection loading can be reduced. When a chemical disinfectant, such as chlorine is used as a subsidiary method, it is better to be installed after an UV system because UV light can degrade some of the chemical disinfectants.

In a pilot-scale study conducted by Rajala and co-workers (40), rapid sand filtration combined with the use of polyaluminum chloride coagulation was used as a pretreatment to improve the quality of wastewater effluent before further treatment with UV irradiation. Rapid sand filtration reduced suspended solids, turbidity, color, and microbes by about 90%, 70–80%, 20–50%, and 90–99%, respectively, which improved the UV transmittance of water by up to 20%. The UV irradiation further reduced the number of microbes. More than 99.9% reduction of MS 2 was achieved with the dose of 140 $\mathrm{mW{\cdot}s/cm^2}$. Rapid sand filtration and the subsequent UV irradiation reduced the number of all the tested microbes to a low level, often below the detection limit.

There are no general regulations and effluent limitations on a UV dose on treated wastewater disinfection. However, a dosage of 50–400 $\mathrm{mJ/cm^2}$ is often adopted in practice. The limit for wastewater reused for irrigation is 100 total coliform/100 mL. In wastewater treatment, a conventional aerobic treatment system including biodegradation and filtration is not sufficient to remove pathogens to a safe level. For example, for water reuse of urban, food crop irrigation, and recreational impoundments, the US EPA suggested disinfected tertiary effluent (filtration of secondary effluent) water quality must meet a pH range 6–9; $\mathrm{BOD_5} < 10$ mg/L; turbidity < 2 NTU; no *E. coli*, and residual $\mathrm{Cl_2} < 1$ mg/L. Because turbidity, some organic substances, and high UV absorbance can significantly affect the performance of UV disinfection, the influent before the UV unit must have high water quality.

7.3. *Environmental Protection*

In addition to potable water and wastewater treatments, UV process can also be used for storm runoff treatment, combined sewer overflow (CSO) treatment, swimming pool water disinfection, and groundwater decontamination. The readers are referred to another book for more information on the applications of UV process in the area of environmental protection.

8. OPERATION AND MAINTENANCE OF UV SYSTEM IN AQUEOUS ENVIRONMENTS

8.1. *UV Lamps*

UV lamp is the most critical element in the disinfection. The most widely used UV lamps can be classified into low-pressure low-intensity lamp, low-pressure high-intensity lamp, medium-pressure high-intensity lamp, high-pressure high-density lamp, and other types of lamps. The details of the typical lamps are listed in Table 3. The low-pressure mercury lamp works in an internal pressure range of 0.001–0.1 torr. Mercury is typically

Table 3
Characteristics of Major UV Lamps

Items	Low-pressure low-output lamp*	Low-pressure high-output lamp*	Medium-pressure high-output lamp*
Advantages	Higher germicidal efficiency, nearly all output at 254 nm; smaller power draw per lamps; Longer lamp life		Higher power output; fewer lamps for a given application; smaller reactors
Disadvantages	More lamps needed		Higher operating temperature can accelerate fouling; shorter lamp life; lower electrical to germicidal conversion efficiency
Germicidal UV light	Monochromatic at 254 nm	Monochromatic at 254 nm	Polychromatic
Power consumption	0.07–0.1 kW	0.2–0.5 kW	2–5 kW
Lamp output at 254 nm	25–27 W	60–400 W	—
Lamp current	350–500 mA	Variable	Variable
Optimum temperature	40°C	40°C	40°C
Efficiency	30–40%	25–35%	10–12%
Temperature	35–45°C	90–150°C	600–800°C
Mercury vapor pressure	0.007 mm Hg	30–30,000 mm Hg	
Lamp length	10–150 m	10–150 m	5–120 m
Lamp diameter	15–20 mm	Variable	Variable
Lamp life	8000–10,000 h	8000–12,000 h	4000–8000 h

*Refs. 3 and 11.

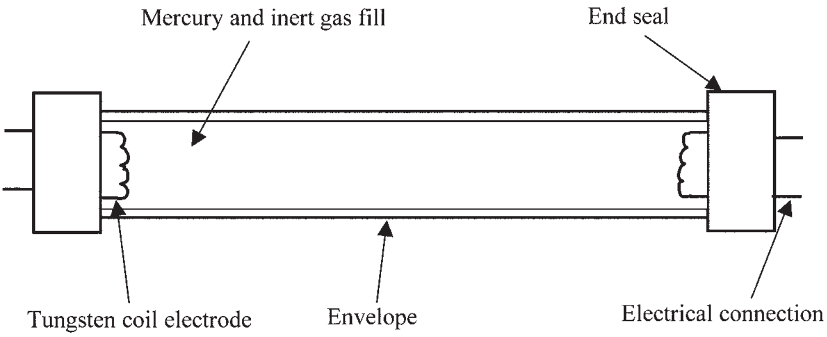

Fig. 12. A schematic of LP mercury lamp.

present in liquid and gas phases. The carrier gas is argon, which is usually in excess of 10–100 times as much as that of mercury vapor inside the low-pressure UV lamps. On the other hand, the medium pressure lamp operates at an internal pressure of 100–10,000 torr. High-pressure mercury lamp, which is less commonly used in aqueous environments, operates at an internal pressure of about 10,000 torr. A typical cylindrical low-pressure mercury lamp is demonstrated in Fig. 12.

The performance of an UV lamp depends on the quality of lamp (mainly material and technologies), lamp temperature, and UV transmission efficiency through lamp wall, voltage, lamp aging, water characteristics of influent, arrangements of lamps, and interference of cluster lamps. As shown in Table 3, low-pressure mercury lamps have a higher emission yield, but comparatively lower output intensity. For all mercury–argon lamps, the optimum emission temperature is that about 40°C and decreases rapidly when the temperature decreases to 10°C. Generally, cold-cathode-type low-pressure mercury–argon lamps are more sensitive to temperature than the hot cathode type in emission intensity. With the aging of UV lamps, the emission intensity decreases. A 1-yr-old lamp can decrease to less than half of the nominal emission intensity.

UV lamps are housed within the lamp sleeves. Quartz is often used to build lamp sleeves with open ends. The sleeve is used to protect, cool, and insulate the UV lamps. The most commonly used lamps in water and wastewater disinfection are low-pressure low-intensity mercury vapor lamps [also termed low-pressure low-output (LPLO) mercury vapor lamps], low-pressure high-intensity mercury vapor lamps (also termed as LPHO mercury vapor lamps), and medium-pressure mercury vapor lamps. Other lamps include electrode-less mercury vapor lamps, metal halide lamps, xenon lamps (pulsed UV), and eximer lamps. UV lamps may be oriented parallel, perpendicular, or diagonal to flow or ground. Orienting MP lamps horizontally relative to the ground prevents differential heating of the lamps and reduces the potential for lamp breakage.

Fouling is a critical problem in UV disinfection. The deposited organic and inorganic compounds on the lamp or sleeve surface can greatly reduce the effectiveness UV of radiation on pathogens. The internal fouling can be reduced by selecting an appropriate material within the lamps. External surface fouling must be removed by a cleaning device or chemicals. Some reactors include automatic cleaning mechanisms to keep the lamp sleeves free of deposits that may form due to contact with the water. UV intensity sensor, flow meters, and UV transmittance monitors are used to monitor dose delivery in the reactor.

Two approaches are often used in lamp cleaning, the off-line chemical cleaning (OCC) and on-line mechanical cleaning (OMC) methods. In the OCC, the reactor is shut down, drained, and flushed with a cleaning solution (e.g., citric acid), rinsed, and reinstalled. LPHO systems typically use the OCC approach. OMC systems are built-in UV reactor components that consist of wipers that are driven by either screws attached to electric motors or pneumatic pistons. There are two types of wipers used in OMC systems: mechanical wipers and physical–chemical wipers. Mechanical wipers may consist of stainless-steel brush collars or Teflon® rings that move along the lamp sleeve. Physical–chemical wipers have a collar filled with a cleaning solution that moves along the lamp sleeve. The wiper physically removes fouling on the lamp sleeve surface, while the cleaning solution within the collar dissolves fouling materials. The use of mechanical and physical–chemical wipers does not require that the UV reactor be drained. Therefore, the reactor can remain on-line while the lamp sleeves are cleaned. Medium pressure mercury vapor lamp systems typically use OMC systems, because the higher lamp temperatures can accelerate fouling with certain water constituents (41).

Ballasts supply the UV lamps with the appropriate power to energize and operate the UV lamps. Ballasts use inductance (e.g., a coil or a transformer), capacitance, and a starting circuit. Power supplies and ballasts are available in many different configurations and are tailored to a unique lamp type and application. UV reactors may use electronic ballasts, magnetic ballasts, or transformers.

UV intensity sensors are photosensitive detectors that measure the UV intensity at a fixed point within the UV reactor. The sensors can indicate dose delivery by providing information related to UV intensity at different points in the reactor. The measurement responds to changes in lamp output due to lamp power setting, lamp aging, lamp sleeve aging, and lamp sleeve fouling. Depending on their position, the sensors may also respond to changes in UV absorbance of the water being treated. UV intensity sensors are composed of optical components, a photodetector, an amplifier, a housing, component, and an electrical connector. The optical components may include monitoring windows, light pipes, diffusers, apertures, and filters. Monitoring windows and light pipes are designed to deliver light to the photodetector. Diffusers and apertures are designed to reduce the amount of UV light reaching the photodetector, thereby reducing sensor degradation that is caused by UV irradiation. Optical filters are used to modify the spectral response, so that the sensor only responds to germicidal wavelengths (i.e., 200–300 nm). UV intensity sensors can be classified as wet or dry. Dry sensors monitor UV light through a monitoring window, whereas wet UV intensity sensors are in direct contact with the water flowing through the reactor. Monitoring windows and the wetted ends of wet sensors can foul with time and require cleaning similar to lamp sleeves.

An UV transmission monitor can measure the UV transmittance [or UV absorbance to calculate UVT by Eqs. (20) and (21)], which is critical to ensure the success of UV disinfection. The UVT can be determined either through grab samples with a laboratory instrument or on-line. The function of a temperature sensor is to protect UV lamp from overheating, and if the surrounding temperature surpasses the recommended operation temperature, the UV system will shut down.

The performance of an operating UV disinfection system must be monitored to demonstrate that adequate disinfection is occurring. Because the concentration of pathogenic organisms cannot be measured continuously in the UV-treated water and dose distribution cannot be measured directly real time, various strategies have been developed to monitor the dose/delivery. The following three important approaches are useful in monitoring the UV disinfection performance:

Approach One is UV intensity set-point approach. In this approach, measurements made by the UV intensity sensor are used to control the UV reactor. The sensor is located in a position that allows it to properly respond to both changes in UV output of the lamps and UVT of the water. The sensor output and the flow rate are used to monitor the dose delivery. The set-point value for UV intensity over a range of flow rates is determined during the validation.

Approach Two is UV intensity and UVT set-point approach. This approach is similar to *Approach One* with an exception. The UV sensor is placed close to the lamp, so that it only responds to changes in UV lamp output and UVT is monitored separately. For a specific flow rate, the UV intensity and UVT measurements are used to monitor the dose/delivery. The set-points for the UV intensity and UVT over a range of flowrates are determined during validation.

Approach Three is calculated UV dose approach. Similar to *Approach Two*, the UV intensity sensor is placed close to the lamp. Flow rate, UVT, and UV intensity are all monitored, and the output values are used to calculate the UV dose via a validated computational algorithm developed by the UV reactor manufacturer.

8.2. Operational Factors

UV absorbing compounds in typical source waters include organic substances [i.e., humic acid, fulvic acids, biochemical oxygen demand (BOD), chemical oxygen demand (COD), TOC, oil and grease, and other organics] and inorganic substances (i.e., iron, manganese, ammonia, nitrite, and nitrate) and other parameters (e.g., pH, total dissolved solids, and total suspended solids). The existence of these matters increases UV absorbance in water. Thus, the UV dose delivered to the microorganism decreases. The UV-absorbing compound concentrations vary due to different locations and season and rainfall conditions. Water treatment processes can reduce the UV absorbance of water. Coagulation, flocculation, and sedimentation remove soluble and particulate material, and filtration removes particles. Chemical oxidation by oxidants such as chlorine and ozone can reduce soluble material, precipitate metals, and reduce UV absorbance. Activated carbon adsorption also reduces soluble organic compounds and some heavy metals such as copper and lead ions. Because these treatment processes reduce UV absorbance, the lowest UV absorbance can be observed at the end of the treatment train. It is therefore recommended that UV disinfection be used after filtration and activated carbon adsorption (if applicable). The UV dose requirements are listed in Table 2. It should be mentioned that the requirements are based on post-filtration water.

Particle content can impact UV disinfection performance. Particles may absorb and scatter light, which reduces the UV intensity delivered to the organisms. Particle-associated microorganisms may be shielded from UV light, effectively reducing disinfection performance and causing a tailing or flattening of the dose–response curve when higher inactivation levels are desired (Fig. 3). Particles in source waters are diverse in composition and size. They include large molecules, microorganisms, clay particles, algae, and flocs. Water treatment unit processes such as coagulation, flocculation, sedimentation, and filtration are designed to remove particles from water. Organisms within coagulated and flocculated particles will be more difficult to inactivate; however, it is not a major concern as they are typically removed during filtration.

Chemicals used in water treatment can affect the UVT of water and the formation of agglomerated particles. They can also cause the fouling problems in water and treatment facilities. Water treatment processes upstream of the UV disinfection units can be operated to control and increase UVT. The design of the UV units can be optimized. Chemicals such as chlorine, ozone, and hydrogen peroxide oxidize UV-absorbing compounds; however, they may absorb UV light, which has some effects on UV absorbance. Among these chemicals, ozone and ferric iron have the greatest potential of impacting the UV absorbance of water. Oxidant residuals can be quenched by chemicals such as sodium thiosulfate and sodium bisulfite. The use of these chemicals, however, can increase the UV absorbance of water.

Wetted components that are contacted with water within an UV reactor can become fouled after it is operated for some time. Fouling on the external surfaces of the lamp sleeve reduces the transmittance of UV light from the lamps into the water, and dose delivery is reduced. Fouling on the UV intensity sensor windows reduces the intensity of UV light measured by the sensors, leading to under-prediction of dose delivery. Fouling on the inside surfaces of the reactor reduces reflection of UV light from those surfaces, which reduces the amount of UV light available for disinfection. Fouling on the wetted surfaces of an UV reactor is attributed to precipitation of organic and inorganic particles and temperature. Because the operation temperature of MP lamps is higher than LP lamps, the MP is more easily to be fouled.

Visible light emitted from UV lamps may promote algae and other organisms' growth in UV reactors and the surrounding piping. Depending on the species, their growth could cause taste and odor problems in the final effluent. Algae growth also depends on water temperature, pH, and nutrient concentration. The growth is a greater issue with MP lamps than LP lamps because MP lamps produce more light in the visible range.

8.3. Maintenance Factors

The most important maintenance factor for the UV reactor performance is the cleanliness of the surfaces through which radiation must pass. Surface fouling can result in inadequate performance, so a strict maintenance schedule is recommended.

An operator determines the need for reactor cleansing by draining and visually inspecting the surfaces. Open reactor systems are easily inspected. Systems with sealed vessels are inspected through portholes or manways in the reactor shell. Surfaces of submerged quartz systems become coated with an inorganic scale, very much like boiler scale. This is a particular problem in areas with hard water. Additionally, the inside surface of the quartz and the outer surfaces of the Teflon tubes eventually develop a grimy dust layer, primarily from airborne dirt and water vapor.

Fouling of the reactor's internal surfaces also is indicated by reduced performance and intensity measured by in-line probes. While these provide some indication of fouling, operators must still visually inspect the surfaces.

The fouled surfaces of lamps and quartz sleeves are cleaned manually with a mild soap solution and then swabbed with a rag soaked in isopropyl alcohol. The transmittance of the lamps and sleeves is measured after cleaning and those that have inadequate measurements are replaced. An inventory allows the plant operator to trace the operation of individual components. Quartz sleeves should last between 4 and 7 yr, but this varies by the application site. In Teflon systems, the lamps are on removable racks and should be cleaned and monitored in the same manner as the quartz systems. The Teflon tubes should also be cleaned with mild soap and swabbed with alcohol. Each tube should be monitored for transmittance, just as with the quartz sleeves. Monitoring may not be as straightforward because of the limited accessibility to the tubes and problems in obtaining direct measurements with a UV radiometer/detector.

9. UV DISINFECTION BY-PRODUCTS AND UV LAMP DISPOSAL

One of the important issues in water and wastewater disinfection is the formation of disinfection by-products, their environmental consequences, and prevention, control, and minimization of them. The major disinfectants are chlorine, chlorine dioxide, ozone, chloramines, and UV irradiation. It is well recognized that disinfection by chlorine, the most commonly used disinfectant, can cause formation of many DBPs, even though it is effective and the cost is low.

Compared to other disinfectants, UV disinfection produces fewer DBPs (3,6,41–43). Conventional UV irradiation does not appear to be of major current concern in the industry. For the treatment of groundwater and filtered drinking water, UV disinfection at typical doses has been shown not to impact the formation of trihalomethanes or haloacetic acids, two categories of DBPs currently regulated by the US EPA. Several studies have demonstrated low-level formation of non-regulated DBPs (e.g., aldehydes) as a result of UV irradiation to wastewater and raw drinking water sources. A study performed with filtered drinking water indicates no significant change in aldehydes, carboxylic acids, or total organic halides (3). The formation of UV DBPs (e.g., nitrophenols and *N*-nitrosoamines) does not occur when the technology is applied for disinfection of secondary municipal effluents that are used agriculture (41). It is therefore acceptable that UV DBPs can be omitted in design consideration. In practice, control and removal of its DBPs are not necessary.

Under some specific conditions, the formation of UV DBPs is worth considering. UV irradiation can cause a series of oxidation reactions, leading to the formation of oxidative by-products, especially if high-pressure UV systems are applied and the organic contents in the water are high (35). Some DBPs can be formed due to the production of powerful free radicals (e.g., OH·) in the water. The resulting concentrations and the types of DBPs depend on the concentrations of the organic substances (e.g., NOM) and the UV dose.

Nitrate, NO_3^-, is a very strong absorber of UV below 250 nm; a characteristic photoreaction of nitrate is reduction to nitrite, NO_2^- (42). The yield of NO_2^- from this reaction during UV disinfection is sensitive to both the dissolved inorganic and organic carbon content of natural water. The amount of NO_2^- formed during UV disinfection is important because public health concerns surrounding this compound have led to its being regulated at fairly low levels. The US EPA has set a MCL for NO_2^- of 1 mg/L (as N), while the comparable European Union Member States standard is 0.11 mg/L (as N).

When LP mercury lamps that emit primarily monochromatic light at 253.7 nm are applied in disinfection, NO_2^- production is negligible. More recent work using MP mercury lamps, which emit a range of UV and visible wavelengths down to approx 200 nm where NO_3^- absorbs very strongly, has shown that NO_2^- production is higher with these lamps (42). The concentration is below US water quality standards. However, the more stringent European Union standard may potentially be violated when these MP lamps are used. Control and minimization of NO_2^- species during UV disinfection with MP lamps are thus of immediate concern.

It is important to note that the spent UV lamps contain mercury, which is highly toxic. The spent UV lamps, therefore, must be properly collected and disposed of in accordance with governmental rules and regulations.

10. UV DISINFECTION OF AIR EMISSIONS

Air can carry various pathogens, like virus and spores. The areas of air disinfection by UV include sensitive areas (e.g., electronic, food, pharmaceutical); household, lab, hospital, clinic, and other public buildings; and odor control (44–48). UV can effectively remove pathogens in moving air and static air. Installing an UV unit before the humidifier in an air ventilation system is an effective method to prevent bacteria and virus from invading through water. In the upper side of some industry tanks and working places, the growth of pathogens is strictly avoided. As a clear disinfection method, an UV disinfection unit is often adopted in these situations.

There are a variety of UV air disinfection systems. Generally, they can be classified into upper-air systems and in-duct systems according to different installations. Upper-air systems are installed at an upper position of a room, where the UV units can be movable or just fixed to room wall, ceiling, or inlet/outlet of air recirculation systems. However, because the air flow and current in upper-air system is usually uncontrolled, it is difficult to establish a theoretical prediction model. In most cases, empirical models are often used. Furthermore, high UV exposure risk to personnel is a concern with upper-air systems. In-duct systems are installed in a ventilating or air conditioning system, where air flow rate, flow paten, and temperature are more easily controlled.

Unlike water-based UV disinfection applications, the UV air disinfection does not have prediction equations. Traditional microorganism under UV exposure decay rate was discussed in Eq. (17). The curve in S/S_0 (residual/initial microorganisms) and negative log format as a function of exposure time were plotted in Fig. 13 (curve 1 and 1', respectively). In UV disinfection in water systems, *E. coli* is used as the valid test microorganism. Also, in UV air disinfection systems, *Serratia marcescens* is recommended as an aerosolization test. In laboratory tests, its airborne rate constant and plate-based rate constant were determined at 0.002909 and 0.000718 $cm^2/\mu W$-s, respectively (51,52). In UV air disinfection, Eq. (15) is often used when mixing is complete and the exposure time is neither too short nor very long (51–53). However, two stages with shoulder region curve is often found in UV air disinfection applications (Fig. 13). The shoulder region changes with the UV intensity on the microorganism. The second stage represents the resistant fraction of microbes with the typical value ranging from 0.1% to 10% (51). Recently, Kowalski developed a mathematical model to predict the response of microorganisms exposed to UV light (51,52):

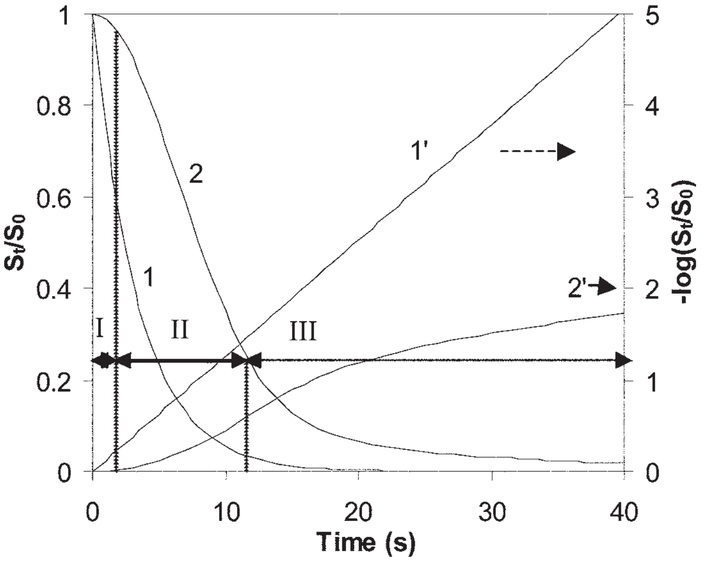

Fig. 13. Different approaches for prediction of UV air disinfection.

$$S(t) = (1-f)e^{-k_f It'} + fe^{-k_s It'} \tag{24}$$

$$t' = \begin{Bmatrix} \dfrac{t^2}{4t_c} & t \le 2t_c \\ (t-t_c) & t \ge 2t_c \end{Bmatrix} \tag{25}$$

where I = Intensity, mW/cm^2; t = exposure time, s; k_f = rate constant for fast decay population, cm^2/mW-s; k_s = rate constant for slow decay population, cm^2/mW-s; t_c = threshold of shoulder, s; f = resistant fraction of population; t_c can be determined by the Eq. (26), where A and B can be obtained through a lab experiment with a typical range being A = 5–12 and B = 0.001–0.1, $s(t)$ = surviving fraction of initial microbial population, and t' = adjusted exposure time, s.

$$t_c = Ae^{-BI} \tag{26}$$

where A = a constant defining the intercept at $I = 0$; B = a constant defining the slope of the plotted line of $\ln(t_c)$ as a function of I. Kowalski further developed a computer model to simulate a three-dimensional intensity field in a rectangular system. The detailed information can be found in related references (51,52,54).

Odor is usually caused by some volatile compounds generated by bacteria. The locations of most concern may be the upper side of sewage treatment basins, sludge treatment tanks, and some meat processing areas. The air emission often brings ammonia, sulfur compounds, indole, skatole, and other odor-causing compounds. Conventional odor control methods include scrubbing, biological filters, and activated carbon adsorption. UV-based oxidation units provide a simple and safe way to control odor. The strong oxidant of hydroxyl radical will oxidize the target odor-causing molecules and transfer them to odorless compounds. Compared to conventional odor-control strategies, a UV system has many advantages, including low cost, short contact time, environmentally friendly operation, and less demand for space. In addition, UV irradiation does not introduce any other chemicals and thus does not need waste disposal. Several approaches for the design of UV disinfection systems and the evaluation of germicidal effects are available in the literature (45,46).

11. UV ENGINEERING CASE HISTORY AND APPLICATIONS

11.1. Engineering Case History

The City of Fort Benton, Montana, USA, obtains drinking water from the Missouri River. The then current filtration plant (20–30 yr old) was in need of upgrading. Rather than building a new filtration plant, the city built a new 0.088 m^3/s (2-MGD) treatment plant in 1987. Water is drawn through collectors installed 6–7.5 m (20–25 ft) below the riverbed, a system that allows the riverbed to naturally filter the raw water. Turbidities of water entering the treatment plant average 0.08 NTU. No *Giardia* cysts have been found in the water (55).

The water is treated with UV radiation for primary disinfection, then chlorinated for secondary disinfection. An applied chlorine dosage of only about 1 mg/L is necessary. The entire water treatment system is housed in a 2.97 m^2 (32 ft^2) building. The UV disinfection system consists of six irradiation chambers, two control cabinets with alarms, chart recorders, relays, hour-run meters, lamp and power on-lights, six thermostats, electrical door interlocks, mimic diagrams, and six UV intensity monitors measuring the total UV output. Each irradiation chamber contains one 2.5-kW mercury vapor, medium-pressure arc tube, generating UV radiation at 253.7 nm.

The initial UV dosage is 41,000 $\mu W{\cdot}s/cm^2$ at a maximum water flow 104 L/s (1650 gal/min) through each irradiation unit. Expected arc tube life is 4500 operating hours, providing a minimum UV dosage of 25,000 $\mu W{\cdot}s/cm^2$. These conditions are designed to reduce concentrations of *E. coli* organisms by a minimum of 5 logs (i.e., 10^5 reduction).

The system is equipped with a telemetry control system and a fully automated backup system. Each bank of three irradiation chambers has two units on line at all times, with the third unit serving as a backup. In the event that the UV intensity decreases below acceptable limits (20,000 $\mu W{\cdot}s/cm^2$) in any of the chambers, the automatic butterfly valve will close, stopping flow through the chamber; at that time, the automatic butterfly valve on the standby unit will open. The alarm system is also activated if UV intensity decreases below acceptable limits in any of the chambers. The UV alarm system is interfaced with the automatic dialer and alarm system. In 1987, total equipment costs for the six-unit UV irradiation system with butterfly valves was US$74,587.

In accordance with the US Environmental Protection Agency, the “CT Values” for inactivation of viruses by UV radiation is independent of temperature, as shown in Table 4.

For the UV facility at Ft. Benton, the initial UV dosage of 41 $mW{\cdot}s/cm^2$ provides in excess of 3-log inactivation of viruses. However, after 4500 h of UV tube operation, the

Table 4
"CT Values" for Inactivation of Viruses by UV radiation

Log virus inactivation	CT values by UV ($mW\cdot s/cm^2$)
2.0	21
3.0	36

Table 5
Technological Status of UV Radiation in Comparison with Other Disinfection Processes

Technological options to meet regulatory requirements	Stage of acceptability	Size suitability	Comments
Chlorine	Established	All	Most widely used method; concerns about health effects of by-products
Chlorine dioxide	Established	All	Relatively new to the United States; concerns about inorganic by-products
Monochloramine	Established	All	Secondary disinfectant only; some by-product concerns
Ozone	Established	All	Very effective and requires a secondary disinfectant
Ultraviolet radiation	Established	All	Simple, no established harmful by-products and requires secondary disinfectant
Advanced oxidation (ozone plus H_2O_2 and ozone plus ultraviolet radiation)	Emerging	All	Not much information concerning disinfection aspects of this process

Source: US EPA.

anticipated decrease in UV dosage (to 25 $mW\cdot s/cm^2$) will provide only 2-log of viral inactivation.

Owing to the success of the UV facility at Ft. Benton, the City of New York is designing a 2020 million gallons per day (MGD) UV disinfection facility, which upon completion will be the largest UV disinfection facility in the world (56–58).

11.2. UV Engineering Aplications

US Environmental Protection Agency has compared ultraviolet radiation with other disinfection processes in terms of their technological status (Table 5), disinfectant production (Table 6), operation and maintenance (Table 7), process advantages and disadvantages (Table 8), and application points (Table 9).

Table 6
Disinfectant Production Considerations

	Chlorine	Chlorine dioxide	Mono-chloramine	Ozone	Ultraviolet radiation
Chemically stable	Yes	Yes	Yes	No	NA
On-site production required	No	Yes	Yes	Yes	Yes
Number of alternative on-site generation techniques	NA	3[a]	2[b]	3[c]	NA

Source: US EPA.

[a] Including:
1. Treating sodium chlorite solution with chlorine gas
2. Treating sodium chlorite solution with sodium hypochlorite and mineral acid
3. Treating sodium chlorite solution with mineral acid

[b] Including:
1. Adding ammonia to a water and chlorine solution
2. Adding chlorine to a water and ammonia solution

[c] Including:
1. Ambient air
2. Pure oxygen
3. Oxygen-enriched air

NA = not applicable.

Table 7
Disinfectant Application Considerations

	Cl_2	ClO_2	Monochloramine	O_3	UV
Optimum water pH	7	6–9	7–8	6	NA
By-products present	Yes	Yes	Yes	Yes	No
Operational simplicity	Yes	No	No	No[a]	Yes
Maintenance required	Low	Low	Low	High	High

Source: US EPA.

[a] Operationally simplified with an automated system.

NA = not applicable.

In comparison with other common disinfectants, such as chlorine, chlorine dioxide, monochloramine, and ozone, UV is simple, produces no harmful by-products (Tables 5–7), requires secondary disinfectant (Tables 5–8), requires on-site production and high maintenance (Tables 6 and 7), is very effective for viruses and bacteria, but inffective for water with *Giardia* cysts, high suspended solids, high color, high turbidity, or soluble organics (Table 8). UV is usually applied toward the end of the water treatment process to minimize presence of other contaminants that interfere with UV (Table 9). According to Wang (57,58), UV is also very effective for dechlorination, dechloramination, or deozonation if it is required in water or wastewater treatment.

Table 8
Advantages and Disadvantages of Five Disinfection Processes

Disinfectant	Advantages	Disadvantages
Chlorine	Effective. Widely used. Variety of possible application points. Inexpensive. Appropriate as both primary and secondary disinfectant.	Harmful halogenated by-products. Potential conflict with corrosion control pH levels, when used as a secondary disinfectant.
Ozone	Very effective. Minimal harmful by-products identified to date. Enhances slow sand and GAC filters. Provides oxidation and disinfection in the same step.	Requires secondary disinfectant. Relatively high cost. More complex operations because it must be generated on-site.
Ultraviolet radiation	Very effective for viruses and bacteria. Readily available. No harmful residuals. Simple operation and maintenance.	Inappropriate for water with *Giardia* cysts, high suspended solids, high color, high turbidity, or soluble organics. Requires a secondary disinfectant.
Chlorine dioxide	Effective. Relatively low cost. Generally does not produce THMs.	Some harmful by-products. Low dosages currently recommended by US EPA may make it ineffective. Must be generated on-site.
Chloramines	Mildly effective for bacteria. Long-lasting residual. Generally does not produce THMs.	Some harmful by-products. Toxic effects for kidney dialysis patients. Only recommended as a secondary disinfectant. Ineffective against viruses and cysts.

Source: US EPA.

Table 9
Desired Points of Disinfectant Application[a]

Chlorine	Toward the end of the water treatement process to minimize THM formation and provide secondary disinfection
Ozone	Prior to the rapid mixing step in all treatment processes, except GAC and conventional treatment processes; prior to filtration for GAC; post-sedimentation for conventional treatment. In addition, sufficient time for biodegradation of the oxidation products of the ozonation of organic compounds is recommended prior to secondary disinfection.
Ultraviolet radiation	Toward the end of the water treatment process to minimize presence of other contaminants that interfere with this disinfectant.
Chlorine dioxide	Prior to filtration; to assure low levels of ClO_2, ClO_2^-, and ClO_3, treat with GAC after disinfection.
Monochloramines	Best applied toward the end of the process as a secondary disinfectant.

[a] In general, disinfectant dosages will be lessened by placing the point of application towards the end of the water treatment process because of the lower levels of contaminants that would interfere with efficient disinfection. However, water plants with short detention times in clear wells and with nearby first customers may be required to move their point of disinfection upstream to attain the appropriate CT value under the Surface Water Treatment Rule.

NOMENCLATURE

a_{10}	Decadal (base 10) absorption coefficient, cm^{-1}
A	A constant defining the intercept at I_0
B	A constant defining the slope of the plotted line of ln(t_c) as a function of I
C	Light speed, 3.0×10^{10} cm/s
d	Thickness of water layer or vertical path length of the water in the Petri dish, cm,
D	UV dose, mJ/cm^2 or mW·s/cm^2
E	Photon energy, J
E_1	Higher-energy status, J
E_0	Lower-energy status, J
h	Planck's constant, 6.626176×10^{-34} J·s
I	UV light intensity in the bulk solution, mW/cm^2
I_{avg}	Average intensity within the suspension, mW/cm^2
I_0	UV intensity measured at the surface of suspension, mW/cm^2
I_{t}	UV intensity transmitted by the sample at the desired UV wavelength, mW/cm^2
I_{ave}	Average intensity of UV light, mW/cm^2
k_f	Rate constant for fast decay population, cm^2/µW·s
k_s	Rate constant for slow decay population, cm^2/mW·s
k	UV inactivation rate coefficient, cm^2/mW·s
k_d	Disinfection rate constant, s^{-1}
L	Distance from the UV lamp to the surface of the cell suspension
N_t	Total number (or density) of pathogens at time t
N_0^p	Total number (or density) of particles (greater than 10 µm)
N_0	Total number (or density) of pathogens prior to UV disinfection, MPN/100 mL
P	Total energy emitted by source matter, W·cm^2
S	Stefan–Boltzmann constant, 5.6703×10^{-12} W·cm^{-2}·K^{-4}
$s(t)$	Surviving fraction of initial microbial population
S_0	Number of microorganisms at time zero
S_t	Number of microorganisms at time t
SS	Suspended solids, mg/L
T	Temperature, K
t	Exposure time, s
t'	Adjusted exposure time, s
t_c	Threshold of shoulder, s
UFT	Unfiltered transmittance at 254 nm
ν	Frequency, Hz
λ	Wavelength, m, or Empirical coefficient
$\alpha\ \beta\ \gamma$	Empirical coefficients
$\pi\ \eta$	Empirical coefficients
AOP	Advanced oxidation process
BER	Base excision repair
BOD	Biochemical Oxygen Demand
BOD$_5$	5-d Biochemical Oxygen Demand
CFD	Computational fluid dynamics
COD	Chemical oxygen demand
DBPs	Disinfection byproducts
DNA	Deoxyribonucleic acid
HPC	Heterotrophic plate count
LP	Low-pressure
LPHO	Low-pressure high-output
LPLO	Low-pressure low-output

MCL	Maximum contaminant level
MCLG	Maximum contaminant level goal
MF	Microfiltration
MGD	Million gallons per day
MP	Medium pressure
MPN	Most probable number
mRNA	messenger RNA
NER	Nucleotide excision repair
NOM	Natural organic matter (NOM)
NWRI	National Water Research Institute
OCC	Off-line chemical cleaning
OMC	On-line mechanical cleaning
PFU	Plaque-forming units
PRE	Photo-reactivating enzyme
RNA	Ribonucleic acid
RO	Reverse osmosis
rRNA	ribosomal RNA
SARS	Severe acute respiratory syndrome
SS	Suspended solids
TDS	Total dissolved solids
THMs	Trihalomethanes
TOC	Total organic carbon
tRNA	transfer RNA
US EPA	United State Environmental Protection Agency
UV	Ultraviolet
UVT	UV Transmittance
WHO	World Health Organization

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11
Water Chlorination and Chloramination

Lawrence K. Wang

CONTENTS

1. INTRODUCTION

Many chemicals function as both oxidizing agents (i.e., oxidants) and disinfecting agents (i.e., disinfectants); therefore, both oxidizing and disinfecting properties must be considered when selecting a chemical. The important characteristics of chlorine, chlorine dioxide, monochloramine, ozone, and UV radiation are described in many chapters of this handbook series (1–3). This chapter places emphasis on chlorination and chloramination of potable water. Chlorination and chloramination of wastewater, sludge, and septage are also important (1–10), but will be introduced in separated chapters of this handbook series.

The process involving the application of chlorine to drinking water, wastewater, industrial effluent, sludge, septage, swimming pool water, etc., to disinfect or to oxidize undesirable pathogens and compounds is termed chlorination (1–10). When chloramines (instead of chlorine) are used as a disinfectant/oxidant, the process is chloramination (1).

When chlorination process is used for treatment of sludge and septage, it can also be called "chlorine stabilization" process (3,5–8).

A device or process equipment that adds any chlorine compounds, in solid, gas, or liquid form, to water, wastewater, or sludge to kill infectious microorganisms or undesirable substances is a chlorinator (8–9). That part of the treatment facility where water, wastewater, or sludge is treated by chlorine for disinfection and oxidation is a chlorine contact chamber (CCC).

Theories and principles of various halogenation processes (including chlorination and chloramination) have been introduced in another chapter, entitled, "Halogenation and Disinfection," in Volume 3 of this handbook series (1). This advanced chapter emphasizes the detailed technical information on the process equipment, various applications,

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and process troubleshooting, etc. In addition, the modern advanced electrolytic technology for on-site hypochlorite production is also introduced.

1.1. Chlorine

Chlorine is an excellent disinfectant and oxidant, and is also a good chlorinating agent. It provides a stable chlorine residual for the potable water distribution system if the water is free of chlorine-demanding ammonia and organic materials (1–22). In addition to potable water disinfection application, chlorine also disinfects and oxidizes the pathogens and contaminants in the wastewater, sludge, septage, cooling tower water, and swimming pool water (23–27). Because chlorine can produce trihalomethanes (THMs) and other halogenated (TOX) and nonhalogenated organic compounds, the use of chlorine should be monitored, particularly when THM and TOX precursors are present. Some of the nonhalogenated oxidation products that result from chlorination of humic and fulvic acids are identical to those produced by other disinfectants/oxidants, such as potassium permanganate, ozone, and chlorine dioxide.

1.2. Monochloramine

Monochloramine is a weak cysticidal disinfectant and a poorer virucide. Therefore, the contact times and concentrations required for adequate primary disinfection of water are much longer and higher than with chlorine, chlorine dioxide, or ozone. When monochloramine is generated, dichloramine can be present. Water containing chloramines can be fatal to individuals on kidney dialysis, so local hospitals and drinking water treatment centers must be warned against using water containing chloramines for these patients. Monochloramine is also a weak oxidant, and its slow dissociation in water to free chlorine produces traces of halogenated organic materials. Monochloramine is not recommended as a primary disinfectant in potable water treatment because its inactivation of *Giardia* cysts is slow and it is a poor virucide (1).

Monochloramine may be produced in three ways: (a) adding ammonia to water containing chlorine, (b) adding chlorine to water containing ammonia, and (c) using a preformed solution of monochloramine. Each technique is discussed in below.

1.2.1. Addition of Ammonia into Water Containing Chlorine

Adding ammonia to water treated with chlorine (the first method) will form THMs and other by-products associated with chlorination during the chlorine contact time used for disinfection or oxidation purposes. In this case, the benefit from using an alternative disinfectant to chlorine is negated. Adding ammonia will arrest THM generation; however, the THM level will remain as produced from the initial chlorination contact time. Chloramination is practiced for both potable water treatment and sludge treatment, although the former is more popular.

1.2.2. Addition of Chlorine into Water Containing Ammonia

Adding chlorine to water already treated with ammonia (the second method), assuming proper mixing, will produce insignificant concentrations of free chlorine and, consequently, lower concentrations of halogenated materials. However, disinfection is less effective because the weak disinfectant monochloramine is performing the disinfection function, rather than free chlorine.

This problem is exacerbated if organic nitrogen materials are already in the water. They react with free chlorine and chloramines to form organic chloramines, and all organic chloramines are even weaker disinfectants than monochloramine. Available field analytical methods do not distinguish between inorganic monochloramine and organic chloramines in water. A utility with raw water containing organic nitrogen materials that adds ammonia and then chlorine to produce monochloramine for primary disinfection may seriously overestimate the degree of disinfection attained.

1.2.3. *Addition of a Performed Monochloramine Solution into Water*

Using a preformed monochloramine solution (the third method) creates the same problem of producing less effective organic chloramines, if organonitrogen compounds are present.

2. POTABLE WATER CHLORINATION

2.1. *Surface Water Treatment Rules*

On June 29, 1989, the Surface Water Treatment Rules (SWTR) and the Coliform Rule were promulgated. According to the SWTR, all public water systems using surface water or groundwater under direct influence of surface water, must disinfect and may be required to filter if certain source water quality requirements and site-specific conditions are not met. The Maximum Contaminant Level Goals (MCLGs) established in the rule are:

- *Giardia lamblia* = 0
- Viruses = 0
- *Legionella* = 0

No MCLGs were set for turbidity and heterotrophic plate count (HPC). Treatment requirements also were established in lieu of MCLs for *Giardia*, viruses, HPC, *Legionella*, and turbidity. Treatment must reliably achieve at least 99.9% removal/inactivation of *Giardia lamblia* cysts and 99.99% removal/inactivation of viruses (1,4,5).

The Coliform Rule requires all public water systems to meet the coliform MCL and monitor total coliform with frequencies depending on population served, and requires small systems to conduct a sanitary survey. To comply with the coliform MCL, no more than 50% of all total coliform samples per month can be total coliform-positive.

The chlorination process applied to the water treatment system before the filtration process is prechlorination, predisinfection, or primary disinfection. When chlorination is applied to water treatment after filtration, it is termed postchlorination, post-disinfection, or secondary disinfection. The disinfectants used in primary disinfection and secondary disinfection are termed primary disinfectant and secondary disinfectant, respectively.

Other primary disinfection technologies—chlorine, chlorine dioxide, ozone, UV radiation, and organic disinfectants—are discussed elsewhere (1–3,17–27) in detail. Because most of the utilities that are affected by the Surface Water Treatment Rules and the Ground-Water Disinfection Treatment Rules serve less than 10,000 persons, this chapter will emphasize the applications of chlorination and chloramination processes to both small and large utilities. Table 1 indicates that both chlorination and chloramination are comparatively simpler than ozonation UV processes.

Table 1
Disinfectant Application Considerations

	Cl_2	ClO_2	Monochloramine	O_3	UV
Optimum water pH	7	6–9	7–8	6	NA
By-products present	Yes	Yes	Yes	Yes	No
Operational simplicity	Yes	No	No	No[a]	Yes
Maintenance required	Low	Low	Low	High	High

Source: US EPA.
NA = not applicable.

2.2. *Potable Water Chlorination Process Description*

Chlorine is the most common primary and secondary disinfectants used in the United States. It is available as a gas, solid, or aqueous solution. Chlorine gas is used most frequently, especially by large utilities, because of its lower cost. Chlorine in its solid form is calcium hypochlorite, $Ca(OCl)_2$; the liquid form is available as sodium hypochlorite solution, NaOCl.

This section describes the chlorination process, including the physical and chemical factors affecting its efficiency and applicability to specific sites. The equipment, chemical, and operating and maintenance considerations relevant to the three physical forms of chlorine are discussed later.

Chlorine undergoes chemical reactions when added to water, and the resulting compounds inactivate or kill undesirable microorganisms. Chlorine gas will form hydrochloric and hypochlorous acids according to the following reaction:

$$Cl_2 + H_2O \rightarrow HCl + HOCl \qquad (1)$$

The hypochlorous acid reacts further depending on the pH of the solution. The higher the pH, the more it will react, as shown below:

$$HOCl \rightarrow (OCl)^- + H^+ \qquad (2)$$

where Cl_2 = chlorine, H_2O = water, HCl = hydrochloric acid, HOCl = hypochlorous acid, $(OCl)^-$ = hypochlorite ion, and H^+ = hydrogen ion.

The concentration of hydrogen ions in the water determines the pH. The more hydrogen ions present, the lower the pH. At neutral pH (pH = 7.0), almost 80% of the chlorine is in its most effective disinfecting form, hypochlorous acid; the remainder exists in the less effective disinfecting form, hypochlorite ion. Increasing pH reduces the total disinfecting strength of the solution because it causes an increasing amount of hypochlorous acid to form more hypochlorite ion. At pH 8.0, for example, nearly 80% of the chlorine is present as the less effective hypochlorite ion. Because pH is extremely sensitive to both chlorination and effluent corrosion control, important corrosion indexes are presented in Appendix A for reference by the readers.

Appendix B gives CT values for inactivation of *Giardia lamblia* cysts with free chlorine (2.0 mg/L). At any given concentration of chlorine, the CT values increase rapidly as the pH rises above 7.0. This is also true at each temperature listed. Appendix C presents the CT values for inactivation of viruses by free chlorination. Figure 1 shows the relationship between pH and the concentration of hypochlorous acid. Effective pH

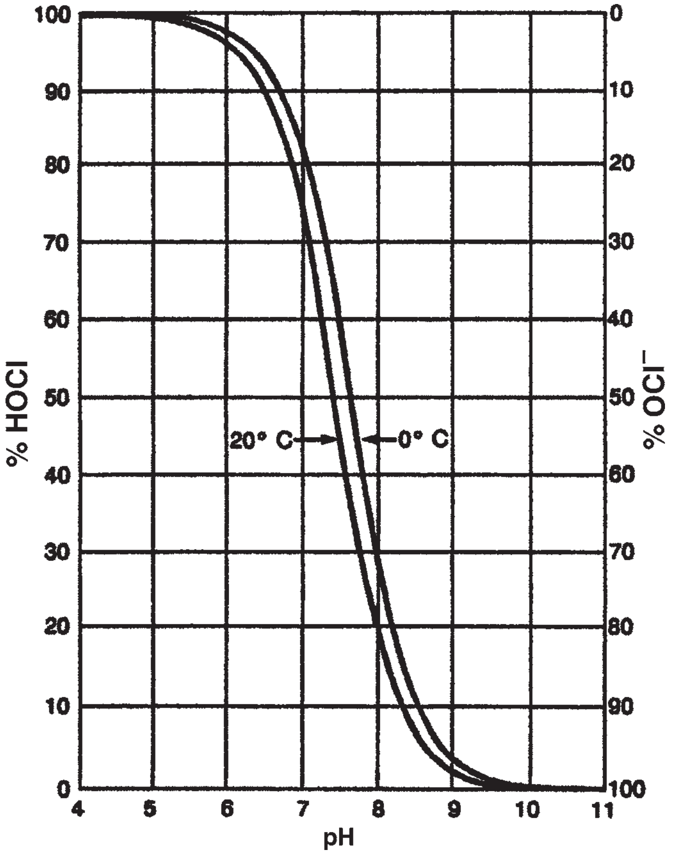

Fig. 1. Distribution of hypochlorous acid and hypochlorite ions in water at different pH values and temperatures of zero to 20°C (US EPA).

control is essential to achieve a desired level of disinfection for systems relying upon chlorination.

When sodium hypochlorite (liquid) or calcium hypochlorite (solid) is used for chlorination, the resulting chemical reactions produce alkaline (basic) compounds as follows:

$$\mathrm{NaOCl + H_2O \rightarrow HOCl + NaOH} \tag{3}$$

$$\mathrm{Ca(OCl)_2 + 2H_2O \rightarrow 2HOCl + Ca(OH)_2} \tag{4}$$

where NaOCl = sodium hypochlorite, NaOH = sodium hydroxide, $Ca(OCl)_2$ = calcium hypochlorite, and $Ca(OH)_2$ = calcium hydroxide.

The resulting hydroxides increase the pH of the water, thereby lowering the concentration of hypochlorous acid and diminishing disinfection efficiencies. Therefore, the ability to adjust and control pH is critical when using the hypochlorite forms of chlorine.

Hypochlorous acid, a strong disinfecting agent, is one of the most powerful oxidizing agents, and an effective chlorinating agent. In addition to acting on target organisms, it reacts with many substances in water, as evidenced by the production of THMs and other halogenated compounds associated with chlorination. Chlorine also produces considerable quantities of nonhalogenated organic oxidation products, e.g., aldehydes, acids, and ketones.

Adequate chlorine concentration will achieve effective disinfection of currently regulated microorganisms. Because chlorine will react with many substances in the water, the "chlorine demand" of these other substances must be satisfied before an excess of free chlorine is available for disinfection. Thus, the amount of chlorine necessary to effectively disinfect must be greater than the chlorine demand of the water.

The "available chlorine residual" is the amount of chlorine that remains available for disinfection after the chlorine demand is satisfied. This is quantified by an approximate analytical testing procedure.

The chlorine residual may be either a free available residual, a combined available residual, or a combination of the two. Free available chlorine refers to the total concentration of hypochlorous acid and hypochlorite ions. Combined available chlorine is the total concentration of mono- and dichloramines, plus nitrogen trichloride and organic nitrogen chlorine–containing compounds (1).

Because of the many complex reactions that take place, the relationship between the amount of chlorine added and the available residual does not become linear until a certain minimum amount of chlorine has been added. In other words, increasing the amount of chlorine does not result in a proportional increase in the available residual until that "chlorine breakpoint" is reached. A series of chemical reactions causes the breakpoint phenomenon. Water may contain small amounts of reduced substances such as sulfides and ferrous iron, as well as organic materials, organic nitrogen materials (amino acids and proteins), and some ammonia, all of which exert a chlorine demand. The initial amount of chlorine added is taken up by reactions with these contaminating substances, leaving no free available chlorine. After the chlorine demands of the reduced substances have been satisfied, the hypochlorous acid will begin to react with ammonia, organic nitrogen materials, and some of the organics present to yield chloramines, oxidized organics, and chlorinated organic compounds. Next, the addition of more chlorine may induce the hypochlorous acid to oxidize or chlorinate some of the same materials it has just created. At this point, a decrease in the amount of residual (combined residual) is observed. When these oxidation reactions are complete, the breakpoint is reached, and adding more chlorine finally increases the available chlorine measured.

Figure 2 shows a "chlorine breakpoint curve," with the amount of chlorine shown on the horizontal scale and the amount of available chlorine shown on the vertical scale. According to the curve, the chlorine residual will not appear until 3 mg/L of chlorine is added. After this point, additional chlorine will result in an increase in residual. However, at about 6 mg/L, further additions of chlorine actually bring about a decrease in residual until the breakpoint is reached (8 mg/L in this diagram). After breakpoint is achieved, additional chlorine finally results in a proportional accumulation of residual free available chlorine.

Actual reactions are considerably more complex than described above because of the time and concentration dependencies of these processes. For these reasons, a breakpoint curve is difficult to recreate and predict; thus, individual tests must be run seasonally, and the data plotted to define the breakpoint for each water supply.

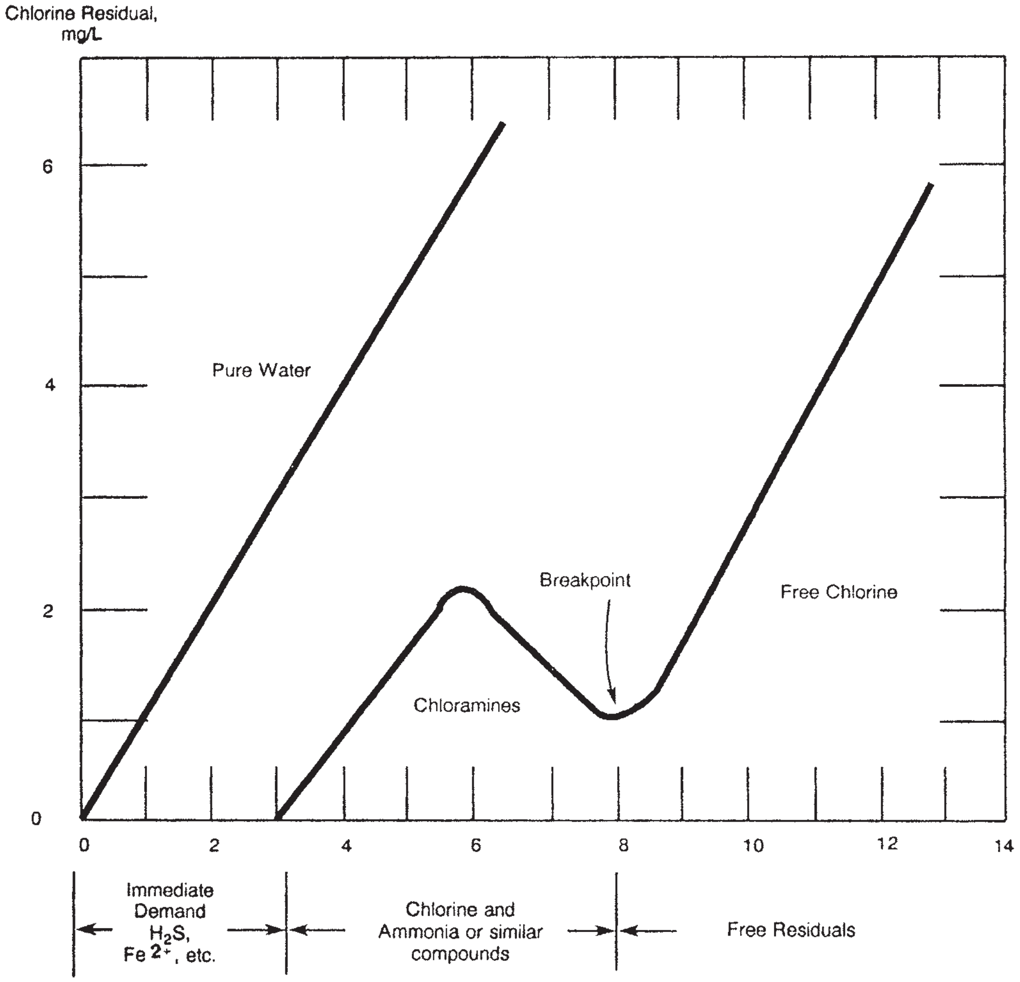

Fig. 2. Graphical representation of the breakpoint chlorination reaction. The straight line at the left shows that chlorine residual is proportional to dosage in pure water. When impurities are present, they exert a chlorine demand (US EPA).

2.3. Design and Operation Considerations

Chlorine in its free state ($HOCl + OCl^-$) is an effective disinfectant and inactivates most microorganisms in a matter of minutes. However, effective disinfection with chlorine requires careful attention to the following factors.

2.3.1. Free Available Chlorine Concentration

Free available chlorine concentration. The concentration must be high enough to always be detectable at the farthest points in the distribution system to effect both primary and secondary disinfection.

2.3.2. pH

The pH should be maintained as close to 7.0 as is practical or consistent with other water quality aspects. This is necessary to maintain as much of the chlorine residual as possible in the hypochlorous acid form. New US Environmental Protection Agency (US EPA) regulatory initiatives, however, are encouraging utilities to adjust the pH of their product water to 8.0 in order to minimize corrosion effects (4). This higher pH will necessitate higher doses of chlorine to attain primary disinfection. The readers are referred to Appendix A for corrosion control when determining the proper pH for secondary disinfection control.

2.3.3. *Chlorine Contact Time*

Chlorine contact time must be long enough to achieve the desired degree of microbial inactivation (i.e., attain the CT value that applies to the concentration of chlorine and the pH and water temperature).

2.3.4. *Mixing*

The chlorine contactor should either contain sufficient baffling to eliminate the possibility of short-circuiting or an external mixing device should be added.

2.3.5. *Temperature*

Temperature also affects the disinfection rate; the higher the temperature, the faster the rate of disinfection. Consequently, at higher temperatures, the CT values become lower.

2.3.6. *Types of Chlorine and Chlorination System*

Chlorine can be in the form of gas, solid, or liquid. Selection of the appropriate type of chlorine and its chlorinator depends on a number of site-specific factors including:

- Availability of chlorine source chemical
- Capital cost of the chlorination system
- Operation and maintenance costs of the equipment
- Chemical costs
- Location of the facility
- Operator skills
- Safety considerations
- Local regulations regarding the storage of chlorine gas

Each chlorination method provides the same disinfecting power on a pound for pound basis of available chlorine at the same pH. The choice of method depends primarily on the availability of each chemical and the construction and annual operating costs for the different systems.

2.4. Process Equipment and Control

2.4.1. *Chlorine Gas*

Elemental chlorine is a toxic, yellow–green gas at standard temperatures and pressures. It is supplied as a liquid in high-strength high-pressure steel cylinders, and vaporizes rapidly when released. As the liquid evaporates, its temperature falls and slows the evaporation rate, necessitating the use of a container manifold or vaporizer.

Chlorine gas can be supplied in cylinders with capacities of 45.4–907.2 kg (100–2000 lb), or in tank cars. The quantities required by small water systems can be purchased from local chemical or swimming pool chemical suppliers.

There are two basic types of gas chlorinators: (a) pressure-operated direct gas feed units and (b) vacuum-operated solution-feed units. Direct gas feed units supply pressurized

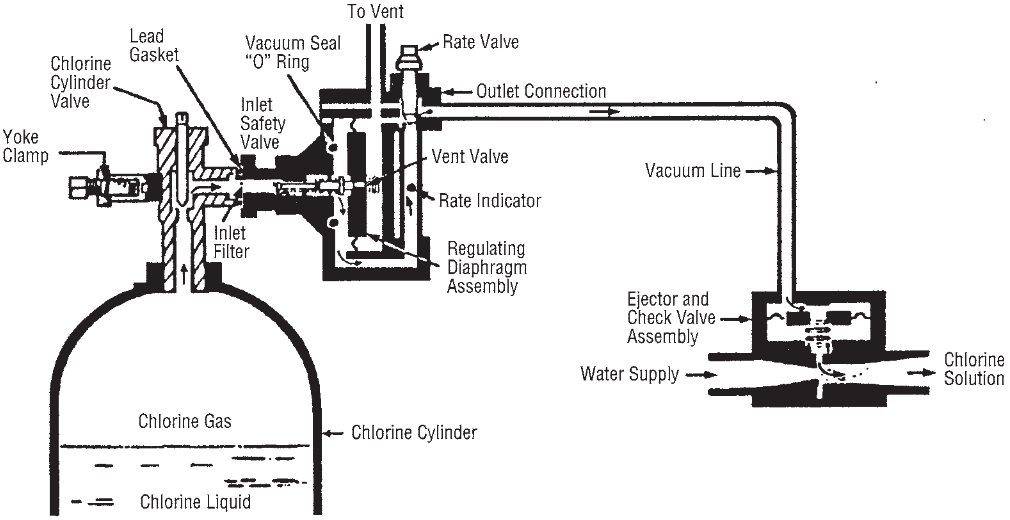

Fig. 3. Solution feed-gas chlorination system (US EPA; Capital Controls).

chlorine gas to the water and are used only when electrical power is unavailable or the water pressure differentials are insufficient to operate a solution feed unit. The solution feed units mix the gas with a side stream of water to form a solution of hypochlorous acid and hypochlorite ion, which is then mixed with the main stream. These units operate on a vacuum-controlled basis, automatically shutting off if the side stream flow is interrupted. The solution feed system is safer to operate and, therefore, is preferred by most operators. Figure 3 shows a solution feed system.

The most sophisticated system includes the basic system plus two scales, a gas mask, a diffuser corporation cock (to allow connection under water line pressure), a flow-pacing chlorine addition system, a flow meter, a booster pump and piping, and a chlorine leak detector.

A small water treatment system is generally sized to treat water volumes up to at least 0.044 m^3/s (1 MGD). For small solution-feed systems treating from 9.5 m^3/d to 0.044 m^3/s (2500 gpd to 1 MGD), operating and maintenance costs for gas chlorination systems are approximately the same. About 1630 kWh each year is required to run the booster pump and approx 2560 kWh annually is required for the building housing the system, assuming a 58.1-m^2 (625-ft^2) building. Maintenance labor cost and material costs for miscellaneous repair of valves, electrical switches, and other equipment replacement cost will be the extra.

2.4.2. Sodium Hypochlorite Solution

Sodium hypochlorite solution is usually supplied commercially in concentrations of 5% and 15% chlorine by weight. It is easier to handle than gaseous chlorine or calcium hypochlorite. Metered chlorinators deliver the solution directly into the water.

Sodium hypochlorite solutions lose their disinfecting (oxidizing) power during storage, and thus should be stored in a cool, dark, dry area. No more than a 1-mo supply of the chemical should be purchased at one time to prevent loss of available chlorine. The material is supplied in glass or plastic bottles, carboys, or lined drums ranging in size from 1.89 to 208.2 L (0.5 to 55 gal). Bulk shipment by tank truck is also a common form of transport.

Sodium hypochlorite solution is more costly per weight (pound) of available chlorine and does not contain the high concentrations of chlorine available from chlorine gas. However, the handling and storage costs are lower than for chlorine gas.

There are two types of process equipment to feed hypochlorite solution: (a) basic system and (b) complex systems. Both basic and complex systems are electrically and hydraulically activated. The basic liquid hypochlorination systems include two metering pumps (one serving as a standby), a solution tank, diffuser, and appropriate quantities of tubing. The more complex system adds a diffuser corporation cock, antisiphon backflow preventer, a safety housing enclosure, a flow pacing system, and a flow meter and signal.

2.4.3. On-Site Generation of Low-Strength Hypochlorite

An on-site generation technique for hypochlorite solutions has recently been developed. This system consists of a two-cell unit, in which a brine solution (salt in water) is electrolyzed, producing a solution of hypochlorous acid in one cell and a solution of caustic (sodium hydroxide) in the other, according to the following equation:

$$Na^+ + Cl^- + 2H_2O + e^- \rightarrow HOCl + NaOH + H_2 \tag{5}$$

where Na^+ = sodium ion, Cl^- = chloride ion, e^- = electron, NaOH = sodium hydroxide, and H_2 = hydrogen.

Using on-site generation avoids the purchase and storage of large volumes of chlorine gas or hypochlorite solutions, but there are significant disadvantages. The generation process produces hydrogen, which poses fire and explosion hazards, and sodium hydroxide, which is a caustic solution that requires proper disposal. Also, the cost per pound of available chlorine is typically much higher for on-site generation. However, certain site-specific considerations may make on-site generation a preferred disinfection technique. The technology for generation of the low-strength sodium hypochlorite solution (0.2–0.8% chlorine by weight) according to the above chemical equation is well established.

2.4.4. On-Site Generation of Chlorine Gas and Caustic and/or Ultra-Pure High-Strength Hypochlorite

Recently modern technologies have been developed for on-site generation of high-strength sodium hypochlorite (13,33). It has not been widely used for on-site generation of low-strength sodium hypochlorite (34). Generation of chlorine gas (at atmospheric pressure) and caustic soda and/or high-strength ultra-pure hypochlorite solution (containing 10–15% chlorine by weight) is the newer technology (13,33). Figures 4–6 illustrate the modern on-site chlorine generation system. As shown in Fig. 4, there is a selective ion-exchange membrane placed between the anode and cathode in the electrolytic cell. The selective membrane will only allow sodium ions to pass to the cathode cell chamber. Brine and water are introduced from the bottom of the cell. In the presence of DC power, sodium ions from the brine in the anode chamber go through the membrane and stay in the cathode chamber where sodium ions react with hydroxide ions forming sodium hydroxide solution. In the cathode chamber, hydroxide ions dissociate from water becoming hydrogen gas on the top of the reactor cell. In the anode cell

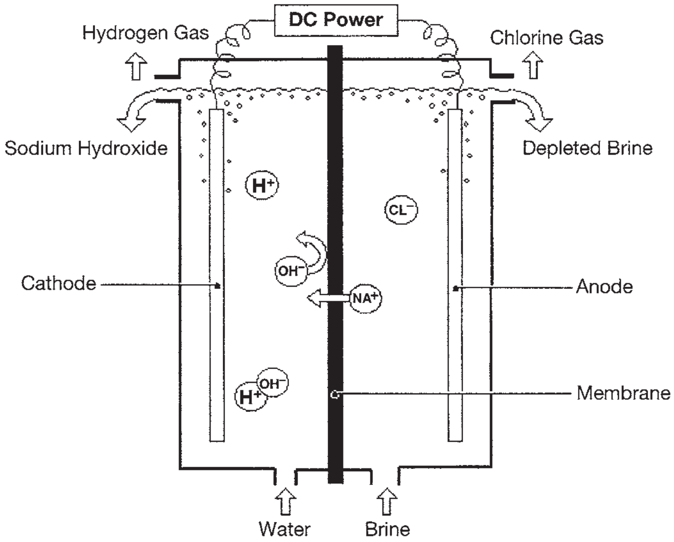

Fig. 4. Typical separated electrolytic cell schematic for on-site chlorine gas generation (Electrolytic Technologies Corporation, North Miami Beach, FL 33179).

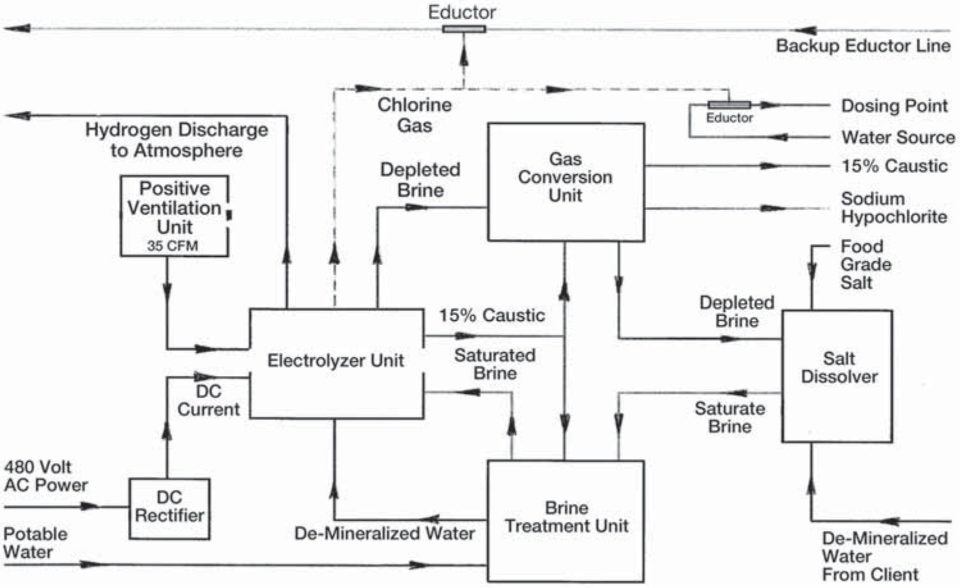

Fig. 5. On-site chlorine gas and caustic generation system schematic (Electrolytic Technologies Corporation, North Miami Beach, FL 33179).

chamber, chloride ions dissociate from brine, forming chlorine gas on the top of the reactor cell. The following are the chemical reactions:

Anode Reactions

$$2NaCl \rightarrow 2Na^+ + 2Cl^- \quad (6)$$

$$2Cl^- \rightarrow Cl_2 \quad (7)$$

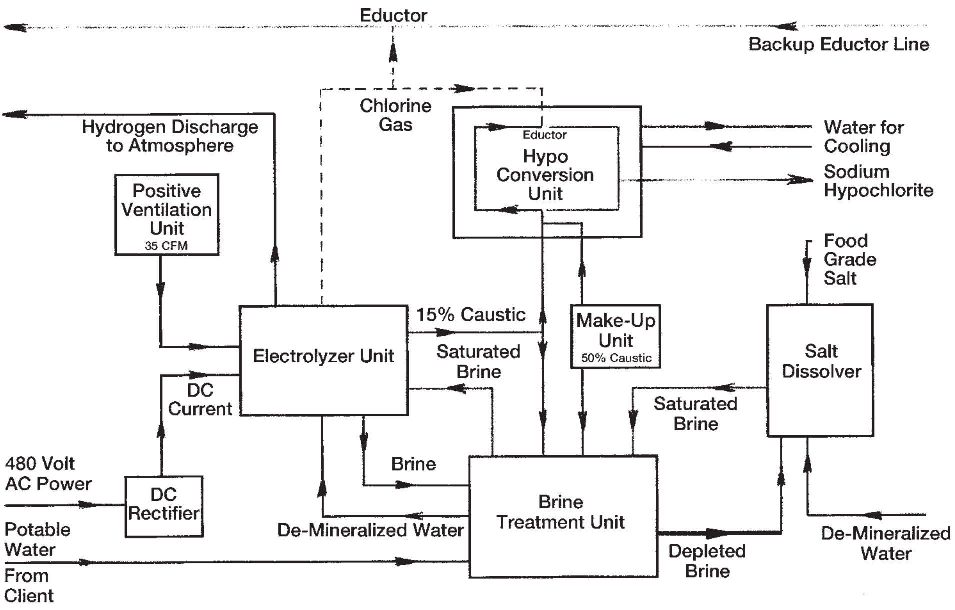

Fig. 6. On-site ultra pure hypochlorite generation system schematic (Electrolytic Technologies Corporation, North Miami Beach, FL 33179).

$2Na^+$ flow through membrane to cathode

Cathode Reactions

$$2H_2O \rightarrow 2H^+ + 2OH^- \tag{8}$$

$$2Na^+ + 2OH^- \rightarrow 2NaOH \tag{9}$$

$$2H^+ \rightarrow H_2 \tag{10}$$

where NaCl = brine solution, Cl_2 = chlorine gas, H_2O = water, NaOH = sodium hydroxide or caustic soda, and H_2 = hydrogen gas.

Figure 5 is the on-site chlorine gas and caustic generation system schematic (13). In this schematic, the produced chlorine gas is directly used in the water treatment plant for disinfection and oxidation. The following are the production steps involving chlorine gas and caustic generation:

- Salt is combined with pre-conditioned water (i.e., low hardness) to form saturated brine.
- The brine is then purified prior to entering the electrolytic cell.
- AC power is rectified to DC and supplied to the electrolytic cell.
- Chlorine gas and sodium hydroxide are primary products of the electrolytic process.
- Brine, saturated with chlorine gas, is discharged from the cell to a separation vessel from which dissolved chlorine gas is extracted by air stripping.
- Sodium hydroxide (caustic soda) is discharged from the cell using a controlled flow of demineralized dilution water to produce a final concentration of 15% solution.

Figure 5 is the on-site ultra-pure hypochlorite generation system schematic (13). The same electrolyzer unit is used in the two schematics (Figs. 5 and 6), except there are a few minor differences; in the new schematic shown in Fig. 6, the chlorine gas and sodium hydroxide can be used independently or combined *in situ* to form high-strength (10–15%) sodium hypochlorite (ultra-pure hypochlorite). Chlorine production is proportional to the power supplied. The following is the chemical reaction for sodium hypochlorite Na(OCl) production:

$$Cl_2 + NaOH \rightarrow Na(OCl) + HCl \quad (11)$$

As this book is being prepared, the Long Beach Water Department (LBWD) is investigating alternatives to pressurize gaseous chlorine at the treatment plant and is testing the feasibility of an on-site "on-demand" chlorine gas generation system. The trial system is approx 700 lb/d and is applied to the raw water for hydrogen sulfide control. If the "on-demand" chlorine gas generator is demonstrated to be feasible, a full-scale system (approx 6000 lb/d) is to be designed and installed at Long Beach's 62.5 MGD treatment plant, which serves approx 500,000 customers in Long Beach, CA (13).

2.4.5. *Solid Calcium Hypochlorite*

Calcium hypochlorite is a white solid that can be purchased in granular, powdered, or tablet form. The chemical is good for small water treatment plant disinfection applications. For disinfection of swimming pool water, the solid calcium hypochlorite is also frequently used .

Dry solid calcium hypochlorite contains 65% available chlorine and is readily soluble in water. The chemical is available in 0.9-, 2.3-, 3.6-, and 15.9-kg (2-, 5-, 8-, and 35-lb) cans and 362.9-kg (800-lb) drums, which are usually resealable. Calcium hypochlorite is a corrosive material with a strong odor and requires proper handling.

When packaged, calcium hypochlorite is very stable; therefore, an annual supply can be purchased in a single procurement. However, it is hygroscopic (readily absorbs moisture), and reacts slowly with atmospheric moisture to form chlorine gas. Therefore, shipping containers must be emptied completely or carefully resealed. Bulk handling systems cannot be used.

Typically, the entire contents of a calcium hypochlorite container are emptied into a mixing tank where they are readily and completely dissolved in water. The resulting corrosive solution is stored in and fed from a stock solution vessel constructed of corrosion-resistant materials such as plastic, ceramic, glass, or rubber-lined steel. Solutions of 1% or 2% available chlorine can be delivered by a diaphragm-type, chemical feed pump or metering pump.

Equipment, operating, and maintenance costs for calcium hypochlorite solution feed systems are similar to those for sodium hypochlorite feed systems. The equipment needed to mix the solution and inject it into the water being treated is the same.

A 9.5-m^3/d (2500-GPD) water treatment plant using a 5 mg/L dosage of chlorine needs 0.104 lb chlorine/d. Because solid calcium hypochlorite contains 65% available chlorine, 15.95 kg/d (0.16 lb/d) is required. (1 GPD = 1 gal/d = 3.785 L/d.)

2.5. Design Example

2.5.1. *Design Criteria*

Water treatment plants employ both primary and secondary disinfection: (a) Primary disinfection achieves the desired level of microorganism kill or inactivation; and (b) secondary disinfection ensures a stable residual concentration of disinfectant in the finished water to prevent microbial growth in the distribution system (4,7,14,17,18).

Major primary disinfectants are chlorine, ozone, chlorine dioxide, and ultraviolet (UV) radiation. Major secondary disinfectants are chlorine and monochloramine. Some disinfectants can be used for both processes.

The 1986 Amendments to the Safe Drinking Water Act (SDWA) require all public water suppliers to disinfect drinking water. In addition, inorganic and organic chemicals will be regulated by means of Maximum Contaminant Levels (MCLs). Since some disinfectants can produce chemical by-products, the dual objective of disinfection is to provide the required level of organism destruction while remaining within the MCLs for by-products set by the US Environmental Protection Agency (US EPA).

Chlorine has been the most widely used disinfectant in the United States; however, it produces trihalomethanes (THMs) and other halogenated organic compounds in drinking water. Because of this, water suppliers are beginning to utilize other disinfectants, such as ozone, chlorine dioxide, and monochioramine, or combinations of disinfectants, such as ozone followed by chlorine.

According to the amendments to the SDWA, all public water suppliers, including those that rely on groundwater, will have to disinfect drinking water before distribution. To ensure compliance with all applicable regulations (both current and anticipated), the specific objectives of disinfection are to (a) ensure 99.9% (3-log) and 99.99% (4-log) inactivation of *Giardia lamblia* cysts and enteric viruses, respectively; (b) ensure control of other harmful microorganisms; (c) not impart toxicity to the disinfected water; (d) minimize the formation of undesirable disinfection by-products; and (e) meet the maximum contaminant levels (MCLs) for the disinfectants used and by-products that may form (4).

Disinfection alone, or a combination of disinfection and filtration, can achieve the minimum mandatory removals and/or inactivation of 99.9% *Giardia* cysts and 99.99% enteric viruses. Primary disinfection systems that use ozone, chlorine, or chlorine dioxide can achieve greater than the above-stated inactivation of enteric viruses when 99.9% inactivation of *Giardia* cysts is attained. Therefore, achieving sufficient *Giardia* cyst inactivation can ensure adequate inactivation of both types of organisms. This is not the case, however, when using chloramination because it is such a poor virucide.

Conventional treatment, which includes coagulation, flocculation, clarification (sedimentation or flotation), and filtration, along with disinfection, can achieve 99.9% inactivation of *Giardia* cysts and 99.99% inactivation of enteric viruses when properly designed and operated. Direct filtration, slow sand filtration, and diatomaceous earth filtration systems, each combined with disinfection, have also achieved these reductions.

Groundwater systems that apply disinfection to comply with regulations may have to add filtration if they contain iron and manganese. Insoluble oxides form when chlorine, chlorine dioxide, or ozone are added to these systems; thus, filters would be needed for their removal. In addition, both ozonation and chlorination may cause flocculation of dissolved organics, thus increasing turbidity and necessitating filtration. The presence of such insoluble substances will require the use of secondary disinfection after filtration as well (4,14).

“CT values” indicate the effectiveness of disinfectants in achieving primary disinfection. They describe the attainable degree of disinfection as the product of the disinfectant residual concentration (in mg/L) and the contact time (in minutes). For chlorine,

chlorine dioxide, or monochloramine, the contact time can be the time required for the water to move from the point at which the disinfectant is applied to the point it reaches the first customer (at peak flow). This is the total time the water is exposed to the disinfectant residual before being used. Ozone, however, has a short half-life in water; therefore, the contact time is considered the time water is exposed to a continuous ozone residual during the water treatment process only.

The US EPA Final Surface Water Treatment Rule (SWTR) states the following: Systems may measure "C" (in mg/L) at different points along the treatment train, and may use this value, with the corresponding "T" (in minutes), to calculate the total percentage inactivation. In determining the total percentage inactivation, the system may calculate the CT at each point where "C" was measured and compare this with the $CT_{99.9}$ value (the CT value necessary to achieve 99.9% inactivation of *Giardia* cysts) in the rule for specified conditions (pH, temperature, and residual disinfectant concentration). Each calculated CT value (CT_{calc}) must be divided by the $CT_{99.9}$ value found in the SWTR tables to determine the inactivation ratio. If the sum of the inactivation ratios, or

$$\text{Summation of } CT_{calc} \,/\, CT_{99.9}$$

at each point prior to the first customer where CT was calculated is equal to or greater than 1.0, i.e., there was a total of at least 99.9% inactivation of *Giardia lamblia*, the system is in compliance with the performance requirement of the SWTR.

For groundwater not under direct influence of surface water, CT is determined in the same manner using enteric viruses or an acceptable viral surrogate as the determinant microorganism, because *Giardia* cysts will not be present.

Appendices B1–B6 of this chapter present the CT values required to attain required reductions of *Giardia* cysts for chlorine. As shown, lower temperatures require higher CT values; with chlorine, an increase in pH also increases the necessary CT values. If more than one disinfectant is used, the percentage inactivation achieved by each is additive and can be included in calculating the total CT value.

When direct filtration is included in the water treatment process, disinfection credit can be taken by the filtration step for a 2-log inactivation of *Giardia* cysts and a 1-log inactivation of viruses. This means that the primary disinfectant must provide an additional 1-log inactivation of *Giardia* cysts and 3-log inactivation of viruses. In the specific instance of a conventional treatment process that includes coagulation, flocculation, sedimentation, and filtration, an inactivation credit of 2.5-logs for *Giardia* cysts and 2-logs for viruses may be taken. This means that the primary disinfectant must provide an additional 0.5-log inactivation of *Giardia* cysts but a 2-log inactivation of viruses.

If a water supply system does not use filtration, the 99.9% inactivation of *Giardia* and 99.99% inactivation of enteric viruses must be achieved by the primary disinfecting agents alone. The CT values for the four disinfectants for achieving 99.9% reductions of *Giardia* cysts, and the CT values for virus inactivation can both found from another chapter of this handbook series (1). Although groundwater disinfection regulations have not been finalized, these values will probably apply to systems treating groundwater determined by the state not to be under direct influence of surface water (4,14).

In the final SWTR, the CT values for ozone have been lowered to levels such that the CT values required to provide 0.5-log inactivation of *Giardia* cysts at the higher water temperatures are below those required to provide 2- or 3-logs of inactivation of enteric viruses. Consequently, the 2- or 3-log virus inactivation CT requirement becomes the pacing parameter for the amount of additional primary disinfection to be provided by ozone during conventional treatment, rather than the 0.5-log inactivation of *Giardia* cysts.

2.5.2. Design Calculations

A 50,000 GPD slow sand filtration water treatment plant supplies a community of 500 people with drinking water from a reservoir in a protected watershed. The raw water supply has the following characteristics: (a) turbidity = 5–10 NTU; (b) total estimated *Giardia* cyst level = less than 1 per 100 mL; (c) pH = 6.5–7.5; (d) temperature = 5–15ºC.

An overall removal/inactivation of 3-logs for *Giardia* and 4-logs for viruses is sufficient for this water treatment system. The Primacy Agency credits the slow sand filter, which produces water with turbidity ranging from 0.6 to 0.8 NTU, with a 2-log *Giardia* and virus removal. Disinfection must achieve an additional 1-log *Giardia* and 2-log virus removal/inactivation to meet overall treatment objectives.

To begin the calculations for determining the adequacy of the inactivation achieved by the disinfection system, the total contact time must be determined.

In this plant, chlorine for disinfection is added prior to the clearwell, which has a 2000-gal capacity. The distance from the plant to the first customer is bridged by a 1000-ft 2-in. transmission main (1 ft = 0.3048 m; 1 in. = 2.54 cm). The contact time provided in both the clearwell basin and the distribution pipe up to the first customer comprises the total contact time for disinfection.

In the calculations, contact time is represented by T_{10}, which is the time needed for 10% of the water to pass through the basin. In other words, T_{10} describes the time, in minutes, that 90% of the water remains in the basin. For the distribution pipe, contact time is 100% of the time that water remains in the pipe.

The contact time multiplied by the concentration (mg/L) of residual chlorine in the water is the calculated CT value for the system. Proven inactivation of *Giardia* and viruses are correlated to calculated CT values in US EPA's *Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources* (28). Appendix B contains excerpts from the CT tables in the manual.

The T_{10} for the clearwell basin can be determined by tracer studies. [Tracer study procedures are described in US EPA's *Guidance Manual* (28).]

On the day represented in this example, the tracer study showed that the T_{10} for the clearwell was 40 min at the peak hourly flow rate. At this flow rate, water travels through the transmission main at 211 ft/min. The distance between the plant and the first customer is 1000 ft. Thus, the T_{10} for the distribution main is 4.7 min (1000 ft divided by 211 ft/min).

Other data required for the calculation are: (a) measured chlorine residual = 2.0 mg/L for the clearwell basin and 1.2 mg/L for the distribution main; (b) water temperature = 5ºC; and (c) water pH = 7.5. The reader should review Appendix A concerning the pH and other related-water quality parameters for corrosion control.

CT values required to achieve various levels of inactivation of *Giardia* and viruses depending on the water temperature, pH, and chlorine residual are provided in the

Guidance Manual (28). The calculated CT values (CT_{calc}) based on actual system data are compared to the CT values in the *Guidance Manual* (28) ($CT_{99.9}$ in the case of a 1-log inactivation) to determine whether the inactivation achieved is adequate.

Because, with free chlorine, a 1-log *Giardia* inactivation provides greater than a 4-log virus inactivation, inactivation of *Giardia* is the controlling factor for determining overall reductions.

The calculation of CT and comparison to CT values for 1-log inactivation of *Giardia* provided below (14):

For the basin:

$$\begin{aligned} CT_{calc} &= \text{Chlorine residual} \times \text{contact time} \\ &= (2.0\ \text{mg/L}) \times (40\ \text{min}) = 80\ \text{mg/L·min} \end{aligned}$$

From Appendix B2 of this chapter, $CT_{99.9}$ (3-log inactivation) is 200 mg/L·min at 5ºC, 2 mg/L chlorine residual, and 7.5 pH.

$$CT_{calc}/CT_{99.9} = (80\ \text{mg/L·min})/(200\ \text{mg/L·min}) = 0.4$$

For the distribution system:

$$CT_{calc} = (1.2\ \text{mg/L}) \times (4.7\ \text{min}) = 5.64\ \text{mg/L·min}$$

From Appendix B2 of this chapter, $CT_{99.9}$ is 183 mg/L·min at 5ºC, 1.2 mg/L chlorine residual, and 7.5 pH.

$$CT_{calc}/CT_{99.9} = (5.64\ \text{mg/L·min})/(183\ \text{mg/L·min}) = 0.03$$

Summing $CT_{calc}/CT_{99.9}$ for both the basin and the main results in 0.43. This is equivalent to a 1.29-log *Giardia* inactivation determined by

$$3 \times (CT_{calc}/CT_{99.9}) = 3 \times 0.43 = 1.29\text{-log}$$

This calculation is based on a 3-log inactivation; therefore, the ratio is multiplied by 3.

Thus, the 1.29-log inactivation achieved by disinfection in this system exceeds the 1-log additional inactivation required to meet overall treatment objectives.

3. POTABLE WATER CHLORAMINATION

Secondary disinfectants provide an essential residual that prevents regrowth in the distribution system. Although chlorine is the most widely used secondary disinfectant, chlorine dioxide and monochloramine are appropriate as well. As secondary disinfectants, chlorine and chlorine dioxide are handled in the same manner as for primary disinfectants. The use of monochloramine as a secondary disinfectant is discussed in detail in this section.

3.1. Potable Water Chloramination Process Description

Chloramination process can be applied to both water treatment and wastewater treatment (1,29). In the field of potable water treatment, chloramine is recommended as a secondary disinfectant because it is ineffective as a virucide, and is only marginally effective against *Giardia* cysts. It is formed from the combination of ammonia and chlorine (hypochlorite or hypochlorous acid). The chemical is generated on site, usually by injecting ammonia gas or adding an ammonium sulfate solution to chlorinated water, or by adding chlorine to water containing ammonia. Ammonia gas can be purchased as an anhydrous liquid in cylinders for small water treatment systems; ammonium sulfate can be purchased as a powder in bags.

This section describes the chloramination process, chloramine residual establishment, system design considerations, and chloramination systems case histories.

When water, chlorine, and ammonia are combined, three different species of chloramine compounds can be generated:

$$NH_3 + HOC1 \rightarrow H_2O + NH_2Cl \tag{12}$$

$$NH_2Cl + HOCl \rightarrow H_2O + NHCl_2 \tag{13}$$

$$NHCl_2 + HOCl \rightarrow H_2O + NCl_3 \tag{14}$$

where NH_3 = ammonia, $HOCl$ = hypochlorous acid, NH_2Cl = monochloramine, $NHCl_2$ = dichloramine, and NCl_3 = nitrogen trichloride.

The mix of species produced depends on the ratio of chlorine to ammonia and the pH of the water. In the pH range of 7–8 with a chlorine-to-ammonia ratio (by weight) of 3 to 1, monochloramine is the principal product. At higher chlorine-to-ammonia ratios or at lower pH values (5–7), some dichloramine will be formed. If the pH drops below 5, some nitrogen trichloride (often erroneously called "trichloramine") may be formed. Nitrogen trichloride formation should be avoided because it imparts undesirable taste and odor to the water. To compare the disinfection efficiencies of secondary chlorination with secondary chloramination, a design engineer should also consider the effect of each process on corrosion control (see Appendix A).

Figure 7 shows the relative percentages of monochloramine and dichloramine produced as the pH changes, for different weight ratios of chlorine to ammonia. At a pH value of about 5.7, approximately equal amounts of mono- and dichloramines are present in solution.

Care should be taken not to exceed chlorine-to-ammonia ratios of 5 to 1. This is the "breakpoint" curve above which all ammonia is removed, chloramines are absent, and free residual chlorine is present.

3.2. Design and Operation Considerations

Establishing a chloramine residual involves a period of mixing the chlorine and ammonia with the water, followed by a short holding time to allow the reactions to take place. Usually, chloramine-forming reactions are at least 99% complete within a few minutes.

The National Academy of Sciences (NAS) recommends adding ammonia to chlorinated water rather than adding chlorine to water containing ammonia. The recommended process produces a residual of free chlorine above that required to oxidize nitrogen (particularly the organic nitrogen compounds). Organic nitrogen compounds will compete successfully with ammonia–nitrogen for chlorine, forming organic chloramines, which are weaker disinfectants than monochloramine. Normal field analytical techniques cannot distinguish between inorganic and organic chloramines. Thus, formation of inorganic chloramines in the presence of organic nitrogen compounds can seriously overstate the actual capability of the chloramine system to provide secondary disinfection.

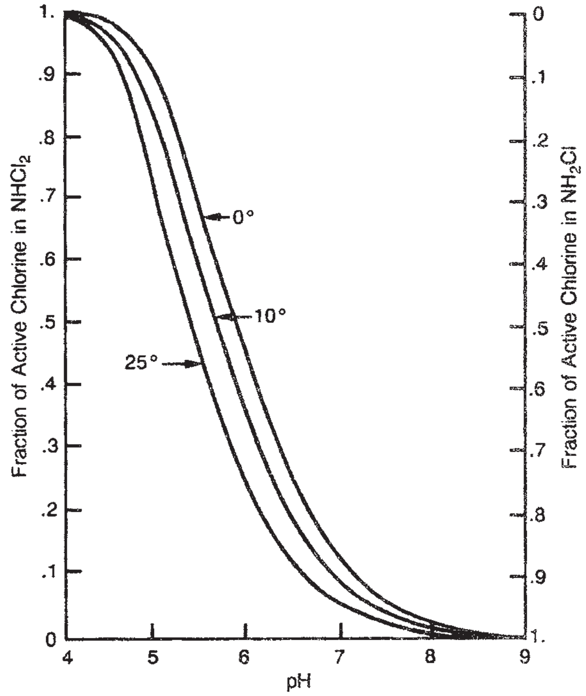

Fig. 7. Proportions of mono- and dichloramines in water with equimolar concentrations of chlorine and ammonia (US EPA; National Academy of Sciences).

Ammonia is available as an anhydrous gas (NH_3), a 29% aqueous solution (aqua ammonia), or as ammonium sulfate powder, $(NH_4)_2SO_4$. Gaseous ammonia is supplied in 68-kg (150-lb) cylinders, aqua ammonia in 208.2-L (55-gal) drums, and ammonium sulfate in 45.4-kg (100-lb) bags (98% pure, 25% available ammonia).

Ammonia gas is injected into treated water using systems and equipment similar to those used for chlorine gas. Aqua ammonia is handled using systems similar to those used for sodium hypochlorite. This form of ammonia is basic and has a strong odor, but is not corrosive. For ammonium sulfate powder, a 25–30% solution is prepared in a plastic or fiberglass container and added to the water by means of a chemical metering pump. Equipment similar to that used for handling calcium hypochlorite can be used for this process. Solutions of ammonium sulfate are stable, but acidic, and, therefore, corrosive to some metals. Materials that withstand dilute sulfuric acid will also withstand the corrosion effects of dilute ammonium sulfate solutions.

3.3. Process Equipment and Control

Generation of chloramines requires the same equipment as chlorination (gaseous or aqueous hypochloramination), plus equipment for adding ammonia (gaseous or aqueous). The information for calculating the corrosion indexes for final corrosion control and for determining the CT values for secondary chloramination process control can be found in Appendix A and Appendixes D–E, respectively.

Table 2
Summary of THM Data at Bloomington, Indiana, with Free Chlorination, August 16, 1984

Sampling point	Chlorine residual (mg/L)	TOC (mg/L)	TTHM (μg/L)	TOX (μg/L)
Raw water	—	4.3	1	23
Settled water	0.25	3.6	48	127
Filtered water	1.0	2.4	81	205
Dist. system #1	1.8	—	110	291
Dist. system #2	0.65	—	151	363

Source: US EPA.

Table 3
Summary of THM Data at Bloomington, Indiana, with Postchloramination, August 26, 1984

Sampling point	Chlorine residual (mg/L)	TOC (mg/L)	TTHM (μg/L)	TOX (μg/L)
Raw water	—	4.1	0	17
Settled water	Trace, free	2.8	53	94
Filtered water	1.2 combined	2.8	55	91
Dist. system #1	1.0 combined	—	52	115
Dist. system #2	0.9 combined	—	57	116

Source: US EPA.

3.4. Application Examples

3.4.1. Example 1: Prechlorination and Postchloramination in Bloomington, Indiana, USA

Bloomington, Indiana, obtains raw water from a lake with TOC levels of 4–6 mg/L. The water is treated with alum coagulation, flocculation, sedimentation, and filtration through pressure filters. Prior to September 1984, chlorine was applied to the raw water and just before the pressure filters. Average chlorine dosages were 1.8 and 1.0 mg/L at each point, respectively. According to quarterly compliance monitoring reports, average TTHM concentrations were exceeding the 100 μg/L limit a majority of the time.

In September 1984, the Bloomington water utility changed from postchlorination to postchloramination. Before the pressure filters, an average 0.54 mg/L of ammonia was applied along with 1.5 mg/L of chlorine. The desired residual chlorine concentration leaving the plant of 1.0 mg/L of free chlorine was changed to 1.5 mg/L of combined chlorine. After the change, quarterly THM levels ranged from 24 to 57 μg/L.

Table 2 summarizes THM and TOX (total organic halide) data for samples collected at points in the treatment train when chlorine was used for both prechlorination and postchlorination. The data show that TOX levels increase with TTHM levels. Table 3 summarizes similar data after postchloramination was instituted. These data show that although the TTHM formation ceases after the addition of ammonia, the production of TOX continues, but at a greatly reduced rate.

Thus, as MCLs for halogenated organic materials other than THMs are promulgated, utilities using postchloramination should plan to determine the makeup of their TOX fraction.

Since switching to postchloramination, the utility has experienced no adverse effects in operations or in finished water quality. According to distribution system monitoring records, the microbiological quality of the water has been maintained.

3.4.2. *Example 2: Prechlorine Dioxide, Prechlorination, and Postchloramination: Philadelphia, Pennsylvania, USA*

The Baxter Water Treatment Plant, Philadelphia, Pennsylvania, is a 12.35-m^3/s (282-MGD) conventional water treatment plant built in 1960. The plant supplies drinking water from the Delaware River to a population of over 800,000. Chemicals used in treatment include chlorine, ferric chloride or ferrous sulfate, lime, fluoride, and ammonia. Powdered activated carbon is used on demand for control of taste and odor, and chloride dioxide is used for control of THMs, tastes, and odors. The chlorine dioxide system was left over from the previous water treatment plant on that site. In the 1950s, it was used to oxidize phenolic compounds found in the watershed, which have since been eliminated.

Prior to 1976, the Baxter plant practiced breakpoint chlorination at the raw water basin and maintained free chlorine in the distribution system. A total of 96 h of free chlorine contact time was typically achieved.

In 1978, analyses of THMs showed peak concentrations above 300 pg/L with an annual average of 140 µg/L. In light of these results, the Philadelphia Water Department began to reevaluate its disinfection strategies. Factors that affected the selection of an alternative included THM, bacterial, taste, odor, algae, and corrosion control; residual duration; and economics.

Modifications were implemented between 1976 and 1983. Chloramination of the finished water was introduced in 1976 to reduce free chlorine contact times and THM levels. Ammonia was added to convert free chlorine to monochloramine. The monochloramine reduced contact time from 96 to 24 h, provided a stable residual in the distribution system, improved the organoleptic properties of the water, and reduced the corrosion rates associated with the use of free chlorine. Adequate disinfection was ensured by maintaining a free chlorine residual of 2–3 mg/L throughout the plant treatment process. THM formation potential within the treatment process was reduced by 40% under summer conditions.

4. CONTROLLING DISINFECTION BY-PRODUCTS IN DRINKING WATER

US Environmental Protection Agency (US EPA) has surveyed 10 operating water utilities for the presence of 22 halogenated disinfection by-products in chlorine-treated water (31). Table 4 presents the frequency and range of concentrations of those by-products of greatest concern. Table 5 summarizes the current knowledge of health effects of selected chlorination by-products. Researchers are continuously studying the by-products associated with ozonation. To date, however, extensive studies of by-products of treatment with ozone, chloramination, and chlorine dioxide have not been conducted.

4.1. Strategies for Controlling Disinfection By-Products

The formation of halogenated by-products is affected by a number of factors, including the concentration and types of organic materials present when chlorine is added, the dosage of chlorine, the temperature and pH of the water, and the reaction time. US EPA

Table 4
Occurrence of Chlorinated Disinfection By-Products at 10 Water Utilities (31)

Compound[a]	Number of locations	Range of values (μg/L)
High Confidence[a]		
Chloroform	10 of 10	2.6 to 594
Bromodichloromethane	10 of 10	2.6 to 77
Chlorodibromomethane	10 of 10	0.1 to 31
Bromoform	6 of 10	0.1 to 2.7
Dichloroacetonitrile	10 of 10	0.2 to 9.5
Dibromoacetonitrile	3 of 7	0.4 to 1.2
Bromochloroacetonitrile	7 of 7	0.2 to 4.0
Chloropicrin	8 of 10	0.2 to 5.6
Low Confidence		
Chloroacetic acid	6 of 10	<10
Dichloroacetic acid	10 of 10	<10 to >100
Trichloroacetic acid	6 of 10	10 to 100
Trichloroacetaldehyde (as chloral hydrate)	10 of 10	10 to 100
1,1,1-Trichloropropanone	10 of 10	10 to 100
2-Chlorophenol	0 of 10	—
2,4-Dichlorophenol	0 of 10	—
2,4,6-Trichlorophenol	0 of 10	—
Qualitative Only		
1,1-Dichloropropanone	0 of 8	—
1,1-Dichloro-2-butanone	0 of 8	—
3,3-Dichloro-2-butanone	1 of 8	—
1,1,1-Trichloro-2-butanone	0 of 8	—
Cyanogen chloride	1 of 7	—
Dichloroacetaldehyde	0 of 10	—

Source: US EPA.

[a] In the first two groups, contaminants are grouped according to whether current knowledge of health effects indicates a high or low confidence that adverse health effects exist; in the third group, current knowledge of health effects is only qualitative to date.

has identified three strategies for controlling formation of halogenated materials during chlorination:

1. Remove the by-products after they are formed; this first approach, removing the by-products after they are formed, can be difficult and costly. Many books discuss the treatment technologies available for organic contaminant removal (1,2).
2. Use alternate disinfectants that do not produce undesirable by-products; this second approach, using alternative disinfectants, is often the most cost-effective.
3. Reduce the concentration of organics in the water before oxidation or chlorination to minimize the formation of by-products. The third approach, reducing the concentrations of organic precursors before adding chlorine or other oxidants, will provide the highest quality finished water.

4.2. *Using Alternative Disinfectants*

This approach, using other than chlorine for disinfection, is sound if the replacements do not produce undesirable by-products of their own and if they perform equally as both

Table 5
Summary of Health Effects Associated With Chlorination By-Products (32)

Chemical class	Example	Toxicological effects
Trihalomethanes	Chloroform	C, H, RT
	Dichlorobromomethane	H, RT
	Dibromochloromethane	H, RT
	Bromoform	H, RT
Haloacetonitriles	Chloroacetonitrile	G, D
	Dichloroacetonitrile	M, G, D
	Trichloroacetonitrile	G, D
	Bromochloroacetonitrile	M, G, D
	Dibromoacetonitrile	G, D
Haloacid derivatives	Dichloroacetic acid	MD, C, N, OL, A
	Trichloroacetic acid	HPP
Chlorophenols	2-Chlorophenol	F, TP
	2,4-Dichlorophenol	F, TP
	2,4,6-Trichlorophenol	C
Chlorinated ketones	1,1-Dichloropropanone	M
	1,1,1-Trichloropropanone	M
	1,1,3,3-Tetrachloropropanone	M
Chlorinated furanones	MX	M, Cl
Chlorinated aldehydes	2-Chloroacetaldehyde	G

Source: US EPA.

Key to toxicological effects: C = Carcinogenic; H = Hepatotoxic; RT = Renal toxic; G = Genotoxic; D = Developmental; M = Mutagenic; MD = Metabolic disturbance; N = Neurotoxic; OL = Ocular lesions; A = Aspermatogenesis; HPP = Hepatic peroxisome proliferation; F = Fetotoxic; TP = Tumor promoter; Cl = clastogenic.

primary and secondary disinfectants. Cost is also a consideration. Alternative disinfectants currently being considered by water treatment specialists are chlorine dioxide, monochloramine, UV radiation, and ozone. Both ozone and UV radiation do not provide stable residuals for the distribution system and, therefore, cannot be used as substitute disinfectants by themselves.

Although extensive studies of ozone by-products have not yet been conducted, many immediate oxidation products of naturally occurring organic materials have been identified repeatedly. For the most part, these by-products are organic aldehydes, acids, and ketones. Oxidation of raw water containing bromide ion will produce hypobromous acid, which can brominate organic precursors.

Because ozone is employed only for primary disinfection, a chlorinated compound (chlorine or chloramine) must be added for secondary disinfection following ozonation, i.e., to provide a residual for the distribution system. Consequently, the "secondary" by-products, those formed by the reaction of chlorine or chloramine with the primary by-products of ozonation, become a concern to water treatment specialists. Although some studies have examined by-products produced by two-step oxidation sequences of this type, no compounds have yet been reported that are not produced by one of the two oxidation processes acting alone.

For example, preozonation may affect the yields of THMs formed by subsequent chlorination. Usually these THM yields are lowered by preozonation, but in some cases, usually with high ozone dosages or at high pH values, they can be enhanced. The yield of chloropicrin (nitrotrichloromethane) can be enhanced if chlorination is preceded by ozonation. Chloramine is known to react with acetaldehyde to produce acetonitrile under drinking water treatment conditions. This and other nitriles might be expected to be produced upon direct chloramination of ozonated waters containing aldehydes.

Chlorine dioxide is effective as a primary and secondary disinfectant, but some chlorite ion is produced. The use of chlorine dioxide has been associated with hematological effects in laboratory animals, which may result from the production of chlorite and chlorate ions. Neurological effects have also been identified.

If a strong chemical reducing agent is added somewhere in the treatment process after chlorine dioxide primary disinfection, then chlorine dioxide and chlorite ions can be reduced to chloride ion. This would leave only traces of chlorate ion in the water. This chemical reduction technique will allow much higher chlorine dioxide dosages to be applied for oxidation and/or primary disinfection than the 1.2–1.4 mg/L currently recommended.

At present, granular activated carbon (GAC) or sulfur dioxide are known to chemically reduce chlorine dioxide and chlorite ion (but not chlorate ion) to the innocuous chloride ion.

The remaining alternative, monochloramine, is a weak disinfectant. The very high CT values required to inactivate 99.9% *Giardia* and 99.99% enteric viruses make monochloramine impractical for use as a primary disinfectant. Therefore, monochloramine should only be considered as a secondary disinfectant.

This chapter only discusses the applications of chlorination and chloramination in potable water treatment. In case the two processes are to be used for wastewater treatment, residual chlorine concentration in the plant effluent may become a regulatory issue (30). Selection of an alternative disinfectant becomes more important. New alternative disinfectants have been studied by Wang (19–25). Wang (35,36) also reported that UV is an effective process for dechlorination, dechloramination, or de-ozonation.

4.3. *Minimizing Precursor Concentrations*

The third approach for controlling disinfection by-products is to reduce the concentration of organic materials before adding chlorine or any oxidant. This approach will minimize the formation of by-products. Another option is to use an oxidant that does not contain chlorine, such as ozone, potassium permanganate, or hydrogen peroxide, before or during rapid mix and/or filtration to partially oxidize organics. This will improve the flocculation and filtration processes that follow.

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Appendix A
Summary of Corrosion Indices (US EPA)

Index	Equation	Parameters	Meaning
Langelier Saturation Index (LSI)	LSI $= pH - pH_s$	Total alkalinity, mg/L as $CaCO_3$ Calcium, mg/L as $CaCO_3$ Hardness, mg/L as $CaCO_3$ Total dissolved solids, mg/L On-site pH On-site temperature	LSI > 0 = Water is supersaturated; tends to precipitate $CaCO_3$ LSI = 0 = Water is saturated (in equilibrium); $CaCO_3$ scale is neither dissolved nor deposited LSI < 0 = Water is undersaturated; tends to dissolve solid $CaCO_3$
Aggressive Index (AI) (for use with asbestos cement)	$AI = pH + \log[(A)(H)]$	Total alkalinity, mg/L as $CaCO_3$ Hardness, mg/L as $CaCO_3$ On-site pH	AI < 10 = Very aggressive AI = 10–12 = Moderately aggressive AI > 12 = Nonaggressive
Ryznar Stability index (RSI)	$RSI = 2pH_s - pH$	Total alkalinity, mg/L as $CaCO_3$ Calcium, mg/L as $CaCO_3$ Hardness, mg/L as $CaCO_3$ Total dissolved solids, mg/L On-site pH On-site temperature	RSI < 6.5 = Water is supersaturated; tends to precipitate $CaCO_3$ 6.5 < RSI < 7.0 = Water is saturated (in equilibrium); $CaCO_3$ scale is neither dissolved nor deposited RSI > 7.0 = Water is undersaturated; tends to dissolve solid $CaCO_3$
Riddick's Corrosion Index (CI)	$\frac{75}{Alk}\left[CO_2 - (1@2)(Hardness - Alk) + Cl^- + 2N\right] \times \left(\frac{10}{SiO_2}\right)\left(\frac{DO + 2}{Sa \times DO}\right)$	CO_2, mg/L Hardness, mg/L as $CaCO_3$ Alkalinity, mg/L as $CaCO_3$ Cl^-, mg/L N, mg/L DO, mg/L Saturation DO (value for oxygen saturation), mg/L	CI = 0–5 Scale forming 6–25 Noncorrosive 26–50 Moderately corrosrve 51–75 Corrosive 76–100 Very corrosive 101+ Extremely corrosive
Driving Force Index (DFI) $CaCO_3$	$\frac{Ca^{2+}(ppm) \times CO_3 = (ppm)}{K_{so} \times 10^{10}}$	Calcium, mg/L as $CaCO_3$ CO_3 = mg/L as $CaCO_3$ K_{so} = solubility product of $CaCO_3$	DFI > 1 = Water supersaturated; tends to precipitate DFI = 1 = Water saturated (in equilibrium); $CaCO_3$ scale is neither dissolved nor deposited DFI < 1 = Water undersaturated; tends to dissolve $CaCO_3$

Source: US EPA

Appendix B1

CT Values for Inactivation of *Giardia* and Viruses by Free Chlorine (US EPA). CT Values for Inactivation of *Giardia* Cysts by Free Chlorine at 0.5°C or Lower[1]

CHLORINE	pH< =6						pH = 6.5						pH = 7.0						pH = 7.5					
CONCENTRATION	Log Inactivations						Log Inactivations						Log Inactivations						Log Inactivations					
(mg/L)	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
< =0.4	23	46	69	91	114	137	27	54	82	109	136	163	33	65	98	130	163	195	40	79	119	158	198	237
0.6	24	47	71	94	118	141	28	56	84	112	140	168	33	67	100	133	167	200	40	80	120	159	199	239
0.8	24	48	73	97	121	145	29	57	86	115	143	172	34	68	103	137	171	205	41	82	123	164	205	246
1	25	49	74	99	123	148	29	59	88	117	147	176	35	70	105	140	175	210	42	84	127	169	211	253
1.2	25	51	76	101	127	152	30	60	90	120	150	180	36	72	108	143	179	215	43	86	130	173	216	259
1.4	26	52	78	103	129	155	31	61	92	123	153	184	37	74	111	147	184	221	44	89	133	177	222	266
1.6	26	52	79	105	131	157	32	63	95	126	158	189	38	75	113	151	188	226	46	91	137	182	228	273
1.8	27	54	81	108	135	162	32	64	97	129	161	193	39	77	116	154	193	231	47	93	140	186	233	279
2	28	55	83	110	138	165	33	66	99	131	164	197	39	79	118	157	197	236	48	95	143	191	238	286
2.2	28	56	85	113	141	169	34	67	101	134	168	201	40	81	121	161	202	242	50	99	149	198	248	297
2.4	29	57	86	115	143	172	34	68	103	137	171	205	41	82	124	165	206	247	50	99	149	199	248	298
2.6	29	58	88	117	146	175	35	70	105	139	174	209	42	84	126	168	210	252	51	101	152	203	253	304
2.8	30	59	89	119	148	178	36	71	107	142	178	213	43	86	129	171	214	257	52	103	155	207	258	310
3	30	60	91	121	151	181	36	72	109	145	181	217	44	87	131	174	218	261	53	105	158	211	263	316

CHLORINE	pH = 8.0						pH = 8.5						pH< =9.0					
CONCENTRATION	Log Inactivations						Log Inactivations						Log Inactivations					
(mg/L)	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
< =0.4	46	92	139	185	231	277	55	110	165	219	274	329	65	130	195	260	325	390
0.6	48	95	143	191	238	286	57	114	171	228	285	342	68	136	204	271	339	407
0.8	49	98	148	197	246	295	59	118	177	236	295	354	70	141	211	281	352	422
1	51	101	152	203	253	304	61	122	183	243	304	365	73	146	219	291	364	437
1.2	52	104	157	209	261	313	63	125	188	251	313	376	75	150	226	301	376	451
1.4	54	107	161	214	268	321	65	129	194	258	323	387	77	155	232	309	387	464
1.6	55	110	165	219	274	329	66	132	199	265	331	397	80	159	239	318	398	477
1.8	56	113	169	225	282	338	68	136	204	271	339	407	82	163	245	326	408	489
2	58	115	173	231	288	346	70	139	209	278	348	417	83	167	250	333	417	500
2.2	59	118	177	235	294	353	71	142	213	284	355	426	85	170	256	341	426	511
2.4	60	120	181	241	301	361	73	145	218	290	363	435	87	174	261	348	435	522
2.6	61	123	184	245	307	368	74	148	222	296	370	444	89	178	267	355	444	533
2.8	63	125	188	250	313	375	75	151	226	301	377	452	91	181	272	362	453	543
3	64	127	191	255	318	382	77	153	230	307	383	460	92	184	276	368	460	552

Note: $CT_{99.9}$ = CT for 3-log inactivation.

Appendix B2
CT Values for Inactivation of *Giardia* Cysts by Free Chlorine at 5°C[1]

CHLORINE CONCENTRATION (mg/L)	pH< =6						pH = 6.5						pH = 7.0						pH = 7.5					
	Log Inactivations						Log Inactivations						Log Inactivations						Log Inactivations					
	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
< =0.4	16	32	49	65	81	97	20	39	59	78	98	117	23	46	70	93	116	139	28	55	83	111	138	166
0.6	17	33	50	67	83	100	20	40	60	80	100	120	24	48	72	95	119	143	29	57	86	114	143	171
0.8	17	34	52	69	86	103	20	41	61	81	102	122	24	49	73	97	122	146	29	58	88	117	146	175
1	18	35	53	70	88	105	21	42	63	83	104	125	25	50	75	99	124	149	30	60	90	119	149	179
1.2	18	36	54	71	89	107	21	42	64	85	106	127	25	51	76	101	127	152	31	61	92	122	153	183
1.4	18	36	55	73	91	109	22	43	65	87	108	130	26	52	78	103	129	155	31	62	94	125	156	187
1.6	19	37	56	74	93	111	22	44	66	88	110	132	26	53	79	105	132	158	32	64	96	128	160	192
1.8	19	38	57	76	95	114	23	45	68	90	113	135	27	54	81	108	135	162	33	65	98	131	163	196
2	19	39	58	77	97	116	23	46	69	92	115	138	28	55	83	110	138	165	33	67	100	133	167	200
2.2	20	39	59	79	98	118	23	47	70	93	117	140	28	56	85	113	141	169	34	68	102	136	170	204
2.4	20	40	60	80	100	120	24	48	72	95	119	143	29	57	86	115	143	172	35	70	105	139	174	209
2.6	20	41	61	81	102	122	24	49	73	97	122	146	29	58	88	117	146	175	36	71	107	142	178	213
2.8	21	41	62	83	103	124	25	49	74	99	123	148	30	59	89	119	148	178	36	72	109	145	181	217
3	21	42	63	84	105	126	25	50	76	101	126	151	30	61	91	121	152	182	37	74	111	147	184	221

CHLORINE CONCENTRATION (mg/L)	pH = 8.0						pH = 8.5						pH< =9.0					
	Log Inactivations						Log Inactivations						Log Inactivations					
	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
< =0.4	33	66	99	132	165	198	39	79	118	157	197	236	47	93	140	186	233	279
0.6	34	68	102	136	170	204	41	81	122	163	203	244	49	97	146	194	243	291
0.8	35	70	105	140	175	210	42	84	126	168	210	252	50	100	151	201	251	301
1	36	72	108	144	180	216	43	87	130	173	217	260	52	104	156	208	260	312
1.2	37	74	111	147	184	221	45	89	134	178	223	267	53	107	160	213	267	320
1.4	38	76	114	151	189	227	46	91	137	183	228	274	55	110	165	219	274	329
1.6	39	77	116	155	193	232	47	94	141	187	234	281	56	112	169	225	281	337
1.8	40	79	119	159	198	238	48	96	144	191	239	287	58	115	173	230	288	345
2	41	81	122	162	203	243	49	98	147	196	245	294	59	118	177	235	294	353
2.2	41	83	124	165	207	248	50	100	150	200	250	300	60	120	181	241	301	361
2.4	42	84	127	169	211	253	51	102	153	204	255	306	61	123	184	245	307	368
2.6	43	86	129	172	215	258	52	104	156	208	260	312	63	125	188	250	313	375
2.8	44	88	132	175	219	263	53	106	159	212	265	318	64	127	191	255	318	382
3	45	89	134	179	223	268	54	108	162	216	270	324	65	130	195	259	324	389

Note: $CT_{99.9}$ = CT for 3-log inactivation.

Appendix B3
CT Values for Inactivation of *Giardia* Cysts by Free Chlorine at 10°C[1]

CHLORINE CONCENTRATION (mg/L)	pH < = 6						pH = 6.5						pH = 7.0						pH = 7.5					
	Log Inactivations						Log Inactivations						Log Inactivations						Log Inactivations					
	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
< =0.4	12	24	37	49	61	73	15	29	44	59	73	88	17	35	52	69	87	104	21	42	63	83	104	125
0.6	13	25	38	50	63	75	15	30	45	60	75	90	18	36	54	71	89	107	21	43	64	85	107	128
0.8	13	26	39	52	65	78	15	31	46	61	77	92	18	37	55	73	92	110	22	44	66	87	109	131
1	13	26	40	53	66	79	16	31	47	63	78	94	19	37	56	75	93	112	22	45	67	89	112	134
1.2	13	27	40	53	67	80	16	32	48	63	79	95	19	38	57	76	95	114	23	46	69	91	114	137
1.4	14	27	41	55	68	82	16	33	49	65	82	98	19	39	58	77	97	116	23	47	70	93	117	140
1.6	14	28	42	55	69	83	17	33	50	66	83	99	20	40	60	79	99	119	24	48	72	96	120	144
1.8	14	29	43	57	72	86	17	34	51	67	84	101	20	41	61	81	102	122	25	49	74	98	123	147
2	15	29	44	58	73	87	17	35	52	69	87	104	21	41	62	83	103	124	25	50	75	100	125	150
2.2	15	30	45	59	74	89	18	35	53	70	88	105	21	42	64	85	106	127	26	51	77	102	128	153
2.4	15	30	45	60	75	90	18	36	54	71	89	107	22	43	65	86	108	129	26	52	79	105	131	157
2.6	15	31	46	61	77	92	18	37	55	73	92	110	22	44	66	87	109	131	27	53	80	107	133	160
2.8	16	31	47	62	78	93	19	37	56	74	93	111	22	45	67	89	112	134	27	54	82	109	136	163
3	16	32	48	63	79	95	19	38	57	75	94	113	23	46	69	91	114	137	28	55	83	111	138	166

CHLORINE CONCENTRATION (mg/L)	pH = 8.0						pH = 8.5						pH < = 9.0					
	Log Inactivations						Log Inactivations						Log Inactivations					
	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
< =0.4	25	50	75	99	124	149	30	59	89	118	148	177	35	70	105	139	174	209
0.6	26	51	77	102	128	153	31	61	92	122	153	183	36	73	109	145	182	218
0.8	26	53	79	105	132	158	32	63	95	126	158	189	38	75	113	151	188	226
1	27	54	81	108	135	162	33	65	98	130	163	195	39	78	117	156	195	234
1.2	28	55	83	111	138	166	33	67	100	133	167	200	40	80	120	160	200	240
1.4	28	57	85	113	142	170	34	69	103	137	172	206	41	82	124	165	206	247
1.6	29	58	87	116	145	174	35	70	106	141	176	211	42	84	127	169	211	253
1.8	30	60	90	119	149	179	36	72	108	143	179	215	43	86	130	173	216	259
2	30	61	91	121	152	182	37	74	111	147	184	221	44	88	133	177	221	265
2.2	31	62	93	124	155	186	38	75	113	150	188	225	45	90	136	181	226	271
2.4	32	63	95	127	158	190	38	77	115	153	192	230	46	92	138	184	230	276
2.6	32	65	97	129	162	194	39	78	117	156	195	234	47	94	141	187	234	281
2.8	33	66	99	131	164	197	40	80	120	159	199	239	48	96	144	191	239	287
3	34	67	101	134	168	201	41	81	122	162	203	243	49	97	146	195	243	292

Note: $CT_{99.9}$ = CT for 3-log inactivation.

Appendix B4
CT Values for Inactivation of *Giardia* Cysts by Free Chlorine at 15°C[1]

CHLORINE CONCENTRATION (mg/L)	pH<=6						pH=6.5						pH=7.0						pH=7.5					
	Log Inactivations						Log Inactivations						Log Inactivations						Log Inactivations					
	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
<=0.4	8	16	25	33	41	49	10	20	30	39	49	59	12	23	35	47	58	70	14	28	42	55	69	83
0.6	8	17	25	33	42	50	10	20	30	40	50	60	12	24	36	48	60	72	14	29	43	57	72	86
0.8	9	17	26	35	43	52	10	20	31	41	51	61	12	24	37	49	61	73	15	29	44	59	73	88
1	9	18	27	35	44	53	11	21	32	42	53	63	13	25	38	50	63	75	15	30	45	60	75	90
1.2	9	18	27	36	45	54	11	21	32	43	53	64	13	25	38	51	63	76	15	31	46	61	77	92
1.4	9	18	28	37	46	55	11	22	33	43	54	65	13	26	39	52	65	78	16	31	47	63	78	94
1.6	9	19	28	37	47	56	11	22	33	44	55	66	13	26	40	53	66	79	16	32	48	64	80	96
1.8	10	19	29	38	48	57	11	23	34	45	57	68	14	27	41	54	68	81	16	33	49	65	82	98
2	10	19	29	39	48	58	12	23	35	46	58	69	14	28	42	55	69	83	17	33	50	67	83	100
2.2	10	20	30	39	49	59	12	23	35	47	58	70	14	28	43	57	71	85	17	34	51	68	85	102
2.4	10	20	30	40	50	60	12	24	36	48	60	72	14	29	43	57	72	86	18	35	53	70	88	105
2.6	10	20	31	41	51	61	12	24	37	49	61	73	15	29	44	59	73	88	18	36	54	71	89	107
2.8	10	21	31	41	52	62	12	25	37	49	62	74	15	30	45	59	74	89	18	36	55	73	91	109
3	11	21	32	42	53	63	13	25	38	51	63	76	15	30	46	61	76	91	19	37	56	74	93	111

CHLORINE CONCENTRATION (mg/L)	pH=8.0						pH=8.5						pH<=9.0					
	Log Inactivations						Log Inactivations						Log Inactivations					
	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
<=0.4	17	33	50	66	83	99	20	39	59	79	98	118	23	47	70	93	117	140
0.6	17	34	51	68	85	102	20	41	61	81	102	122	24	49	73	97	122	146
0.8	18	35	53	70	88	105	21	42	63	84	105	126	25	50	76	101	126	151
1	18	36	54	72	90	108	22	43	65	87	108	130	26	52	78	104	130	156
1.2	19	37	56	74	93	111	22	45	67	89	112	134	27	53	80	107	133	160
1.4	19	38	57	76	95	114	23	46	69	91	114	137	28	55	83	110	138	165
1.6	19	39	58	77	97	116	24	47	71	94	118	141	28	56	85	113	141	169
1.8	20	40	60	79	99	119	24	48	72	96	120	144	29	58	87	115	144	173
2	20	41	61	81	102	122	25	49	74	98	123	147	30	59	89	118	148	177
2.2	21	41	62	83	103	124	25	50	75	100	125	150	30	60	91	121	151	181
2.4	21	42	64	85	106	127	26	51	77	102	128	153	31	61	92	123	153	184
2.6	22	43	65	86	108	129	26	52	78	104	130	156	31	63	94	125	157	188
2.8	22	44	66	88	110	132	27	53	80	106	133	159	32	64	96	127	159	191
3	22	45	67	89	112	134	27	54	81	108	135	162	33	65	98	130	163	195

Note: $CT_{99.9}$ = CT for 3-log inactivation.

Appendix B5

CT Values for Inactivation of *Giardia* Cysts by Free Chlorine at 20°C[1]

CHLORINE CONCENTRATION (mg/L)	pH < =6						pH = 6.5						pH = 7.0						pH = 7.5					
	Log Inactivations						Log Inactivations						Log Inactivations						Log Inactivations					
	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
< =0.4	6	12	18	24	30	36	7	15	22	29	37	44	9	17	26	35	43	52	10	21	31	41	52	62
0.6	6	13	19	25	32	38	8	15	23	30	38	45	9	18	27	36	45	54	11	21	32	43	53	64
0.8	7	13	20	26	33	39	8	15	23	31	38	46	9	18	28	37	46	55	11	22	33	44	55	66
1	7	13	20	26	33	39	8	16	24	31	39	47	9	19	28	37	47	56	11	22	34	45	56	67
1.2	7	13	20	27	33	40	8	16	24	32	40	48	10	19	29	38	48	57	12	23	35	46	58	69
1.4	7	14	21	27	34	41	8	16	25	33	41	49	10	19	29	39	48	58	12	23	35	47	58	70
1.6	7	14	21	28	35	42	8	17	25	33	42	50	10	20	30	39	49	59	12	24	36	48	60	72
1.8	7	14	22	29	36	43	9	17	26	34	43	51	10	20	31	41	51	61	12	25	37	49	62	74
2	7	15	22	29	37	44	9	17	26	35	43	52	10	21	31	41	52	62	13	25	38	50	63	75
2.2	7	15	22	29	37	44	9	18	27	35	44	53	11	21	32	42	53	63	13	26	39	51	64	77
2.4	8	15	23	30	38	45	9	18	27	36	45	54	11	22	33	43	54	65	13	26	39	52	65	78
2.6	8	15	23	31	38	46	9	18	28	37	46	55	11	22	33	44	55	66	13	27	40	53	67	80
2.8	8	16	24	31	39	47	9	19	28	37	47	56	11	22	34	45	56	67	14	27	41	54	68	81
3	8	16	24	31	39	47	10	19	29	38	48	57	11	23	34	45	57	68	14	28	42	55	69	83

CHLORINE CONCENTRATION (mg/L)	pH = 8.0						pH = 8.5						pH < =9.0					
	Log Inactivations						Log Inactivations						Log Inactivations					
	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
< =0.4	12	25	37	49	62	74	15	30	45	59	74	89	18	35	53	70	88	105
0.6	13	26	39	51	64	77	15	31	46	61	77	92	18	36	55	73	91	109
0.8	13	26	40	53	66	79	16	32	48	63	79	95	19	38	57	75	94	113
1	14	27	41	54	68	81	16	33	49	65	82	98	20	39	59	78	98	117
1.2	14	28	42	55	69	83	17	33	50	67	83	100	20	40	60	80	100	120
1.4	14	28	43	57	71	85	17	34	52	69	86	103	21	41	62	82	103	123
1.6	15	29	44	58	73	87	18	35	53	70	88	105	21	42	63	84	105	126
1.8	15	30	45	59	74	89	18	36	54	72	90	108	22	43	65	86	108	129
2	15	30	46	61	76	91	18	37	55	73	92	110	22	44	66	88	110	132
2.2	16	31	47	62	78	93	19	38	57	75	94	113	23	45	68	90	113	135
2.4	16	32	48	63	79	95	19	38	58	77	96	115	23	46	69	92	115	138
2.6	16	32	49	65	81	97	20	39	59	78	98	117	24	47	71	94	118	141
2.8	17	33	50	66	83	99	20	40	60	79	99	119	24	48	72	95	119	143
3	17	34	51	67	84	101	20	41	61	81	102	122	24	49	73	97	122	146

Note: $CT_{99.9}$ = CT for 3-log inactivation.

Appendix B6
CT Values for Inactivation of *Giardia* Cysts by Free Chlorine at 25°C[1]

CHLORINE CONCENTRATION (mg/L)	pH< =6 Log Inactivations						pH =6.5 Log Inactivations						pH =7.0 Log Inactivations						pH =7.5 Log Inactivations					
	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
< =0.4	4	8	12	16	20	24	5	10	15	19	24	29	6	12	18	23	29	35	7	14	21	28	35	42
0.6	4	8	13	17	21	25	5	10	15	20	25	30	6	12	18	24	30	36	7	14	22	29	36	43
0.8	4	9	13	17	22	26	5	10	16	21	26	31	6	12	19	25	31	37	7	15	22	29	37	44
1	4	9	13	17	22	26	5	10	16	21	26	31	6	12	19	25	31	37	8	15	23	30	38	45
1.2	5	9	14	18	23	27	5	11	16	21	27	32	6	13	19	25	32	38	8	15	23	31	38	46
1.4	5	9	14	18	23	27	6	11	17	22	28	33	7	13	20	26	33	39	8	16	24	31	39	47
1.6	5	9	14	19	23	28	6	11	17	22	28	33	7	13	20	27	33	40	8	16	24	32	40	48
1.8	5	10	15	19	24	29	6	11	17	23	28	34	7	14	21	27	34	41	8	16	25	33	41	49
2	5	10	15	19	24	29	6	12	18	23	29	35	7	14	21	27	34	41	8	17	25	33	42	50
2.2	5	10	15	20	25	30	6	12	18	23	29	35	7	14	21	28	35	42	9	17	26	34	43	51
2.4	5	10	15	20	25	30	6	12	18	24	30	36	7	14	22	29	36	43	9	17	26	35	43	52
2.6	5	10	16	21	26	31	6	12	19	25	31	37	7	15	22	29	37	44	9	18	27	35	44	53
2.8	5	10	16	21	26	31	6	12	19	25	31	37	8	15	23	30	38	45	9	18	27	36	45	54
3	5	11	16	21	27	32	6	13	19	25	32	38	8	15	23	31	38	46	9	18	28	37	46	55

CHLORINE CONCENTRATION (mg/L)	pH =8.0 Log Inactivations						pH =8.5 Log Inactivations						pH< =9.0 Log Inactivations					
	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0	0.5	1.0	1.5	2.0	2.5	3.0
< =0.4	8	17	25	33	42	50	10	20	30	39	49	59	12	23	35	47	58	70
0.6	9	17	26	34	43	51	10	20	31	41	51	61	12	24	37	49	61	73
0.8	9	18	27	35	44	53	11	21	32	42	53	63	13	25	38	50	63	75
1	9	18	27	36	45	54	11	22	33	43	54	65	13	26	39	52	65	78
1.2	9	18	28	37	46	55	11	22	34	45	56	67	13	27	40	53	67	80
1.4	10	19	29	38	48	57	12	23	35	46	58	69	14	27	41	55	68	82
1.6	10	19	29	39	48	58	12	23	35	47	58	70	14	28	42	56	70	84
1.8	10	20	30	40	50	60	12	24	36	48	60	72	14	29	43	57	72	86
2	10	20	31	41	51	61	12	25	37	49	62	74	15	29	44	59	73	88
2.2	10	21	31	41	52	62	13	25	38	50	63	75	15	30	45	60	75	90
2.4	11	21	32	42	53	63	13	26	39	51	64	77	15	31	46	61	77	92
2.6	11	22	33	43	54	65	13	26	39	52	65	78	16	31	47	63	78	94
2.8	11	22	33	44	55	66	13	27	40	53	67	80	16	32	48	64	80	96
3	11	22	34	45	56	67	14	27	41	54	68	81	16	32	49	65	81	97

Note: $CT_{99.9}$ = CT for 3-log inactivation.

Appendix C
CT Values for Inactivation of Viruses by Free Chlorine

	Log inactivation					
	2.0 pH		3.0 pH		4.0 pH	
Temperature (°C)	6–9	10	6–9	10	6–9	10
0.5	6	45	9	66	12	90
5	4	30	6	44	8	60
10	3	22	4	33	6	45
15	2	15	3	22	4	30
20	1	11	2	16	3	22
25	1	7	1	11	2	15

Source: US EPA.

Appendix D
CT Values for Inactivation of *Giardia* Cysts by Chloramine, pH 6–9

	Temperature (°C)					
Inactivation	≤1	5	10	15	20	25
0.5-log	635	365	310	250	185	125
1-log	1270	735	615	500	370	250
1.5-log	1900	1100	930	750	550	375
2-log	2535	1470	1230	1000	735	500
2.5-log	3170	1830	1540	1250	915	625
3-log	3800	2200	1850	1500	1100	750

Source: US EPA.

Appendix E
CT Values for Inactivation of Viruses by Chloramine

	Temperature (°C)					
Inactivation	≤1	5	10	15	20	25
2-log	1243	857	643	428	321	214
3-log	2063	1423	1067	712	534	356
4-log	2883	1988	1491	994	746	497

Source: US EPA.

Appendix F
On-Site Sodium Hypochlorite Generation System

Comparison of High Strength 12% to Low Strength 0.8%

Product/design	12% Hypo solution high strength system	0.8% Hypo solution low strength system
Sodium hypochlorite degradation U.L. Certifiable	• Usage and production are "on demand" thus degradation does not apply	• Usage and production are "on demand" thus degradation does not apply
pH	• 10–12	• 9–9.5
Chlorine gas	• 98% chlorine gas with 20–30% moisture	• Does not produce chlorine gas
Sodium hydroxide	• 15% sodium hydroxide "membrane" grade	• Does not produce sodium hydroxide
Production	• Production is scalable	• Production is not scalable
Brine	• Spent brine is recovered	• Only 1/3 (33%) of sodium is converted, remaining 2/3 (67%) will stay in the weak solution
Electrolyzer design	• Membrane separates anode and cathode	• No membrane

Storage	12% Hypo solution high strength system	0.8% Hypo low solution strength system
	• 1 gallon of solution per pound of chlorine with 12% trade	• 15 gallons of solution per pound of chlorine

Consumption per lb of chlorine generated	12% Hypo solution high strength system	0.8% Hypo low solution strength system
Power (kWh)	1.75	2.5
Water (gal)	0.95	15.0
Salt, food grade (lb)	1.65	3.5

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Waste Chlorination and Stabilization

Lawrence K. Wang

CONTENTS

1. INTRODUCTION

1.1. *Process Introduction*

Chlorine is an efficient disinfectant as well as an oxidizing agent, and perhaps is the most frequently used chemical by environmental engineers and scientists since 1800s. The oldest water treatment facilities used only chlorine for water disinfection, which became the foundation of our industrial development. Today chlorine has been used in various forms for sanitary, commercial, industrial, and military applications. This chapter is a sister chapter to the following book chapters in the *Handbook of Environmental Engineering* series:

1. "Halogenation and Disinfection" chapter introduces various disinfection processes, such as chlorination, chlorine dioxide disinfection, bromination, and iodination which all involve the use of halogens (1).
2. "Potable Water Chlorination and Chloramination" chapter introduces the detailed engineering procedures for calculation of CT values for disinfection, and both conventional and innovative process equipment, including the on-site chlorine gas and hypochlorite generation facilities (2).
3. "Ozonation" chapter and "UV Disinfection" chapter introduce the disinfection/oxidation processes which use ozone and UV, respectively (1,2).
4. "Inorganic Chemical Conditioning and Stabilization" chapter introduces various chemical conditioning and stabilization processes (including chlorine stabilization) for sludge treatment (3).
5. "Pressurized Ozonation" chapter introduces a modern process involving the use of ozone and oxygen in a pressurized reactor for sludge disinfection, oxidation and stabilization (3).

From: *Handbook of Environmental Engineering, Volume 4: Advanced Physicochemical Treatment Processes*
Edited by: L. K. Wang, Y.-T. Hung, and N. K. Shammas © The Humana Press Inc., Totowa, NJ

This chapter deals with the same topic of chemical oxidation and disinfection, but at the advanced level. Specifically the engineering design and applications of chlorination processes for treatment of wastewater, biosolids, and septage are introduced in detail.

1.2. Glossary

The process involving the application of chlorine to drinking water, wastewater, industrial effluent, sludge, septage, swimming pool water, etc., to disinfect or to oxidize undesirable pathogens and compounds is termed chlorination (1–10). When chloramines (instead of chlorine) are used as the disinfectant/oxidant, the process is termed chloramination (1,8).

When wastewater is treated by chlorine, the treatment process is termed "wastewater chlorination," or simply "chlorination."

When chlorination process is used for treatment of sludge and septage, it can be called "sludge chlorination" and "septage chlorination," respectively. Either sludge chlorination or septage chlorination is a "chlorine stabilization" process (3,5–8). A device or process equipment that adds any chlorine compounds, in solid, gas, or liquid form, to water, wastewater, or sludge to kill infectious microorganisms or undesirable substances is a chlorinator (8–9). A part of treatment facility where water, wastewater, or sludge is treated by chlorine for disinfection and oxidation is a chlorine contact chamber (CCC).

Chlorine stabilization is one of a number of chemical stabilization processes, involving the use of chlorine. For instance, if lime is used in a chemical stabilization process for sludge treatment, it is a lime stabilization process.

Chlorine dosage is the amount of chlorine required to oxidize the target substance to be treated (such as water, wastewater, sludge, or septage) plus the desired chlorine residual. The target substance to be treated is termed chlorine demand. Usually the chlorine dosage is computed as mg/L concentration and the chlorine feed system set at the equivalent lb/d feed rate.

Given a desired chlorine residual of 300 mg/L and a chlorine demand of 800 mg/L, the chlorine dosage and resulting feed rate (for 12,000 gal/d throughput) are computed as follows:

$$\text{Chlorine dosage} = \text{Chlorine demand} + \text{Desired chlorine residual} \tag{1}$$

$$\text{Chlorine dosage} = 300\ \text{mg/L} + 800\ \text{mg/L} = 1100\ \text{mg/L}$$

$$\begin{aligned}\text{Feed rate, lb/d} &= (1100\ \text{mg/L}) \times (8.34\ \text{lb/MG/mg/L}) \times (0.012\ \text{MGD})\\ &= 110\ \text{lb/d}\end{aligned}$$

Throughput rate is the gallons of sludge fed to the unit per unit time (gpm or gpd). If the sludge is treated by chlorine (a disinfectant/oxidizing agent), the oxidized sludge is the chemical oxidation effluent. Chlorination is an oxidation process.

A total chemical process step for changing, adjusting, modifying, and improving the characteristics of sludge or septage prior to a dewatering process is termed "chemical conditioning." If only chlorine is used for the sludge or septage treatment, chlorination (or chlorine oxidation) is a "chemical conditioning" process. If the chlorine-treated sludge (or septage) needs to be further treated by another chemical (such as a neutralizing agent), then chlorination is only an intermediate process. The chlorine-treated sludge (or treated septage) is the oxidized sludge (or oxidized septage). In this case, the

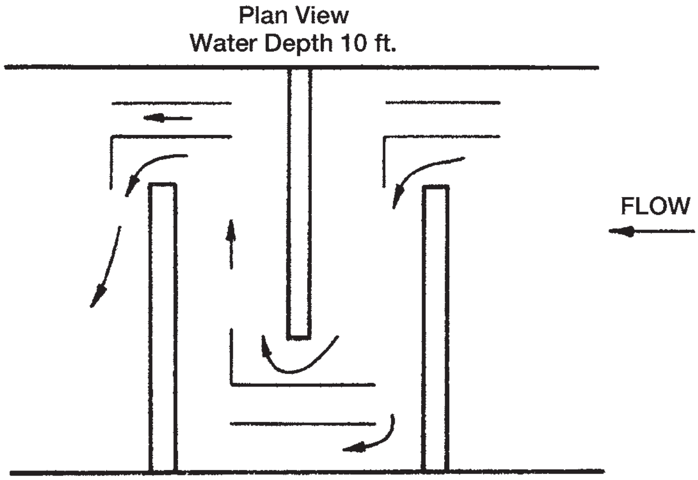

Fig. 1. Chlorine contact chamber with end-around baffles and vanes.

conditioned sludge will be the oxidized sludge that has also been conditioned by a holding tank or further chemical treatment to raise the pH and reduce the chlorine residual.

Nascent oxygen is uncombined oxygen in molecular form (O). Oxidant is an agent which oxidizes a substance by removing one or more electrons from an atom, ion, or molecule.

2. WASTEWATER CHLORINATION

2.1. Process Description

The most common use of chlorine in sewage treatment is for disinfection, which usually is the last treatment step in a secondary biological wastewater treatment plant. Where the treated secondary effluent is fed into a stream to be used for water supply or for recreational purposes, chlorination is effective in destroying the disease-producing pathogens found in treated wastewater. Other principal uses of chlorine are odor control and control of bulking in activated sludge.

Chlorine may be fed into the wastewater automatically, with the dosage depending on the degree of treatment. The wastewater then flows into a tank, where it usually is held for about 30 min to allow the chlorine to react with the pathogens (Fig. 1). Chlorine often is used either as a gas, or a solid or liquid compound. Liquid chlorine, or hypochlorite, has been used mostly in small systems (fewer than 5000 persons), or in large systems, where safety concerns related to handling chlorine gas outweigh economic concerns. The use of chlorine has proven to be a very effective means of disinfection.

Chlorine is also used in advanced wastewater treatment (AWT) for nitrogen removal, through a process known as “breakpoint chlorination.” For nitrogen removal, enough chlorine is added to the wastewater to convert all the ammonium nitrogen to nitrogen gas. To do this, about 10 mg/L of chlorine must be added per mg/L of ammonia nitrogen in the wastewater—about 40 or 50 times more chlorine than normally used in a wastewater plant for disinfection only.

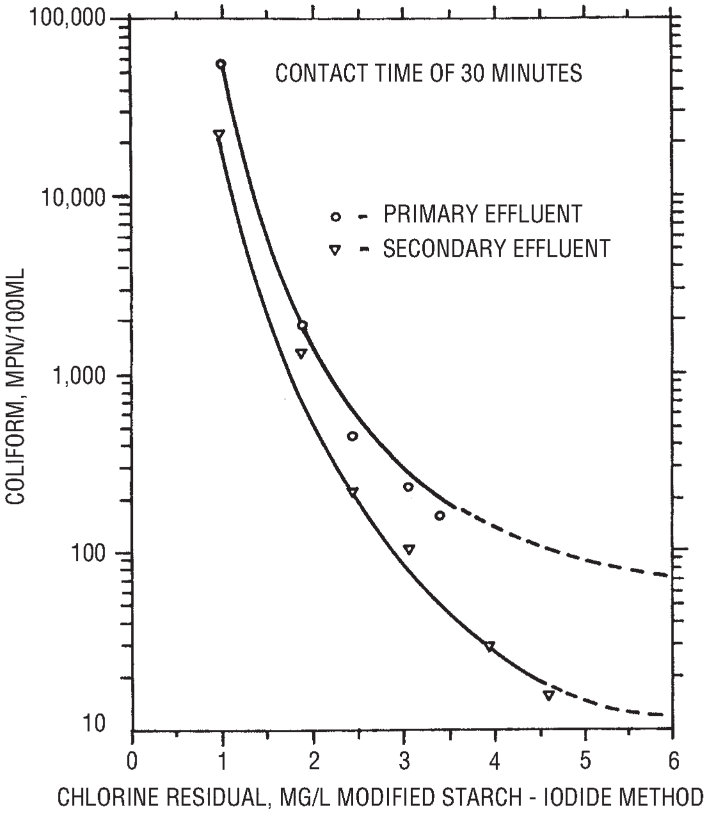

Fig. 2. MPN coliform vs. chlorine residual.

The facilities required for the chlorination process are simple. Wastewater (after secondary or tertiary treatment) flows into a mixing tank where the chlorine is added and complete mixing is provided. Because a large amount of chlorine is used and has an acidic effect on the wastewater, alkaline chemicals (such as lime) may be added to the same chamber to neutralize this acidic effect. The nitrogen gas that is formed is then released to the atmosphere. The amount of chlorine used for nitrogen control provides very effective disinfection. Because the process is just as effective in removing 1 mg/L as 20 mg/L of ammonium, breakpoint chlorination often is used as a polishing step downstream of other nitrogen removal processes.

2.2. Design and Operation Considerations

2.2.1. General Considerations

Figure 2 shows how residual chlorine affects coliform number. The curves show the most probable number (MPN) of coliforms remaining after 30 min of chlorine contact in a well-designed chlorine contact tank. These results should not be considered as being exact. Table 1 lists chlorine dosages often used for disinfection of raw and partially-treated sewage.

In breakpoint chlorination, about 10 mg/L of chlorine must be added for each mg/L of ammonia nitrogen present in the wastewater. Studies show that better pretreatment will

Table 1
Chlorine Dosage Ranges

Waste	Chlorine dosage (mg/L)
Raw sewage	6–12
Raw sewage (septic)	12–25
Clarified sewage	5–10
Clarified sewage (septic)	12–40
Chemical precipitation effluent	3–10
Trickling filter effluent	3–10
Activated sludge effluent	2–8
Sand filter effluent	1–5

Source: US EPA.

Table 2
Effect of Pretreatment on Chlorine and Ammonia Nitrogen Breakpoint Ratio

Sample	Breakpoint pH	Initial NH_4^+-N (mg/L)	Final NH_4^+-N (mg/L)	Irreducible minimum residual (mg/L as Cl_2)	Breakpoint ratio Cl_2:NH_4^+-N (weight basis)
Laboratory Tests					
Buffered water	6–7	20	0.1	0.6	8 : 1
Raw wastewater	6.5–7.5	15	0.2	7	9 : 1–10 : 1
Lime clarified raw wastewater	6.5–7.5	11.2	0.1	7	8 : 1–9 : 1
Secondary effluent	6.5–7.5	8.1	0.2	3	8 : 1–9 : 1
Lime clarified secondary effluent	6.5–7.5	9.2	0.1	4	8 : 1
Ferric chloride clarified raw wastewater	3.2	10.2	0.1	20	8.2 : 1
Pilot Plant Test					
Filtered secondary effluent	6–8	12.9–21.0	0.1	2–8.5	8.4 : 1–9.2 : 1
Lime clarified raw wastewater—filtered	7.0–7.3	9.7–12.5	0.4–1.2	–	9 : 1
Alum clarified oxidation pond effluent—filtered	6.6	20.6	0.1	7.6	9.6 : 1

reduce the amount of chlorine needed to reach breakpoint. Table 2 shows how different pretreatment processes affect the chlorine to ammonia–nitrogen ratio needed for breakpoint chlorination. The breakpoint process can result in 99+% removal of ammonium nitrogen, reducing concentrations to less than 0.1 mg/L (as N).

To evaluate the performance of a chlorination system, an environmental engineer should check the contact time, chlorine residual, and MPN of coliform organisms after chlorination. This can be done easily in the following steps:

1. Obtain typical operating data for the chlorination system being studied. For example: (a) type of effluent = activated sludge; (b) peak plant flow = 5 MGD; (c) volume of chlorine contact chamber (CCC), v = 13,926 ft^3; (d) chlorine dosage = 6 mg/L; (e) chlorine residual = 1 mg/L.
2. Determine the contact time for the chlorine contact chamber based on peak flow:

$$\text{Contact time, h} = (\text{V in ft}^3) \times (7.48\ \text{gal/ft}^3) \times (24\ \text{h/d})/(\text{Flow in gpd}) \tag{2}$$

$$\begin{aligned}\text{Contact time, h} &= (13{,}926)\ (7.48)\ (24)/(5 \times 10^6)\\ &= 0.45\ \text{h} = 27\ \text{min}\end{aligned}$$

3. Examine the daily disinfection log sheet for chlorine feed rates and chlorine residual patterns. Compare both contact time and chlorine residual with those required by the proper regulatory agency. As a general rule, residuals between 0.2 and 1.0 mg/L after 15–30 min contact times provide good disinfection. As shown in the example, the 27 min contact time and 1.0 mg/L chlorine residual should be generally sufficient.
4. If the chlorination system does not perform as expected, the shortcomings and troubleshooting guide should be studied.

2.2.2. Specific Design Procedures

For wastewater treatment, the recommended chlorine dosage for disinfection purposes should produce a chlorine residual of 0.5–1 mg/L after a specified contact time. Effective contact time of not less than 15 min at peak flow is recommended. Practical chlorine dosages recommended for wastewater disinfection and odor control are presented in below:

(a) Untreated wastewater (prechlorination) = 6–25 mg/L
(b) Primary clarification = 5–20 mg/L
(c) Chemical precipitation plant = 2–6 mg/L
(d) Trickling filter plant = 3–15 mg/L
(e) Activated sludge plant = 2–8 mg/L
(f) Multimedia filter following activated sludge plant = 1–5 mg/L

The required input data include: (a) chlorine contact tank influent flow, MGD; (b) peak flow, MGD; and (c) average flow, MGD. The design parameters include: (a) contact time at maximum flow, min; (b) length-to-width ratio; (c) number of chlorine contact tanks; (d) chlorine dosage, mg/L.

The following is recommended design procedure. The first step is to select contact time at peak flow and calculate volume of contact tank:

$$\text{VCT} = [Q_p(\text{CT})\ (10^6)]/(\ 24 \times 60) \tag{3}$$

where VCT = volume of contact tank, gal, Q_p = peak flow, MGD, and CT = contact time at maximum flow, min.

The second step in design is to select a side water depth and calculate surface area:

$$\text{SA} = \text{VCT}/[7.48\ \text{SWD}] \tag{4}$$

where SA = surface area, ft^2, VCT = volume of contact tank, gal, and SWD = side water depth = 8 ft.

The third step in design is to select a length-to-width ratio and calculate dimensions by the following equations:

$$\mathrm{CTW} = [\mathrm{SA}/\mathrm{RLW}]^{0.5} \tag{5}$$

$$\mathrm{CTL} = \mathrm{SA}/\mathrm{CTW} \tag{6}$$

where CTW = contact tank width, ft, SA = surface area, ft^2, RLW = length-to-width ratio, and CTL = contact tank length, ft.

The fourth step in design is to select chlorine dosage according to the recommended chlorine dosages in this section, and then calculate chlorine requirements:

$$\mathrm{CR} = (Q_a)(\mathrm{CD})(8.34) \tag{7}$$

where CR = chlorine requirement, lb/d, Q_a = average flow, MGD, and CD = chlorine dosage, mg/L.

The fifth step in design is to calculate peak chlorine requirements by the following equation:

$$\mathrm{PCR} = (\mathrm{CR})(Q_p)/Q_a \tag{8}$$

where PCR = peak chlorine requirements, lb/d, CR = chlorine requirements, lb/d, Q_p = peak flow, MGD, and Q_a = average flow, MGD.

The output data of wastewater disinfection design will be:

(a) Maximum flow, MGD (1 MGD = 3.785×10^6 L/d).
(b) Average flow, MGD.
(c) Contact time, min.
(d) Volume of contact tank, gal (1 gal = 3.785 L).
(e) Average chlorine requirement, lb/d (1 lb = 454 g).
(f) Peak chlorine requirement, lb/d.
(g) Tank dimensions.

2.3. *Process Equipment and Control*

The process equipment used for wastewater chlorination are similar to that for potable water chlorination, in terms of chlorine generation facilities and feeding system (1–17). The difference of the wastewater chlorination and water chlorination is their chlorine contact equipment. Many government rules and regulations specify the minimum detention time, depth, cover, mixing intensity, etc., for different types of oxidizing agents or disinfectants (17–20). The chlorine contact chamber for potable water treatment can be either indoors or outdoors, but usually is of indoors. The chlorine contact chamber for wastewater treatment is always an outdoor hydraulic structure. In general, the better the wastewater treatment plant is operated, the easier it will be to disinfect the plant effluent. Any failure to provide adequate treatment will increase the bacterial count and the chlorine requirement. High solids content and soluble organic loads increase the amount of chlorine required. Effective chlorine disinfection is dependent on the combined effect of chlorine dosage, mixing, and contact time with the wastewater. Enough disinfectant should be added to always meet the bacterial quality required by the regulatory agency. Control of the disinfection process is accomplished by measurement of the chlorine residual. General theories and process control of chlorination, disinfection, oxidation, and stabilization processes can be found from the literature (21–25).

Table 3
Common Design Shortcomings of Wastewater Chlorination and Solutions

Shortcomings	Solution
1. Big changes in effluent chlorine residual when chlorine flow proportioning control device is operating properly.	1. Install a continuous chlorine residual analyzer to control the feed rate automatically, or use a closed-loop system.
2. Short-circuiting in chlorine contact tank.	2. Make channels very narrow or Provide thorough baffling in the channel to ensure complete mixing and a sufficient contact time.
3. High residual chlorine concentrations in the effluent toxic to aquatic life.	3. Install dechlorinating systems (activated carbon, hydrogen peroxide, sulfur dioxide, sodium metabisulfite, or UV).
4. Sodium hypochlorite cannot be stored for long periods of time without deteriorating.	4. If long storage periods cannot be avoided, dilute the sodium hypochloride to slow down the rate of deterioration, or use liquid (gas) chlorine as an alternate source.
5. Lack of mixing.	5. Install mechanical mixer.

Proper mixing is one of the most important factors in chlorine disinfection. Applying chlorine to wastewater in a well-mixed system produces a much better effluent than a system where chlorine is fed without rapid mixing, even with adequate residual and contact time. However, sufficient contact time (usually 30 min) between the chlorine and the wastewater is also needed to provide good disinfection. Usually, longer contact times are more important than higher residuals in wastewater treatment.

In breakpoint chlorination, the system must be able to meet quick changes in ammonia nitrogen concentrations, chlorine demand, pH, alkalinity, and flow. Failure to properly control chlorine dosage can result in poor nitrogen removal and chlorine overdoses. Overdoses of chlorine are a direct waste of this chemical and cause problems in adjusting the operation of the dechlorination equipment. Overdoses also can cause the direct discharge of high concentrations of chlorine residuals to the receiving water, and can result in the undesirable formation of $NC1_3$.

Usually, a base chemical is added to the breakpoint process to neutralize some of the acidity resulting from the chlorine addition. The base requirements depend on wastewater alkalinity, individual treatment processes used before breakpoint chlorination, as well as effluent pH or alkalinity restrictions by regulatory agencies.

Another consideration in breakpoint chlorination is dechlorination to remove the chlorine residual from the final effluents before it is discharged. Very often, dechlorination using sulfur dioxide or activated carbon may be needed when the breakpoint chlorination process is used. A new dechlorination technology has been introduced in another chapter of this handbook series (2). UV dechlorination is recommended by Wang (45).

In most cases, control of breakpoint chlorination requires the use of accurate and reliable automatic equipment to reduce the need for manual process control by operators. However, the operator must give special attention to this equipment and monitoring devices in order to ensure their proper operation. Table 3 indicates how the common process shortcomings can be compensated and improved. Table 4 is a wastewater chlorination process trouble-shooting guide for use by practicing environmental engineers.

Table 4
Troubleshooting Guide for Wastewater Chlorination Process

Indicators/observations	Probable cause	Check or monitor	Solutions
1. Low chlorine gas pressure at chlorinator.	1a. Insufficient number of cylinders connected to system.	1a. Reduce feed rate and note if pressure rises appreciably after short period of time. If so, 1a is the cause.	1a. Connect enough cylinders to the system so that chlorine feed rate does not exeed the withdrawal rate from the cylinders.
	1b. Stoppage or flow restriction between cylinders and chlorinators.	1b. Reduce feed rate and note if icing and cooling effect on supply lines continues.	1b. Disassemble chlorine header system at point where cooling begins, locate stoppage and clean with solvent.
2. No chlorine gas pressure at chlorinator.	2a. Chlorine cylinders empty or not connected to system.	2a. Visual inspection.	2a. Connect cylinders or replace empty cylinders.
	2b. Plugged or damaged pressure reducing valve.	2b. Inspect valve.	2b. Repair the reducing valve after shutting off cylinder valves, and decreasing gas in the header systems.
3. Chlorinator will not feed any chlorine.	3a. Pressure reducing valve in chlorinator is dirty.	3a. Visual inspection.	3a. 1. Disassemble chlorinator and clean valve stem and seat. 2. Precede valve with a filter-sediment trap.
	3b. Chlorine cylinder hotter than chlorine control apparatus.	3b. Cylinder area temperature	3b. 1. Reduce temperature in cylinder area. 2. Do not connect a new cylinder which has been sitting in the sun.
4. Chlorine gas escaping from chlorine pressure reducing valve (CPRV).	4a. Main diaphragm of CPRV ruptured due to: 1. Improper assembly or fatigue. 2. Corrosion	4a. Place ammonia bottle near termination of CPRV vent line to confirm leak.	4a. 1. Disassemble valve and diaphragm. 2. Inspect chlorine supply systems for moisture intrusion.

(Continued)

Table 4 (*Continued*)

Indicators/observations	Probable cause	Check or monitor	Solutions
5. Inability to maintain chlorine feed rate without icing of chlorine system.	5a. Insufficient evaporator capacity.	5a. Reduce feed rate to about 75% of evaporator capacity. If this eliminates problem 5a is the cause.	
	5b. External CPRV cartridge is clogged.	5b. Inspect cartridge.	5b. Flush and clean cartridge.
6. Chlorination system unable to maintain water-batch temperature sufficient to keep external CPRV open.	6a. Heating element malfunction.	6a. Evaporator water-batch temperature.	6a. Remove and replace heating element.
7. Inability to obtain maximum feed rate from chlorinator.	7a. Inadequate chlorine gas pressure.	7a. Gas pressure.	7a. Increase pressure—replace empty or low cylinders.
	7b. Water pump injector clogged with deposits.	7b. Inspect injector.	7b. Clean injector parts using muriatic acid. Rinse with fresh water and replace in service.
	7c. Leak in vacuum relief valve.	7c. Disconnect vent line at chlorinator; place hand over vent connection to vacuum relief valve, observe if this results in more vacuum and higher chlorine feed rate.	7c. Disassemble vacuum relief valve and replace all springs.
	7d. Vacuum leak in joints, gaskets, tubing, etc. in chlorinator system.	7d. Moisten joints with ammonia solution, or put paper containing orthotolidine at each joint in order to detect leak.	7d. Repair all vacuum leaks by tightening joints, replacing gaskets, replacing tubing and/or compression nuts.
8. Inability to maintain adequate chlorine feed rate.	8a. Malfunction or deterioration of water supply pump.	8a. Inspect pump.	8a. Overhaul pump (if turbine pump is used, try closing down needle valve to maintain proper discharge pressure).

9. Wide variation in chlorine residual produced in effluent.	9a. Chlorine flow proportion meter capacity inadequate to meet plant flow.	9a. Check chlorine meter capacity against plant flow meter capacity.	9a. Replace with higher capacity chlorinator meter.
	9b. Malfunctioning automatic controls.	9b.	9b. Call manufacturer's field service personnel.
	9c. Solids settled in chlorine contact chamber.	9c. Solids in contact chamber.	9c. Clean chlorine contact chamber.
	9d. Flow proportioning control device not zeroed or spanned correctly.	9d. Check zero and span of control device on chlorinator.	9d. Re-zero and span the device in accordance with manufacturer's instructions.
10. Chlorine residual analyzer recorder controller does not control chlorine residual properly.	10a. Electrodes fouled.	10a. Visual inspection.	10a. Clean electrodes.
	10b. Loop-time too long.	10b. Check loop-time.	10b. Reduce loop time by doing the following: 1. Move injector closer to point of application. 2. Increase velocity in sample line to analyzer cell. 3. Move cell closer to sample point. 4. Move sample point closer to point of application.
	10c. Insufficient potassium iodide being added for amount of residual being measured.	10c. Potassium iodide dosage.	10c. Adjust potassium iodide feed to correspond with residual being measured.
	10d. Buffer additive system malfunctioning.	10d. See if pH of sample going through cell is maintained.	10d. Repair buffer additive system.
	10e. Malfunctioning of analyzer cell.	10e. Disconnect analyzer cell and apply a simulated signal to recorder mechanism.	10e. Call authorized service personnel to repair electrical components.

(*Continued*)

Table 4 (*Continued*)

Indicators/observations	Probable cause	Check or monitor	Solutions
	10f. Poor mixing of chlorine at point of application.	10f. Set chlorine feed rate at constant dosage and analyze a series of grab samples for consistency.	10f. Install mixing device to cause turbulence at point of application.
	10g. Rotameter tube range is improperly set.	10g. Check tube range to see if it gives too small or too large an incremental change in feed rate.	10g. Replace with a proper range of feed rate.
11. Coliform count fails to meet required standards for disinfection.	11a. Inadequate chlorination equipment capacity.	11a. Check capacity of equipment.	11a. Replace equipment as necessary to provide treatment based on maximum flow through plant.
	11b. Inadequate chlorine residual control.	11b. Continuously record residual in effluent.	11b. Use chlorine residual analyzer to monitor and control the chlorine dosage automatically.
	11c. Short-circuiting in contact chamber.	11c. Contact time.	11c. 1. Install baffling in contact chamber. 2. Install mixing device in contact chamber.
	11d. Solids build-up in contact chamber.	11d. Visual inspection.	11d. Clean contact chamber to reduce solids build-up.
	11e. Chlorine residual too low.	11e. Chorine residual.	11e. Increase contact time and/or increase chlorine feed rate.
12. Chlorine residual too high in plant effluent to meet requirements.	12a. Chlorine residual too high.	12a. Determine toxicity level by bioassay procedures.	12a. Install dechlorination facility (See Shortcomings).

2.4. Design Example—Design of a Wastewater Chlorine Contact Chamber

Design a chlorine contact chamber for wastewater disinfection based on the following given data and equations.

The first step is to select contact time at peak flow and calculate volume of chlorine contact chamber (1) [use Eq. (3)]:

$$\mathrm{VCT} = [Q_p(\mathrm{CT})\ (10^6)]/(\ 24 \times 60)$$

where VCT = volume of contact tank, gal, Q_p = peak flow, 2 MGD, and CT = contact time at maximum flow, 15 min; then

$$\mathrm{VCT} = [Q_p(\mathrm{CT})\ (10^6)]/(\ 24 \times 60) = 2\ (15)\ (106)/(24 \times 60) = 20{,}833 \text{ gal}$$

The second step in design is to select a side water depth and calculate surface area [use Eq (4)]:

$$\mathrm{SA} = \mathrm{VCT}/[7.48\ \mathrm{SWD}]$$

where SA = surface area, ft^2, VCT = volume of contact tank, 20,833 gal, and SWD = side water depth = 8 ft; then

$$\mathrm{SA} = \mathrm{VCT}/[7.48 \times \mathrm{SWD}] = 20{,}833/[7.48 \times 8] = 348 \text{ ft}^2$$

The third step in design is to select a length-to-width ratio and calculate dimensions [use Eqs. (5) and (6)]:

$$\mathrm{CTW} = [\mathrm{SA}/\mathrm{RLW}]^{0.5}$$
$$\mathrm{CTL} = \mathrm{SA}/\mathrm{CTW}$$

where CTW = contact tank width, ft, SA = surface area, 348 ft^2, RLW = length-to-width ratio = select 40, and CTL = contact tank length, ft; then

$$\mathrm{CTW} = [\mathrm{SA}/\mathrm{RLW}]^{0.5} = [348/40]^{0.5} = 2.95 \text{ ft}$$
$$\mathrm{CTL} = \mathrm{SA}/\mathrm{CTW} = 348/2.95 = 118 \text{ ft}$$

The fourth step in design is to select chlorine dosage according to the recommended chlorine dosages in this section, and then calculate chlorine requirements [use Eq. (7)]:

$$\mathrm{CR} = (Q_a)(\mathrm{CD})(8.34)$$

where CR = chlorine requirement, lb/d, Q_a = average flow, 1 MGD, and CD = chlorine dosage, 8 mg/L; then

$$\mathrm{CR} = (Q_a)(\mathrm{CD})(8.34) = 1 \times 8 \times 8.34 = 66.7 \text{ lb/d}$$

The fifth step in design is to calculate peak chlorine requirements [use Eq. (8)]:

$$\mathrm{PCR} = (\mathrm{CR})(Q_p)/Q_a$$

where PCR = peak chlorine requirements, lb/d, CR = chlorine requirements, 66.7 lb/d, Q_p = peak flow, 2 MGD, and Q_a = average flow, 1 MGD; then

$$\mathrm{PCR} = (\mathrm{CR})(Q_p)/Q_a = (66.7 \times 2\ )/(1) = 133.4 \text{ lb/d}$$

Finally, the output data of wastewater disinfection design will be:

(a) Maximum flow, 2 MGD.
(b) Average flow, 1 MGD.
(c) Contact time, 15 min.
(d) Volume of contact tank, 20,833 gal.
(e) Average chlorine requirement, 66.7 lb/d.
(f) Peak chlorine requirement, 133.4 lb/d.
(g) Tank dimensions: surface area = 348 ft^2; side water depth = 8 ft; length–width ratio = 40; contact tank length = 118 ft.

2.5. Application Example—Coxsackie Sewage Treatment Plant, Coxsackie, NY, USA

This project was initiated in 1970s when the New York State Department of Health (NYSDOH) and the New York State Department of Correction (NYSDOC) undertook a program of research and development in the area of advanced biological sewage treatment at one of its correctional facilities. With a view to the impending program of sewage treatment plant construction in the entire New York State, it was decided to build an advanced sewage treatment plant and a research laboratory on the grounds of the Coxsackie Correctional Facility at West Coxsackie, New York. The plant has been performing successfully as a role model to the New York municipalities since 1973. This section only reports the operational and R&D data generated by Leo J. Hetling, Carl Beer, and Lawrence K. Wang, who were Research Director, Project Manager, and Operator (NYSDEC Senior Sanitary Engineer), respectively, in 1973–1977. The plant data introduce how a typical single-sludge activated-sludge plant performs for carbonaceous oxidation, nitrification, denitrification, and phosphors removal, wastewater chlorination, and sludge chlorine stabilization (37–42).

The Coxsackie Correctional Facility is an institution for young male delinquents aged 16–21. The average age of the inmates is l8. The design inmate population is 750. During the period covered by the full analytical data of this report, the inmate population was near capacity. In addition to the inmates, approx 350 prison personnel are in daytime or nighttime residence at the facility. A 306 ha (750 acres) farming operation is part of the correctional facility. Farm products are milk, vegetables, apples, and beef. The institution is located south of Albany, NY. The effluent of the single-sludge biological treatment plant is discharged to the Coxsackie Creek, a short tributary of the Hudson River. The Coxsackie Creek is classified as an intermittent stream. The New York State effluent requirements for sewage treatment plant discharging to intermittent streams are as follows: (1) 5-d BOD = 5 mg/L, maximum; (2) ammonia nitrogen, NH_3 = 2 mg/L maximum; and (3) DO = 7.5 mg/L minimum.

The detailed operational data can be found in another handbook by Wang, Shammas, and Hung (35). This chapter introduces the Coxsackie Sewage Treatment Plant (STP), its wastewater chlorination facility and its structural improvement. Figure 3 shows the flow diagram of Coxsackie STP, in which wastewater chlorine contact chamber (CCC) is the last unit process from where the plant effluent is discharged to the receiving stream, Coxsackie Creek. The hydraulic structure of CCC, illustrated by Fig. 4, consists of mixing chamber, influent plenum, flow-through chamber, and effluent plenum.

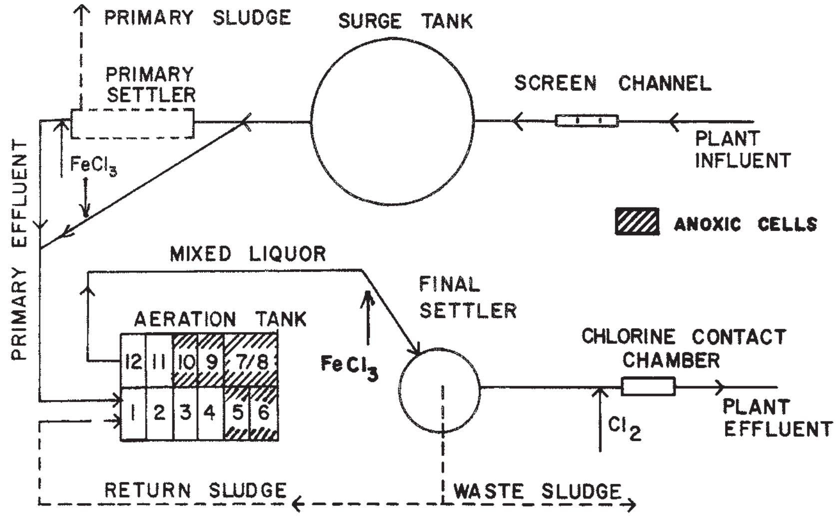

Fig. 3. Process flow diagram of Coxsackie Sewage Treatment Plant, Coxsackie, NY, USA.

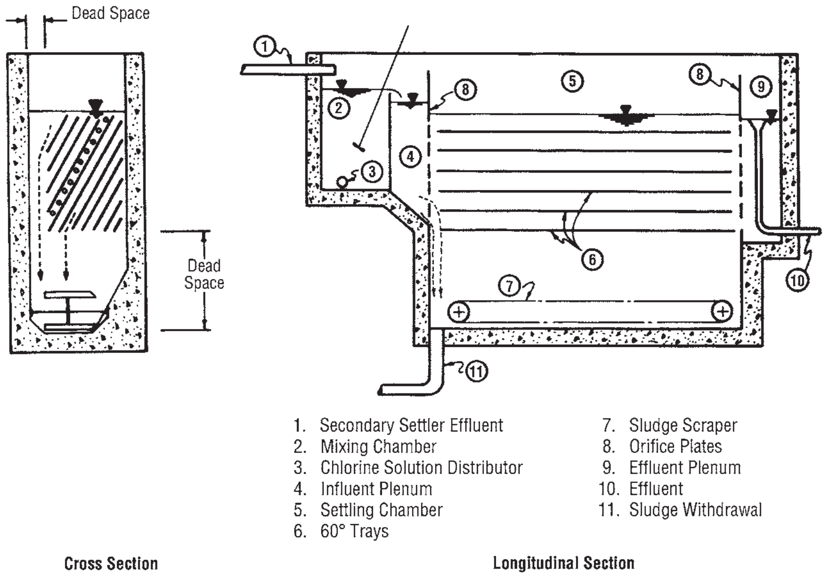

Fig. 4. Chlorine contact chamber and second-phase settler combination.

In the CCC, chlorine solution is admixed to the final settler effluent. The chamber is equipped with a 0.25-kW (1/3 hp), 330-rpm mixer. The two plenums serve to distribute the process water over the cross section of the flow-through chamber with the help of two orifice plates mounted at the entrance and exit of that chamber. Each orifice plate carries 40 orifices of 12.7 mm (1/2 in.) diameter. The flow-through chamber is 1.52 m × 1.52 m (5 ft × 5 ft) in cross section and 4.88 m (16 ft) long.

Baffle cages were installed in the combined CCC and second-phase final settler unit (refer to Fig. 4). The baffle cages carry Plexiglass baffles 3.2 mm (1/8 in.) thick that are

Table 5
Effect of Chlorine Contact Chamber and Second-Phase Settler Combination on Suspended Solids Removal

Date 1975	Influent SS (mg/L)	Effluent SS (mg/L)	Date 1975	Influent SS (mg/L)	Effluent SS (mg/L)
June 28	2.0	2.6	July 16	3.6	2.7
29	5.1	3.4	17	4.2	2.9
30	7.3	3.1	18	6.2	2.9
July 1	5.2	N.AV.	19	3.8	2.7
2	3.8	2.7	20	6.3	4.5
3	N.AV.	2.7	21	5.1	3.8
4	7.9	1.3	22	5.5	3.9
5	5.5	4.7	23	6.7	4.6
6	6.3	5.1	24	7.6	5.9
7	4.5	3.9	25	7.2	4.5
8	5.6	4.7	26	4.9	4.0
9	6.8	4.5	27	5.8	3.7
10	5.0	4.5	28	11.4	3.7
11	5.4	3.7	29	5.4	4.1
12	5.1	3.5	30	4.3	3.1
13	3.8	3.3	31	4.9	3.8
14	6.0	4.4	Aug. 1	6.9	3.9
15	4.8	3.5	Ave.	5.4	3.6

inclined by 60° to the horizontal and spaced 152 mm (6 in.) on center or 305 mm (12 in.) vertically.

The data in Table 5 for the 5-wk period of June 28 to August 1, 1975, indicate an average 33% reduction in suspended solids (SS) from 5.4 mg/L down to 3.6 mg/L was achieved across the unit.

During the 5 wk period ending August 1, 1975, the following operating conditions prevailed: (a) average daily flow = 629 m^3 /d (166,000 gpd); (b) average flow rate = 7.28 L/s (0.255 cfs); (c) average flow velocity taken over the l.525 m × 1.525 m (5 ft × 5 ft) cross section = 0.0031 m/s (0.0102 ft/s); and (d) average flow-through time for 4.88 rn (l6 ft) length = 26 min.

It has been proven that the operation of the subject combination unit can be improved by using corrugated sheets instead of the flat Plexiglass sheets as baffles. Using corrugated sheets drastically cut down the accumulation time of the solids on the baffles. Solids accumulate on the baffles until a certain thickness is reached. At that point, the solids slide off.

The orifice plates must be cleaned periodically of scraps of papers and bits of rags. In order to prevent such a manual operation, a combined second-phase settler and chlorine contact chamber is protected by a traveling screen.

3. SLUDGE CHLORINATION AND STABILIZATION

3.1. Process Description

Stabilization by chlorine addition has been developed and is marketed under the registered trade name Purifax. The chlorine conditioning of sludge varies greatly from the more traditional methods of biological digestion or heat conditioning. First, the reaction is almost instantaneous. Second, there is very little volatile solids reduction in the sludge. There is some breakdown of organic material and formation of carbon dioxide and nitrogen; however, most of the conditioning is by the substitution or addition of chlorine to the organic compound to form new compounds that are biologically inert. The sludge to be chlorinated can be either biosolids or chemical sludge.

The chemical form in which chlorine is present in wastewater is directly related to pH. The first reaction of chlorine is with ammonia (combined available chlorine). However, this is a small portion of the chlorine added for this process. Most of the chlorine (free available chlorine) ends up as either hydrochloric acid, HCl, or hypochlorous acid, HOCl. The HOCl subsequently breaks down into nascent oxygen, O, and HCl. Below pH 5, molecular chlorine, Cl_2, appears in solution and increases in concentration with decreasing pH. The equations for the reaction of free available chlorine in water can be summarized as follows:

$$Cl_2 + 2\ H_2O \rightarrow HOCl + HCl + H_2O \tag{9}$$

Hypochlorous acid, HOCl, its subsequent by-product nascent oxygen, O, and molecular chlorine are all strong oxidants. The hydrochloric acid is not an oxidant or a disinfectant, but does lower the pH of the solution. Generally, the entire process consists of a macerator, flow meter, recirculation pump, two reaction tanks, a chlorine eductor, chlorinator, evaporator, a pressure control pump, and two holding tanks. Variations are possible with the selection of the individual units depending on the nature of the sludge. Conventional grit removal equipment used for the plant influent will suffice for grit reduction of sludge processed through the oxidation unit. If grit removal equipment has not been provided for the plant, then it should be added to this system. The type of macerator selected depends on the type of sludge being stabilized. The resulting maximum particle size should not exceed 1/4 in. To provide optimum utilization of chlorine, the system should be preceded by a sludge holding tank, which includes some means of mixing or agitation. This is especially necessary for treating primary sludge. The primary sludge solids concentration is typically higher at the beginning of a pumping cycle and lower near the end of the cycle. Without provision of the holding tank, the chlorine requirement would be variable and over-chlorination or under-chlorination a possibility. With the holding tank in use, the chlorine requirement can be set at a constant rate. Use of sludge thickeners ahead of the conditioning unit is optional. The sludge processing rate will be reduced for thicker sludge; specifically for primary sludge or primary sludge plus trickling filter sludge greater than 4%, primary sludge plus waste-activated sludge greater than 2.6%, or waste activated sludge greater than 1%. The lower processing rates offset the reduction in volume obtained by thickening, so there is no advantage in thickening to concentrations greater than those given above for the different types of sludge.

3.2. Design and Operation Considerations

A schematic of the sludge chlorination process (Purifax process) is shown in Fig. 5. The sludge is first pumped through a macerator to reduce the particle size for optimum chlorine exposure. It is then mixed with conditioned sludge ahead of the recirculation pump at a ratio of 3.8 gal of recirculated sludge for each gallon of raw sludge.

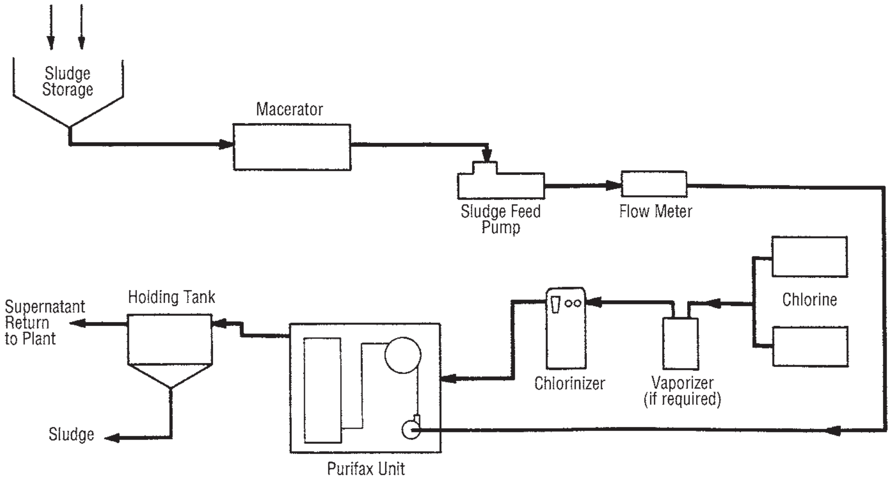

Fig. 5. Schematic of a waste sludge chlorination process system (BIF).

The combined flow is then pumped through the first reaction tank where it is thoroughly mixed. A portion of the sludge then flows to the second reaction tank while the remainder is recirculated. Recirculation of a portion of the sludge aids in mixing and provides better utilization of the chlorine. The recirculation rate is normally held constant. A pressure control pump at the discharge end of the second reaction tank maintains a pressure of 30–40 psi on the entire system.

Chlorine is added to the recirculated sludge line ahead of the recirculation pump. The passage of the conditioned sludge through the eductor creates a vacuum that causes chlorine gas to move from the chlorine supply into the sludge line. The recirculation of the conditioned sludge through the eductor satisfies the dilution requirements of the chlorine gas without introducing additional water into the system. The recirculation pump acts as a mixer for the raw and conditioned sludge. Almost all of the reaction between the sludge and chlorine takes place in the first reaction tank. This tank provides 3 min of detention time at design flow. The second reaction tank provides an additional 1.5 min of detention time. Operating the system under pressure forces the chlorine to penetrate into the sludge particles to insure a complete reaction.

Chlorine is supplied to the unit from a separate chlorinator located in the same room as the chlorinators for disinfecting the plant effluent. Because of the large volumes of chlorine required for the sludge chlorination (Purifax) unit, an evaporator is used ahead of the chlorinator. The sidestreams that require further treatment result from the thickening and/or dewatering processes that follow the oxidation unit. The characteristics of the supernatant vary with the type of sludge being treated and the method of thickening or dewatering. The oxidized sludge should be contained in a holding tank or reservoir for at least 48 h. This will allow time for the chlorine residual to approach zero and the pH to rise from 3.5 or 4.0 to 5.0 or 6.0. The BOD_5 and suspended solids (SS) concentrations obviously are quite variable but each should be less than 350 mg/L. The supernatant or filtrate sidestreams are routed to the plant headworks for treatment with the incoming sewage.

Table 6
Solids Loading Rates

Type of sludge	Solids concentration (%)	gpm/hp
Primary	≤4	2–3.5
Primary and trickling filter	≤4	2–3.5
Primary and waste activated sludge	≤2.6	2–3.5
Primary and waste activated sludge	4.0	1.5–2.5
Primary and waste activated sludge	5.0	1.1–2.1
Waste activated sludge	1.0	2.9–5.1
Waste activated sludge	2.0	2.2–3.9
Waste activated sludge	3.0	1.5–2.6
Waste activated sludge	4.0	0.8–1.3
Anaerobic digester supernatant	0.2	2.9–5.1
Anaerobic digester supernatant	0.3	2.5–4.5
Anaerobic digester supernatant	0.4	2.1–3.8
Anaerobic digester supernatant	0.5	1.8–3.2
Septic tank sludge	2.0	2.9–5.1
Septic tank sludge	3.0	2.5–4.5
Septic tank sludge	4.0	2.2–3.9
Trickling filter humus	2.0	2.9–5.1
Trickling filter humus	3.0	2.5–4.6
Trickling filter humus	4.0	2.2–4.0

If the oxidized sludge is dewatered without provisions for the holding tank, then sodium hydroxide or lime must be added to raise the pH. The quantities of filtrate or supernatant to be treated vary with the type of process(es) used. In general, the quantity of supernatant or filtrate to be treated is minor in terms of the total treatment plant capacity. The loading rates shown in Table 6 apply to standard Purifax units. Chlorine dosages range from 600 to 4800 mg/L depending on the type of sludge and solids concentration. Generally, the units should be operated with the lowest concentration shown for each sludge type shown in Table 6. At these concentrations the chlorine dosage varies from 600 to 2000 mg/L or 0.005 to 0.017 pounds per gallon. The actual dosage used must be adjusted for each individual plant.

The stabilized sludge will have a pH of 2.5–4.5 and chlorine residual of 200–400 mg/L. The stabilized sludge will have chlorine smell and light brown color. Total solids, suspended solids, and volatile solids concentrations will be about the same as the raw sludge. When stored for 48 h, the chlorine residual will have fallen to 0 and the pH will have increased to 4.5–6.0. The organics will normally not decompose even after several days of storage.

Table 7 shows the expected characteristics for sidestreams from typical thickening and dewatering operations as applied to the conditioned sludge.

3.3. Process Equipment and Control

3.3.1. Process Equipment

The process equipment for sludge chlorination or stabilization is commercially available from BIF Corporation.

Table 7
Sidestream Characteristics

Supernatant from Conditioned Sludge Holding	
BOD_5	50–150 mg/L
Suspended solids	50–200 mg/L
pH	4.5–6.0
Chlorine residual	0
Filtrate from Vacuum Filter	
BOD_5	100–350
Suspended solids	50–150
pH (with 20–30 lb/ton NaoH)	4.5–5.5
Chlorine residual	200–400 (unless stored)
Centrate from Solid Bowl Centrifuge	
BOD_5	200–400
Suspended solids	300–500
pH (with 20–30 lb/ton NaOH)	4.5–5.5
Chlorine residual	200–400 (unless stored)

3.3.2. *Staffing Requirements*

The staff requirements shown below apply to the Purifax process, macerator, pumps, and chlorination system. Dewatering or thickening operation and maintenance are not included. The labor requirements of a package chlorine treatment unit are listed below: (a) Operation = 2 h/shift/unit; and (b) maintenance = 3 h/shift/unit.

The chemical oxidation process (i.e., chlorination) is automated. The main effort is visually checking the process and operating the ancillary equipment. Most of the systems now in operation are package-type units.

3.3.3. *Monitoring*

The oxidized sludge should have a faint chlorine odor after processing, with no chlorine odor after 2 d storage.

The material should be light gray in color. If these characteristics change, the process control parameters should be checked. Each individual plant will result in processed sludge that has slightly different sensory characteristics. After the wastewater plant has operated for several weeks, then the sensory observations can be more critically reviewed. Major differences in chlorine odor may result with too little or too much chlorine. Darkening of the sludge color may result if the process is not properly operating. If either of the above occur, the chlorine residual and system pressure should be checked immediately. If these parameters are within acceptable ranges, then check for changes in the incoming sludge.

3.3.4. *Normal Operating Procedures*

3.3.4.1. PRE-STARTUP AND STARTUP

The following are the pre-startup procedures: (a) Check operation of the chlorine pressure reducing valve (PRV) by turning ON the power switch on the sludge oxidation unit control panel. Turn the chlorine valve switch to the OPEN position, observe operation of valve actuator; (b) turn switch to the CLOSED position; and (c) adjust time delay relays according to the manufacturer's instruction manual.

The following are the startup procedures: (a) Adjust the chlorinator feed rate to a low setting; (b) close the chlorine pressure-reducing valve bypass valve; (c) turn on the chlorine supply to the chlorinator; (d) turn the feed pump and macerator motor starter selector switches to AUTO; (e) turn both selector switches in the PURIFAX motor starter panel to AUTO; (f) turn the power switch and alarm switch ON and the chlorine valve switch to AUTO; (g) depress the START pushbutton. When the motors start, adjust the speed of the pressure control pump to produce 30 psi at the process pressure gauge. If this is not done before the timing relay times out, the system will automatically shut down. (h) The vacuum gauge should read approx 20 in. of mercury. The vacuum gauge on the chlorinator should read the same. The pump suction gauge should read approx 5 psi. The pump discharge gauge should read approx 30 psi. (i) Check the oxidation unit for obvious sludge leaks. (j) Belt adjustment—adjust takeup on the recirculation pump belts until only a slight bow appears in the slack side. (k) Recheck the tension of new belts several times within the first 50 h of operation and adjust if necessary. (l) Thereafter check the tension periodically. (m) Install belt guard. (n) When sludge is introduced into the system, it may be necessary to readjust the speed of the pressure control pump. (o) Adjust the chlorinator feed rate to the calculated rate; and (p) check for water at each pump seal by disconnecting the seal water tubing.

3.3.4.2. ROUTINE AND SHUTDOWN OPERATIONS

The system routine operation is automatic after startup. Should a problem develop causing deviation from established operating limits, the system will automatically shutdown. The system cannot be restarted until the problem causing the shutdown has been corrected. The system should be checked twice a shift.

Normal shutdown is a sequential operation initiated by depressing the STOP pushbutton. The sequence of operation is as follows:

1. Depressing the STOP pushbutton causes immediate interruption of the circuit to the chlorine pressure-reducing valve causing it to close and shut off the chlorine gas supply.
2. The chlorine pressure switch senses the loss of chlorine gas pressure and its contacts open. After a sufficient time has elapsed to evacuate chlorine gas from the piping, an OFF delay relay, 3TR, is de-energized, closing the vacuum line valve.
3. When the vacuum valve closes, its auxiliary contacts open causing interruption of the circuits to the recirculation pump and pressure control pump motor starters. Auxiliary contacts in the starters open, interrupting the circuit to the seal flushing water solenoid valve and the remotely mounted control relay. The control relay is de-energized stopping the feed pump and macerator.

3.3.5. Process Control Considerations

The control system is automatic, with little operator attention required. There are three variables that affect operation. They are throughput rate, chlorine feed rate, and system pressure. The throughput rate has been designed for an expected solids concentration. The process chlorine feed is set based on the expected rate of solids fed to the oxidation unit. If the actual solids concentration increases, the throughput rate should be lowered.

The chlorine feed rate is also adjusted based on throughput rate solids concentration and/or monitoring results. If the chlorine residual increases or decreases beyond the limits of the recommended range, check the chlorine demand and reset the chlorine feed.

If the above parameters are correct and the oxidized sludge characteristics are not within recommended limits, check the unit pressure. This should be between 30 and 40 psi.

3.3.6. Emergency Operating Procedures

The chlorine oxidation unit will not operate without power. Raw sludge must be hauled to a landfill site or temporarily stored if facilities are available. If stored, the sludge must be processed when power is restored.

Other treatment units that affect the oxidation unit include raw sludge thickening and oxidized sludge dewatering. If the raw sludge thickener is out of service, the throughput rate will not be affected unless the maximum capacity is exceeded. If this occurs, the unit hours of operation will have to be extended. The chlorine feed rate should be adjusted. The amount of adjustment is determined by the results of a chlorine demand test.

If the oxidized sludge dewatering unit is out of service, then the disposal transport system and disposal site must be expanded to handle the increased volume.

Should an emergency occur requiring immediate shutdown and over-ride of normal sequential shutdown, an EMERGENCY STOP pushbutton is provided for this purpose. This device interrupts power to all components in the oxidation unit control circuit, shuts down all motors, and closes the vacuum line valve and the chlorine pressure-reducing valve (PRV). The EMERGENCY STOP pushbutton is also used as a reset device to restore the system to normal operating status after an alarm situation has occurred.

The control system is designed to sense certain component and system failures. Pressure switches are located to sense overpressure, excessive suction, low chlorine pressure, and low eductor vacuum. A flow switch senses low flow. Motor starters sense motor overloading. Evaporator low-temperature switch senses low water temperature.

Whenever deviation from established operating limits is sensed, lights indicating the cause of the problem will be activated, an audible alarm will call attention to the problem, and the system will be automatically shutdown until the problem is corrected. The audible alarm may be switched off. The indicating lamps remain lighted until the problem is corrected and the system is reset.

A lock-out relay is included in the circuit that allows indicating alarm lamps to light, the audible alarm to sound, and prevents restarting without resetting the system when shutdown occurs in an alarm situation. It also prevents alarm devices from functioning during normal shutdown.

3.3.7. Common Process Shortcomings and Solutions

Table 8 indicates the common process shortcomings and their respective solutions. Table 9 is a sludge chlorination trouble shooting guide.

3.3.8. Maintenance Considerations

Inspect motors at regular intervals; keep motors clean and ventilation openings clear. Check valve may become clogged causing sludge to backup into chlorinator. Periodically disassemble and clean. Replace diaphragm and spring if they are deteriorated. Valve ball and seats may become scored causing sludge to back-up into diaphragm check valve. Periodically disassemble by unscrewing union nuts, with valve in CLOSED position, remove carrier and ball by pressing on flat spot on ball. Replace ball and seats if scored.

Table 8
Common Design Shortcomings of Sludge Chlorination and Solutions

Shortcoming	Solution
1. Unit improperly sized.	1. Change operating time.
2. Inadequate holding tank capacity.	2a. Add another holding tank. 2b. Use chemicals for pH adjustment and chlorine removal.
3. Inadequate storage for new sludge during power outage or shutdown.	3a. Store sludge in clarifiers (temporary). 3b. Haul sludge to landfill.

When reassembling valve, use caution. Only hand tighten union nuts. Check the macerator twice daily for debris.

The major concerns are contact with the low pH and the high chlorine concentration of the oxidized sludge. Human contact with the oxidized sludge should be avoided. If this occurs, shower immediately.

The macerator can be dangerous if maintenance is attempted while the unit is turned on. Be sure the power is off before doing maintenance work.

Safety practices for handling chlorine are contained in "Safety Practice for Water Utilities," AWWA Manual M3 and an AWWA/WEF/APHA handbook (24,25). The readers are referred to Section 5 for more information on safety considerations of all chlorination processes.

Generation of chlorinated hydrocarbons may be a problem (26), but the magnitude of any such problem cannot be determined at this time. The feasibility of using a chlorination step to reduce excess sludge in an activated-sludge process has been studied by Saby et al. (27). The ultimate disposal of excess waste-activated sludge (WAS) from a biological treatment plant has been a problem. Ozonation works well, but is a costly option. It was observed that the WAS production could readily be reduced by 65% once the sludge chlorination treatment was involved (27). However, the chlorination treatment also caused some problems: (a) it resulted in poor sludge settleability when part of the treated sludge was returned to the aeration tank and (b) it increased soluble COD in the plant effluent. Saby et al. (27) discovered that by integrating the immersed membrane into the activated-sludge process, these difficulties can be overcome effectively. Wang and his associates (28–35) have studied other alternative disinfectants (quaternary ammonium compounds) and oxidizing agents (ozone, chlorine dioxide) for sludge stabilization with preliminary success. Continuous research along this direction will be be needed.

3.4. Application Example—Coxsackie Sewage Treatment Plant, Coxsackie, NY, USA

Figure 3 in introduces the Coxsackie Sewage Treatment Plant (STP). The plant's special wastewater chlorination facility, a combined chlorine contact chamber (CCC) & second-phase final settler unit, is shown in Fig. 4. This section introduces the sludge chlorination facility of Coxsackie STP and its operational data. At Coxsackie STP, data generated during 19 batches of sludge chlorination are summarized in Tables 10–12. Characteristics of the underflow from the sludge dewatering beds for nine of those

Table 9
Troubleshooting Guide for Sludge Chlorination Process

Indicators/observations	Probable cause	Check or monitor	Solutions
1. Oxidation unit shuts down (low chlorine supply pressure).	1a. No chlorine supply pressure.	1a. (1) Check chlorine tanks. (2) Check all manual valves in supply piping. (3) Check evaporator.	1a. (1) If empty, replenish supply. (2) Should be fully open. (3) See manufacturer's instructions.
	1b. Failure of electric chlorine pressure-reducing and shut-off valve to open.	1b. Check chlorine valve switch on control panel (should be in AUTO position).	1b. (1) Turn chlorine valve switch on control panel to OPEN position. If valve opens, and if chlorine pressure is indicated at chlorinator, the problem is in the control panel. (2) If valve remains closed, the problem is in the valve or valve operator.
	1c. Failure of chlorine pressure switch to close.	1c. (1) Check position of relay. (2) Check pressure setting and switch contacts.	1c. (1) Should be de-energized. (2) Adjust as needed.
	1d. Electrical failure in control panel.	1d. See wiring diagram.	1d. Correct where necessary.
2. Oxidation unit shutdown.	2a. Failure of feed pump motor to operate.	2a. (1) Check selector switch on motor starter. (2) Check motor overload heaters. (3) Check control relay.	2a. (1) Should be in AUTO position. (2) Correct if overloaded. (3) Should be energized, if not, problem is in control panel or control relay. If relay is energized, relay has failed.
	2b. Failure of feed pump to pump.	2b. (1) Check lines for obstructions. (2) Check valves. (3) Pull pump.	2b. (1) Clean lines. (2) Open if necessary. (3) Repair per manufacturer's instructions.
	2c. Failure of flow meter receiver contacts to close.	2c. (1) Check setting of auxiliary contacts. (2) Check valve in discharge piping.	2c. (1) Should be set for approximately 50% of the minimum system throughput rate. (2) Should be fully open.

	2d. Process pressure switch contacts opened.	2d. (1) Check valve in discharge piping. (2) Monitor pressure control pump speed.	2d. (1) Should be fully open. (2) Reduce speed.
	2e. Pump suction pressure switch contacts opened.	2e. Obstruction in inlet piping.	2e. Remove obstruction.
3. Oxidation unit shuts down (low vacuum).	3a. Break or leak in chlorine vacuum line piping.	3a. Locate leak.	3a. Repair.
	3b. Plugged eductor body.	3b. Disassemble and inspect.	3b. Remove two pipe plugs, vacuum gauge, switch assembly and vacuum line valve. Clean all openings.
	3c. Recirculation pump fails to deliver required dynamic head of 30 psi. (discharge pressure minus suction pressure).	3c. (1) Check drive belt tension. (2) Check for worn impeller. (3) Check for air in piping.	3c. (1) Adjust. (2) Replace. (3) Bleed off air at vent plugs.
	3d. Failure of pressure control pump to maintain pressure in the system.	3d. (1) Check pump speed. (2) Check for worn impeller.	3d. (1) Increase speed. (2) Replace.
	3e. Failure of pressure control pump motor or recirculation pump motor to operate.	3e. (1) Check selector switches on the starter panel. (2) Check motor starter overloads.	3e. (1) Set on AUTO position. (2) Reset.
	3f. Failure of vacuum switch contacts to close.	3f. (1) Check switch assembly and vacuum gauge. (2) Check vacuum setting and switch contact. (3) Check for loss of oil.	3f. (1) Replace. (2) Clean and reset. (3) Fix leak and/or refill.
	3g. Electrical failure in control panel.	3g. Check wiring diagram.	3g. Repair.

(*Continued*)

Table 9 (*Continued*)

Indicators/observations	Probable cause	Check or monitor	Solutions
4. Macerator stopped.	4. Jammed with debris.	4. Inspect.	4. Turn off power, remove obstruction.
5. Indication of vacuum at oxidation unit but none at chlorinator.	5a. Diaphragm check valve plugs.	5a. Inspect.	5a. Disassemble and clean.
	5b. Failure of vacuum line valve ball to open.	5b. Inspect.	5b. (1) Replace with spare valve. (2) Disassemble and replace broken ball or shaft.
6. Depressing STOP button on control panel, unit continues to run longer than normal shutdown time.	6a. Failure of electric chlorine pressure-reducing and shut-off valve to close.	6a. Check chlorine pressure at chlorinator.	6a. (1) If there is pressure, turn chlorine valve switch on control panel to the closed position. (2) If there is still pressure, the valve is stuck open-replace. (3) If there is no pressure, the problem is in the control panel (correct wiring or fuse).
	6b. Failure of chlorine pressure switch contacts to open.	6b. Check position of relay.	6b. If energized, the pressure switch is stuck open.
	6c. Failure of vacuum line valve limit switch contacts to open.	6c. (1) Inspect. (2) Check valve operator.	6c. (1) Replace with spare valve. (2) If in the OPEN position, problem is in motor, gearing, limit switches, or cams. (3) If closed, problem is in the limit switch or cam.

Table 10
Chlorine Dosages Used During Sludge Chlorination Treatment

Batch	Volume of sludge chlorinated		Cl_2 used		SS of sludge before treatement	Dry sludge treated		Chlorine Dosage	Chlorine % of dry solids
No.	(m^3)	(gal)	(kg)	(lb)	(mg/L)	(kg)	(lb)	(mg/L)	
1	31.8	(8400)	22	(48)	9200	293	(645)	685	7
2	31.0	(8200)	27	(60)	7400	230	(506)	877	12
3	31.4	(8300)	25	(54)	10,100	318	(699)	780	8
4	22.4	(6000)	24	(52)	8700	198	(435)	1039	12
5	33.7	(8900)	36	(78)	10,700	361	(794)	1051	10
6	33.7	(8900)	33	(72)	12,700	429	(943)	970	8
7	37.8	(10,000)	21	(46)	8700	330	(726)	552	6
8	32.6	(8600)	24	(54)	13,400	437	(961)	753	6
9	23.5	(6200)	25	(55)	9600	225	(496)	1064	11
10	31.0	(8200)	36	(80)	9700	301	(663)	1170	12
11	32.6	(8600)	18	(40)	9800	320	(703)	558	6
12	68.6	(18,100)	59	(129)	7300	501	(1102)	855	12
13	22.7	(6000)	24	(52)	7400	168	(370)	1039	14
14	51.9	(13,700)	38	(84)	6300	327	(720)	735	12
15	37.8	(10,000)	35	(76)	7100	269	(592)	911	13
16	45.0	(11,900)	30	(66)	5400	244	(536)	665	12
17	45.0	(11,900)	24	(54)	5600	253	(556)	544	10
18	22.7	(6000)	24	(54)	7200	164	(360)	1079	15
19	42.4	(11,200)	39	(87)	4200	178	(392)	931	22
Total	678.0	(179,100)	564	(1241)		5546	(12,199)	831*	10*

Batch 18: Primary sludge; all other batches were a mixture of primary sludge and WAS.
*Weighted mean.

batches are presented in Table 13. The batch size varied somewhat according to the solids concentration of the sludge treated and also according to the sludge storage space available. A typical batch consisted of 34 m^3 (9000 gal) applied to 111 m^2 (1200 ft^2) of sand bed, resulting in an average sludge slurry dose of 0.31 m (1 ft). However, such a depth was never attained because drainage occurred immediately upon application. At most, approx 15 cm (6 in.) of chlorinated sludge slurry were seen standing on the bed. Usually, all visible liquid had drained away by the morning following application (37–42).

The slurry was treated at a rate of approx 2.5 L/s (40 gpm). The weighted average of the chlorine dosage was 830 mg/L or 10% of the dry weight of the sludge chlorinated. The chlorine dosage was adjusted to produce a pH of 2.3–2.8 in the chlorinated slurry. The pH of the unchlorinated slurry indicates that considerable nitrification had occurred on some batches before treatment.

During chlorination, samples of unchlorinated and chlorinated sludge slurry were withdrawn and subjected to the tests reflected in Tables 10–12. Glass fiber filters were used to determine some of the parameters in Table 13.

Table 11
Effect of Sludge Chlorination on Solids Concentration, Filterability, and pH

	SS			VSS			Filterability			pH	
Batch no.	Before (mg/L)	After (mg/L)	Change (%)	Before (mg/L)	After (mg/L)	Change (%)	Before (mL/30 sec)	After (mL/30 sec)	Change (%)	Before	After
1	9190	8680	–6	4950	5020	+1	122	182	+49	6.45	2.6
2	7400	7240	–2	3780	3680	–3	124	172	+40	6.3	2.65
3	10,100	9540	–6	5680	5580	–2	20	97	+385	7.0	2.5
4	8730	8070	–8	5100	5030	–1	158	230	+46	6.7	2.5
5	10,690	10,420	–3	6190	6470	+5	16	69	+331	6.75	2.7
6	12,705	11,765	–7	7480	7390	–1	12	67	+458	7.1	2.4
7	8680	8020	–8	4100	4440	+8	120	162	+35	6.0	2.5
8	13,440	12,620	–6	7040	7420	+5	14	63	+350	6.4	3.0
9	9590	9220	–4	5910	6010	+2	10	64	+540	6.6	3.1
10	9680	9720	–	5640	6080	+8	34	76	+124	6.7	2.75
11	9780	9460	–3	5550	5600	+9	68	99	+46	6.0	3.0
12	7300	6920	–5	4860	4820	–1	16	67	+319	6.5	2.6
13	7360	5920	–20	4720	4130	–13	88	144	+64	5.85	2.4
14	6260	6710	–7	4100	4890	+19	84	152	+80	6.9	3.2
15	7050	6330	–10	4220	4030	–5	50	84	+68	6.8	2.4
16	5440	4950	–9	3320	3340	–	51	82	+61	6.9	2.3
17	5600	5430	–3	3460	3560	+3	30	77	+157	6.9	2.5
18	7220	6940	–4	4580	4820	+5	10	83	+730	7.2	2.25
19	4220	4020	–5	2780	2920	–5	22	24	+10	7.4	2.7
Weighted mean	8180	7760	–5	4790	4900	+2	52	101	+49		

Table 12
Effect of Sludge Chlorination on Slurry Filtrate Quality

	TOC			NH_4^+			NO_2^-+NO_3^-N			Dissolved orthophosphorus			Chlorine residual
Batch no.	Before (mg/L)	After (mg/L)	Change (mg/L)	Before (%)	After (mg/L)	Change (mg/L)	Before (mg/L)	After (mg/L)	Change (mg/L)	Before (mg/L)	After (mg/L)	Change (mg/L)	After (mg/L)
1	17.5	63.5	+363	1.3	2.3	+1.0	42.0	42.0	0	0.5	2.4	+1.9	133
2				0.6	1.2	+0.6	74.0	71.5	–2.5	1.8	8.8	+7.0	102
3				8.9	9.2	+0.3	0.2	1.0	+0.8	2.1	1.6	–0.5	111
4				1.0	1.7	+0.7	35.5	34.5	–1.0	1.9	6.1	+4.2	233
5				9.5	13.6	+4.1	37.5	31.2	–6.3	2.2	2.2	—	142
6	115	184	+183	20.5	19.6	–0.9	5.7	0.4	–4.3	1.6	2.0	+0.4	164
7	11	71	+545	0.5	2.2	+1.7	59.0	56.0	–3.0	0.6	2.6	+2.0	191
8	150	188	+253	22.0	22.0	0	62.5	83.5	+21.0	5.1	3.0	–2.1	121
9				72.6	61.2	–11.1	0.3	0.3	—	4.7	1.3	–3.4	22
10				1.3	3.6	–2.3	5.1	19.9	+14.8	0.8	0.8	—	89
11				2.8	28.5	+25.7	3.8	15.0	+11.2	0.4	1.6	+1.2	150
12				1.7	0.2	–1.5	7.6	4.0	–3.6	0.92	1.5	+0.6	126
13	20.5	46	+124	1.6	2.4	+0.8	2.7	0.8	–1.9	0.20	3.15	+3.0	244
14	24	61.5	+156	8.8	11.7	+2.9	0.8	6.9	+6.1	0.31	1.40	+1.1	121
15	66	74.5	+13	0.1	9.1	+9.0	6.5	4.3	–2.2	4.53	5.65	+1.1	171
16	20	49	+145	0.4	0.5	+0.1	0.5	1.5	+1.0	0.33	4.70	+4.4	197
17	39	50	+28	0.2	0.1	–0.1	3.8	3.7	–0.1	0.61	1.95	+1.3	74
18				0.1	0.3	+0.2	1.7	0.9	–0.8	3.32	5.50	+2.2	315
19				0.2	0.2	—	8.7	0.6	–8.1	0.92	3.96	+3.0	168
Weighted mean				6.7	8.7	+2.0	17.6	18.4	+0.8	1.6	3.0	+1.4	146

Table 13
Quality of Sludge Dewatering Bed Underflow During Sludge Chlorination Treatment

			Constituents of bed filtrate**									
Batch no.	Type of bed*	Chlorine dosage (mg/L)	SS (mg/L)	VSS (mg/L)	pH	Chlorine residual (mg/L)	TOC (mg/L)	COD (mg/L)	Total alk. (mg/L as $CaCO_3$)	NH_4^+-N (mg/L)	NO_2^-+ NO_3^-N (mg/L)	Dissolved orthophosphorus (mg/L)
11	CTF	558	21	13	6.6	2.7	N. AV.	193	78	8	5	1.4
12	CTF	855	76	24	6.2	0.7	N. AV.	208	115	12	15	1.2
13	SSB	1039	29	12	5.2	0.1	43	147	42	36	11	1.8
14	CTF	735	14	N. AV.	6.3	2.7	39	110	130	11	1	0.4
15	CTF	911	40	19	6.7	0.1	44	241	90	24	17	1.3
16	SSB	665	9	2	5.8	5.3	51	142	87	12	14	0.5
17	CTF	544	64	43	6.7	0.1	60	178	73	15	12	1.0
18	CTF	1079	25	22	6.3	0.1	N. AV.	199	52	21	8	1.0
19	CTF	931	55	27	6.9	2.7	N. AV.	211	127	6	15	1.3

*CTF = Converted trickling filter.
SSB = Standard sand drying bed.
**Grab samples.

There was only a slight reduction in SS due to chlorination, approx 5%. It should be noted in this connection that solids reduction due to acidification with H_2SO_4 to pH 2 was found to be between 50 and 60% in unrelated laboratory tests on the waste sludge of this plant.

The increase in filterability, 49% on the average, was of course the most important change in sludge characteristics brought about by sludge chlorination. The increase of filterability was greater for sludge of a low initial filterability. The weighted average filterability was increased from 52 to 101 mL/30 s. The mechanisms of this increase remain to be explained.

The changes in nutrient concentration were somewhat erratic but on the average negligible, i.e., under 3 mg/L.

The chlorine residual in the chlorinated sludge was approx 150 mg/L. A significant increase in the TOC of the sludge supernatant was observed from a range of 11–150 mg/L to a range of 46–188 mg/L. The sludge dewatering beds underflow did not impose any significant load on the Coxsackie activated sludge system. The following constituent ranges were determined: (a) SS = 9–76 mg/L; (b) VSS = 2–43 mg/L; (c) pH = 5.2–6.9; (d) chlorine residual = 0.1–5.3 mg/L; (e) TOC = 39–60 mg/L; (f) COD = 142–241 mg/L; (g) alkalinity = 42–130 mg/L as $CaCO_3$; (h) ammonia–N = 6–36 mg/L; (i) nitrate–nitrite–N = 1–17 mg/L; and (h) dissolved orthophosphorus = 0.4–1.8 mg/L.

4. SEPTIC CHLORINATION AND STABILIZATION

4.1. Process Description

The septage chlorination process (Purifax) utilizes chlorine gas in solution to oxidize various types of waste sludge (biosolids), including septage. Chlorination is one type of chemical oxidation process that stabilizes sludge and septage both by reducing the number of organisms present and by making organic substrates less suitable for bacterial metabolism and growth.

The septage chlorination process involves disinfection and oxidation of several septage constituents with high dosages of chlorine gas, which is applied directly to the septage in an enclosed reactor for a short time. Because of the reaction of chlorine gas with the septage, significant quantities of hydrochloric acid are formed, and the stablilized septage has low pH (about 2). The reactor vessel is moderately pressurized (30–40 psi) to ensure more complete absorption of the chlorine gas as well as adequate chlorination penetration into the larger particles in the sludge. At these pressures, the gases formed are supersaturated in the treated septage. When discharged from the reactor vessel at atmospheric pressure, these gases come out of solution as fine bubbles that float the septage solids. The process is followed by dewatering, generally on sand beds. Septage chlorination is also termed chlorine stabilization, which, like lime stabilization, does not completely destroy organic matter or solids during septage treatment. It can, however, produce a relatively biologically stable end-product, which is dewaterable and which does not have an offensive odor. Because chlorine reactions with sludge and septage are very rapid, reactor volumes are relatively small; therefore, compared with biological digestion processes, septage chlorination system sizes are generally smaller, and capital costs may be lower, depending on the site-specific circumstances. In addition, septage chlorination systems can be run intermittently (unlike biological processes) so long as

Table 14
Bacteriological Data Generated From Chlorination Treatment of Septage[a]

	Total coliform (counts/100 mL)	Fecal coliform (counts/100 mL)
Raw septage	4.4×10^7	5.3×10^6
Purifax™ treated septage[b]	200	200
Sand bed underdrainage	6.9×10^6	3.2×10^4

[a] Values are averages of four runs.
[b] Dewatered solids
Source: US EPA.

sufficient storage volume is available both upstream and downstream of the reactor. As a result, operating costs are more directly dependent on septage production rates. Septage treatment facilities utilizing chlorination include Babylon, NY; Ventura, CA; Putnam, CT; and Bridgeport, CT, all in USA.

4.2. Design and Operation Considerations

An investigation, of the septage chlorination process were conducted at the Lebanon, Ohio, USA treatment plant which addressed chlorine requirements, dewatering rate, and sand bed underdrainage quality (43). The study concluded the following:

1. The chlorination process, in conjunction with sand bed dewatering, was an effective septage treatment method.
2. The sand bed underdrainage quality, compared with untreated septage, indicated the following removals: COD, 98%; BOD_5, 95–97%; total phosphorus, 99%; ammonia, 55–75%.
3. Mass balance calculations indicate that the sand dewatering beds following the chlorination process were the site of the majority of the organic and nutrient removal. It is possible that after repeated application, the removal capacity of the sand would be exhausted.
4. Large dosages of chlorine (1000–3000 mg/L) were required for the process to operate satisfactorily.
5. Chlorinated organics formed during processing appeared to be tied up in the sludge solids. The ultimate fate of these organics and their effects on the environment are not well documented.

The study (43) also showed that chlorine treatment of septage produced a solids fraction with greatly reduced total and fecal coliform concentrations, although coliform concentrations in the sand bed underdrainage were quite high, as summarized in Table 14. The average chlorine dose used during the study was 0.0021 kg chlorine per liter septage or 0.115 kg chlorine per kg dry solids.

A schematic diagram of a chlorine oxidation system is shown in Fig. 6. The heart of the septage chlorination (Purifax) system consists of a disintegrator, a recirculation pump, two reaction tanks, a chlorine eductor, and a pressure-control pump. The chlorine can be fed to the system through a chlorinator and/or evaporator. An influent feed pump and flow meter should also be provided.

Raw septage is pumped through the disintegrator to reduce particle size and increase particle surface area for contact with the chlorine. Chlorinated septage from the first reactor is mixed with raw septage just prior to reaching the recirculation pump. The combined flow then passes through the first reaction tank. Chlorine is added to the system by means of an eductor in the recirculation loop. Recirculation aids mixing and

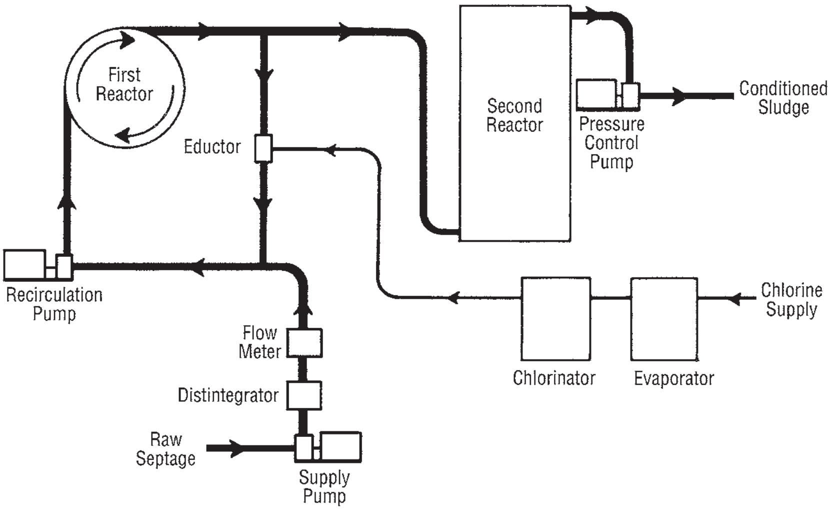

Fig. 6. Schematic of a septage chlorination system (US EPA).

efficient chlorine use. The ratio of recirculated reacted product to raw septage is normally about 7 to 1. System pressure (30–40 psi) is maintained by a pressure-control pump located at the discharge of the second reactor tank, which has been provided to increase system detention time to allow for a more complete reaction between septage and chlorine.

A holding/equalization tank should be provided upstream of the oxidation system. Mechanical mixing can be used, although air mixing is preferable because it enhances aerobic conditions and reduces odors. A particular benefit of septage chlorination treatment is that odor can be controlled in the holding tank by returning a portion of the filtrate or supernatant from the dewatering process. Ventilation of such tanks must be provided. A downstream holding tank is beneficial in that it ensures optimum functioning of subsequent processes, and it allows the chlorine residual to drop from approx 200 mg/L to about 0, and the pH to rise to between 4.5 and 6.5. This process takes approx 48 h.

4.3. Process Equipment and Control

The septage chlorination process equipment (Purifax) is commercially available over a wide range of flow capacities from 55 m^3/d (10 gpm) to a theoretically unlimited maximum. Sizing information is available from the manufacturer of Purifax. The system can be dimensioned such that the daily volume of septage is treated in 4–6 h. Most septage chlorination units are of a prefabricated, modular design, completely self-contained and skid-mounted.

Chlorine dosages vary from 700 to 3000 mg/L, depending on the solids content of the septage and the amount of chlorine-demanding substances present. (9). These substances include ammonia, amino acids, proteins, carbonaceous material, and hydrogen sulfide. The Babylon, New York septage treatment facility uses about 0.6 kg Cl_2/L influent (5 lb per 1000 gal).

The chlorine dosage is approx 0.7 kg Cl_2/L influent (6 lb/1000 gal) for septage with a suspended solids concentration of 1.2%. The chlorine demand varies in proportion to the solids concentration. For example, if the solids concentration were to double, the chlorine concentration would double as well.

4.4. Design Criteria

A summary of the typical design criteria for chlorine stabilization of septage is presented in below:

Chlorination system size = to treat daily septage volume within 4–6 h

Chlorine dosage = 0.7 kg/L for 1.2% TS, chlorine demand varies directly with TS

Limitations of the chlorine stabilization process center on chemical, operational, and environmental factors. From a chemical standpoint, the low pH of chlorine-stabilized septage may require neutralization prior to mechanical dewatering or before being applied to acid soils. Costs of neutralization are in addition to chlorine costs. Chlorine stabilization does not reduce sludge mass nor produce methane gas as a by-product for energy generation. The process consumes relatively large amounts of chlorine. Special safety and handling precautions must be used when employing this system. If high alkalinity wastes are processed, CO_2 generated during chlorination may promote cavitation in downstream pumps. The potential for production of carcinogenic compounds by the chlorination process has been a major concern, because these compounds may leach into the ground or contaminate surface waters as a result of sludge or liquid effluent disposal.

The effluent (filtrate, supernatant) from the dewatering step is not suitable for direct discharge into surface waters. Infiltration/percolation beds have been used for effluent disposal. Alternative disposal methods have included direct recycle to a treatment plant or direct discharge following activated carbon adsorption .

The major parameters used to control the septage chlorination process are treated septage color, effluent pH, and effluent chlorine residual. The chlorine dose can be adjusted until the effluent stream is a light buff color with a pH of 2–2.5, and a chlorine residual of 150–200 mg/L (43).

5. SAFETY CONSIDERATIONS OF CHLORINATION PROCESSES

Each safety program should include a list of safety rules for all employees to learn and use. An inspector cannot enforce safety rules but a written set of safety rules should be available to all employees. The safety rules should include the following areas:

1. Personal hygiene
2. Fire protection
3. Protection around openings
4. Tools and safety equipment
5. Accidents and first aid
6. Safety drill procedures
7. Gases
8. Created hazards
9. Accident prevention
10. Driving safety
11. In-plant traffic
12. Machinery guards
13. Ventilation

14. Gas utilization
15. Structures
16. Housekeeping
17. Safe operation
18. Electrical equipment
19. Procedures for one-man shifts
20. Laboratory

A detailed, well-written safety manual should include the above plus specific rules for individual unit processes.

Chlorine is a highly toxic gas, which may be fatal if inhaled in sufficient quantity. The presence of chlorine is easily detected however. A concentration of 3.5 parts per million of chlorine by volume is detectable. At concentrations between 15 and 30 parts per million, significant irritation of the mucus membranes and nasal linings will occur. Exposure to chlorine at a concentration of 1000 parts per million will result in fatalities in a very short exposure time. Most chlorination facilities using gaseous or liquid chlorine are designed to rigorous safety standards presenting minimum hazards to operating personnel. An adequately designed facility will have continuously monitoring chlorine leak detectors, which sound an alarm in the event of a leak. The following safety requirements should be met for any chlorine application facility.

1. Chlorination equipment should always be placed in an adequately ventilated room and isolated from other working areas. Ventilation should be provided with fan at floor level since chlorine is heavier than air. Access should be from an outside door.
2. Provisions should be made to continuously ventilate the area surrounding the chlorine cylinders and the chlorination equipment.
3. Equipment should be provided for continuous monitoring of the air in chlorine storage and application area.
4. Proper instructions and supervision to workers charged with responsibility of chlorination equipment should be provided.
5. Proper and approved self-contained breathing apparatus for persons working where there is a possibility of exposure to chlorine gas fumes should be provided, should be stored outside the area of danger, and should be quickly accessible.
6. Combustible or inflammable materials should never be stored near chlorine containers or application equipment.
7. Heat should never be applied to any chlorine container.
8. A water supply to keep chlorine containers cool in case of fire should be provided.
9. Several appropriate emergency container leak repair kits should be stored near the chlorine application facility.
10. Plant safety rules should require that any leak in storage cylinders or application equipment be attended by at least two persons wearing self-contained breathing apparatus.
11. Emergency shower and eye wash facilities should be provided adjacent to entry doors into chlorine storage or application facility.
12. First aid procedures should be developed and all personnel handling chlorine should be familiar with their application. These procedures should be posted in the chlorine area.
13. Fire protection should be provided by class C fire extinguishers (for energized electrical equipment) and located in the area immediately adjacent to the chlorination room.
14. Procedures should be developed to handle chlorine leaks from storage cylinders or application equipment. Periodically operating personnel should review these procedures in a hypothetical emergency situation.

NOMENCLATURE

CD	chlorine dosage, mg/L
CR	chlorine requirement, lb/d
CT	contact time at maximum flow, min
CTL	contact tank length, ft
CTW	contact tank width, ft
PCR	peak chlorine requirements, lb/d
Q_a	average flow, MGD
Q_p	peak flow, MGD
RLW	length-to-width ratio
SA	surface area, ft^2
SWD	side water depth, ft
V	volume, ft^3
VCT	volume of contact tank, gal

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13
Dechlorination

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CONTENTS

1. BACKGROUND

1.1. Chlorination of Potable Waters

Chlorine has been used as a disinfectant in potable water systems for over 100 yr. Free chlorine and combined chlorine (chloramines) are the two forms of chlorine widely used for the disinfection. Free chlorine is added as chlorine gas or sodium/calcium hypochlorite to the water. The reaction of chlorine in water produces hypochlorous acid and hydrochloric acid:

$$\underset{\text{Chlorine}}{Cl_2} + H_2O \leftrightarrow \underset{\text{Hypochlorous acid}}{HOCl} + \underset{\text{Hydrochloric acid}}{HCl}$$

Hypochlorous acid, in turn, dissociates into hydrogen ion and hypochlorite ion:

$$\underset{\text{Hypochlorous acid}}{HOCl} \leftrightarrow H^+ + \underset{\text{Hypochlorite}}{OCl^-}$$

Free chlorine is highly reactive and *relatively* unstable. Utilities using free chlorine for disinfection have been known to use secondary chlorination stations to maintain residual chlorine concentrations in the potable water distribution system as regulated by the Clean Water Act (CWA). One of the key concerns in using free chlorine for disinfection is that, under certain conditions, free chlorine may react with organic substances in water to form carcinogenic trihalomethanes (THMs) (1,2).

Combined chlorine is produced by adding chlorine and ammonia to the water. Usually a chlorine to ammonia ratio of 3:1 to 6:1 is used. Ammonia forms monochloramine, dichloramine, and trichloramine species with chlorine, as per the following reactions:

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$$\underset{\text{Hypochlorous acid}}{\mathrm{HOCl}} + \underset{\text{Ammonia}}{\mathrm{NH_3}} \leftrightarrow \underset{\text{Monochloramine}}{\mathrm{NH_2Cl}} + \mathrm{H_2O}$$

$$\underset{\text{Hypochlorous acid}}{\mathrm{HOCl}} + \underset{\text{Monochloramine}}{\mathrm{NH_2Cl}} \leftrightarrow \underset{\text{Dichloramine}}{\mathrm{NHCl_2}} + \mathrm{H_2O}$$

$$\underset{\text{Hypochlorous acid}}{\mathrm{HOCl}} + \underset{\text{Dichloramine}}{\mathrm{NHCl_2}} \leftrightarrow \underset{\text{Trichloramine}}{\mathrm{NCl_3}} + \mathrm{H_2O}$$

Monochloramine is a more effective oxidizing agent than di- and trichloramines. In potable water systems, monochloramine is often the predominant species present. Combined chlorine is less aggressive, more persistent, and reacts more slowly with oxidizable materials and bacteria (3). Some utilities prefer chloramines over free chlorine for disinfection because it has a lower potential to form THMs and has less taste and odor problems. Also, it travels further in the typical distribution system.

1.2. *Release of Chlorinated Water and Concerns*

Chlorinated water from potable water sources is released to the environment through various planned and unplanned activities (e.g., water main flushing, disinfection of new mains and storage tanks, hydrant testing, main breaks, filter backwash). In addition, the concentrations of chlorine in these releases may vary from 50 mg/L (e.g., new main disinfection) to less than 1 mg/L (e.g., hydrant testing). The volume of chlorinated water release also varies from several thousand gallons (e.g., reservoir cleaning) to less than a few hundred gallons (e.g., temporary by-pass lines). Although chlorine protects humans from pathogens in the water, release of chlorinated waters may be detrimental to the existence of several endangered aquatic species. Free and combined chlorines are reported to be toxic to several aquatic species at or below 0.1 mg/L. The Clean Water Act has defined the water quality criterion for total residual chlorine to be as low as 11 μg/L for some waters. Release of free chlorine is also a concern in some cases with respect to potential formation of THMs upon reaction with receiving stream organics. In addition to chlorine, ammonia is also toxic to several aquatic species at very low concentrations (0.1–0.2 mg/L) (4). Federal and state regulations have developed water quality criteria for un-ionized ammonia and total ammonia to be as low as 0.002 and 0.08 mg/L, respectively, for some waters.

2. DECHLORINATION OF WATER RELEASES

Dechlorination is the process of converting highly reactive chlorine from these waters into less reactive chloride ions prior to disposal into receiving streams. Various chemical and nonchemical techniques are currently used for disposal of chlorinated waters by water and wastewater agencies. For example, wastewater treatment plants use sulfur dioxide gas or sodium metabisulfate to dechlorinate treated effluent prior to release into receiving streams. Many water utilities often use passive, non-chemical methods such as discharge to sanitary sewers for disposal of chlorinated waters. Impurities such as organics, iron, and sulfide in the sanitary sewer exert a chlorine demand and neutralize chlorine in the released water.

Dechlorination is an evolving practice in the water industry. Currently, there is no industry guidance or American Water Works Association (AWWA) standard for disposal of chlorinated water (5–7). The AWWA standard for disinfection of water mains (C651-92) provides some information on disposal of chlorinated waters. This information, presented as an appendix, is not a part of the standard. Regulations and permit programs for disposal of chlorinated waters vary widely among the states and provinces.

The effectiveness of various passive non-chemical methods as well dechlorination chemicals for disposal of chlorinated water is discussed in this section. Furthermore, water quality impacts, health and safety concerns, and dose calculations for dechlorination of both free and combined chlorine using these techniques are discussed. Utilities must verify the chlorine levels (measured as total chlorine) of discharged water prior to release to receiving streams regardless of the method chosen for dechlorination.

2.1. Non-chemical Methods for Chlorine Dissipation

The non-chemical methods for chlorinated water discharges vary from retention in holding tanks to discharge through hay bails or into sanitary sewers. The advantage of dissipating chlorine passively is that such a process does not involve chemical addition. Hence, utilities do not have to be concerned with the effects of neutralizing chemicals in the receiving streams. Also avoided are cost, health, and safety concerns related to storage, transportation, and handling of dechlorination chemicals.

2.1.1. Retention in Holding Tanks

The chlorine concentration in stored water gradually decreases with time due to aeration, reaction with sunlight, and reaction with surfaces of holding tanks. A number of utilities store filter backwash water and main disinfection water in holding tanks to allow for residual chlorine decay. On some occasions the chlorine demand of the water is reduced by retention in a holding tank for some time, prior to dechlorination using chemicals.

Although this method can remove chlorine from the water, there are several limitations. First, chlorine decay through natural reactions is extremely slow. Free chlorine decay in a distribution system is reported to be a first-order reaction with a decay coefficient varying from 0.85 to 0.1 d^{-1} (8). These values indicate that decay of free chlorine at concentrations typically found in distribution systems (0.5–2 mg/L) will take several hours to a few days to meet regulatory discharge limits (0.002–0.1 mg/L). Second, activities such as reservoir cleaning and large main dewatering produce a large volume of chlorinated water, requiring very large tanks for storage.

Combined chlorine is more stable than free chlorine in the environment. Hence, decay of combined chlorine in holding tanks will require much longer retention times than those of free chlorine.

2.1.2. Land Application of Chlorinated Water

Organic and inorganic impurities in soil and pavements exert a significant amount of chlorine demand and rapidly neutralize chlorine in waters. Hence, spraying chlorinated waters onto soils or pavements can be a very effective method for disposing of chlorine-containing waters. The presence of impurities in the soil typically increases decay rates compared with those observed in holding tanks.

However, potential drainage of partially dechlorinated waters, frequently caused by release on recently cleaned roads and pavements, into storm drains, and receiving waters is a matter of concern while using this method. Also, land application of large volumes of water may lead to soil erosion. In general, this technique appears to be more effective for discharging small amounts of water, in locations far from storm drainage and receiving streams.

2.1.3. Discharging Through Hay Bales and Other Natural Obstructions

Treatment plant backwash waters and planned water releases from the distribution system may be allowed to flow through hay bales or other obstructions to dissipate chlorine prior to discharging receiving waters. However, elaborate arrangements required to construct such barriers, practical difficulties in construction of such barriers at various field discharge points, and potential soil erosion while discharging waters are some of the concerns in using this technique.

2.1.4. Discharge to Storm Sewers

Discharging chlorinated water into storm sewers may be an effective way to dissipate chlorine from some potable water releases. However, there are several limitations and risks in releasing chlorinated waters into storm drains. Although storm waters may contain some organic and inorganic impurities, their concentrations may not be sufficient to completely dechlorinate the water released. Lower chlorine demand in storm waters may require a longer travel time for chlorine neutralization. Storm waters are usually discharged directly into receiving streams or waters leading to aquatic species–bearing streams. In some instances, therefore, chlorinated waters released into storm sewers may not undergo sufficient dechlorination before being discharged to nearby receiving streams.

2.1.5. Discharge of Chlorinated Waters in Sanitary Sewers

The release of chlorinated water into sanitary sewers is a very safe and effective means of disposing chlorinated waters in most cases. Most of the water utilities prefer this method as their first option for releasing chlorinated potable waters. A very high demand exerted by sulfide and other inorganic and organic pollutants in sewage rapidly neutralizes chlorine. In addition, because the water is not directly released to receiving streams, utilities do not have to be concerned with meeting receiving NPDES discharge limits.

The availability of a sanitary sewer near the point of chlorinated water release, and the capacities of the sanitary sewer and the wastewater treatment plant to handle the additional load, are the primary limitations in this method. Potential upset of treatment plant operations due to chlorinated water release must also be evaluated. A backflow prevention device or an air gap method must be used to prevent cross-connection problems.

2.1.6. Dechlorination Using Activated Carbon

Activated carbon has been used in water and wastewater treatment facilities and industries for dechlorination (9). Free as well as combined chlorine from water can be removed by activated carbon. In water treatment plants carbon filters effectively remove dissolved organic matter in addition to removing chlorine.

Free chlorine is removed in carbon filters by the following reactions:

$$\underset{\text{Active carbon}}{\mathrm{C^*}} + \underset{\text{Hypochlorous acid}}{\mathrm{HOCl}} \rightarrow \underset{\text{Surface oxide on carbon}}{\mathrm{CO^*}} + \underset{\text{Hydrochloric acid}}{\mathrm{HCl}}$$

Under certain conditions reaction of chlorine with surface CO* group may release carbon as CO or CO_2 gas (9):

$$\underset{\text{Carbon}}{\mathrm{C^*}} + \underset{\text{Chlorine}}{\mathrm{2Cl_2}} + \mathrm{2H_2O} \rightarrow \underset{\text{Hydrochloric acid}}{\mathrm{4HCl}} + \underset{\text{Carbon dioxide}}{\mathrm{CO_2}}$$

A fraction of carbon is permanently destroyed during this reaction. According to stoichiometry, one part of chlorine can destroy 0.00845 parts of carbon by this reaction.

Carbon undergoes the following reactions with mono- and dichloramines:

$$\underset{\text{Monochloramine}}{\mathrm{NH_2Cl}} + \mathrm{H_2O} + \underset{\text{Carbon}}{\mathrm{C^*}} \rightarrow \underset{\text{Ammonia}}{\mathrm{NH_3}} + \underset{\text{Hydrochloric acid}}{\mathrm{HCl}} + \underset{\text{Surface oxide on carbon}}{\mathrm{CO^*}}$$

$$\underset{\text{Dichloramine}}{\mathrm{2NHCl_2}} + \mathrm{H_2O} + \underset{\text{Carbon}}{\mathrm{C^*}} \rightarrow \underset{\text{Nitrogen}}{\mathrm{N_2}} + \underset{\text{Hydrochloric acid}}{\mathrm{4HCl}} + \underset{\text{Surface oxide on carbon}}{\mathrm{CO^*}}$$

Chloramine reactions do not release CO_2 gas or destroy the integrity of the carbon. However, chloramine reactions are much slower than chlorine reactions with activated carbon. Finally, although carbon can effectively remove chlorine from potable water, it is more expensive than other dechlorination methods (9,10).

2.1.7. Catalytic Carbon

Catalytic carbon can be an effective technology for removing chloramines from waters. Catalytic carbon is developed by an advanced process where the electron structure of bituminous coal–based granular activated carbon is altered. Alteration of the electronic structure provides the carbon a wide range of chemical reactions not found in conventional carbons. One such reaction is neutralization of chloramines according to the following reactions:

$$\underset{\text{Monochloramine}}{\mathrm{NH_2Cl}} + \mathrm{H_2O} + \underset{\text{Carbon}}{\mathrm{C^*}} \rightarrow \underset{\text{Ammonia}}{\mathrm{NH_3}} + \mathrm{H^+} + \mathrm{Cl^-} + \underset{\text{Surface oxide on carbon}}{\mathrm{CO^*}}$$

$$\underset{\text{Monochloramine}}{\mathrm{2NH_2Cl}} + \mathrm{CO^*} \rightarrow \mathrm{N_2} + \mathrm{2H^+} + \mathrm{2Cl^-} + \mathrm{H_2O}$$

The chloramine removal efficiency of catalytic carbon is reported to be an order of magnitude greater than that of conventional activated carbons used for dechlorination. Various factors such as empty bed contact time (EBCT), influent chloramine concentration, particle size, and temperature influence treatment efficiency using catalytic carbon (11,12). In a study using water containing 2 mg/L influent chloramine concentration, an increase in EBCT from 10 to 30 s increased the volume of water treated to below 0.1 mg/L chloramine from 250 bed volumes to 11,000 bed volumes. In a different study, reducing the mesh size from 20 × 50 to 30 × 70 increased the bed volumes treated from 11,000 to 28,000 at a 30 s EBCT and 2 mg/L influent chloramine concentration. Also, an increase in influent chloramine concentration from 2 to 5 mg/L decreased the amount of bed volumes treated from 11,000 to 4,000 at 30 s EBCT.

The limitations to using catalytic carbon for potable water dechlorination include (i) inability to dechlorinate free chlorine (only chloramines are removed by catalytic carbon) and (ii) potential loss of carbon life due to fouling by organic compounds or oxidation by various compounds. Furthermore, catalytic carbons are generally more expensive than activated carbon as well as other dechlorination methods currently available.

2.1.8. Dechlorination Using UV

Recently UV treatment is also reported as an effective non-chemical dechlorination method for free and combined chlorine (25).

2.2. Dechlorination Using Chemicals

Whenever it is not possible to dispose of chlorinated waters safely by non-chemical methods, chlorine must be neutralized using dechlorination chemicals. Several solid, liquid, and gaseous dechlorination chemicals are commercially available and are widely used by water and wastewater utilities. Benefits and limitations of various chemicals used for dechlorination are summarized below.

2.2.1. Sulfur Dioxide (SO_2)

Sulfur dioxide is widely used in water and wastewater treatment plants for dechlorinating backwash water and wastewaters containing chlorine. It is a colorless gas with a suffocating pungent odor. Sulfite ion, which is formed when SO_2 gas dissolves in water, reacts instantaneously with free and combined chlorine according to the following stoichiometry (13):

$$\underset{\text{Sulfur dioxide}}{SO_2} + H_2O + \underset{\text{Hypochlorous acid}}{HOCl} \rightarrow \underset{\text{Sulfate}}{SO_4^{2-}} + Cl^- + 3H^+$$

$$\underset{\text{Sulfur dioxide}}{SO_2} + \underset{\text{Monochloramine}}{NH_2Cl} + 2H_2O \rightarrow \underset{\text{Sulfate}}{SO_4^{2-}} + Cl^- + \underset{\text{Ammonium}}{NH_4^+} + 2H^+$$

The mass ratio of SO_2 to available chlorine is 0.9:1. In the field, nearly 1.1 parts of SO_2 are required to neutralize 1 part of chlorine (14). Dechlorination using sulfur dioxide produces a small amount of acid. Approximately 2.8 mg of alkalinity as $CaCO_3$ is consumed per milligram of chlorine reduced. SO_2 is also an oxygen scavenger. It can deplete dissolved oxygen in the discharge water and in the receiving stream.

Sulfur dioxide is a toxic chemical subject to reporting requirements of the Superfund Amendments and Reauthorization Act (SARA), Title III, Section 313. It has a National Fire Protection Association (NFPA) rating of 2, 0, and 0 for health, fire, and reactivity, respectively. (Hazard rating is from 0 to 4, with 0 indicating no hazard and 4 indicating extremely hazardous.) It may cause various degrees of irritation to mucous membranes of the eyes, nose, throat, and lungs. Contact with sulfur dioxide liquid may produce freezing of the skin because the liquid absorbs the heat of vaporization from the skin. Concentrations above 500 mg/L can cause acute irritation to the upper respiratory system and cause a sense of suffocation. The Threshold Limit Value, Time Weighted Average (TLV:TWA) is 2 ppm and the Short Term Exposure Limit (STEL) value of SO_2 is 5 ppm. Great caution is required in transporting cylinders of SO_2 gas. Care must be taken to design storage and handling facilities to avoid accidental exposure to gas release. Although it is suitable for use in facilities such as treatment plants and pumping stations, it is not best suited for field applications.

2.2.2. *Sodium Thiosulfate* ($Na_2S_2O_3$)

Sodium thiosulfate is a colorless, transparent monoclinic crystal widely used by utilities for dechlorination. The reactions of sodium thiosulfate with free and combined chlorine varies with solution pH (13,15). Reaction of sodium thiosulfate with chlorine yields the following:

$$\underset{\text{Sodium thiosulfate}}{Na_2S_2O_3} + \underset{\text{Hypochlorous acid}}{4HOCl} + H_2O \rightarrow \underset{\text{Sodium bisulfate}}{2NaHSO_4} + \underset{\text{Hydrochloric acid}}{4HCl}$$

$$\underset{\text{Sodium thiosulfate}}{Na_2S_2O_3} + \underset{\text{Hypochlorous acid}}{HOCl} \rightarrow \underset{\text{Sodium sulfate}}{Na_2SO_4} + S + \underset{\text{Hydrochloric acid}}{HCl}$$

$$\underset{\text{Sodium thiosulfate}}{2Na_2S_2O_3} + \underset{\text{Hypochlorous acid}}{HOCl} \rightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + \underset{\text{Sodium chloride}}{NaCl} + \underset{\text{Sodium hydroxide}}{NaOH}$$

Sodium thiosulfate undergoes the following reactions with monochloramines:

$$\underset{\text{Monochloramine}}{4NH_2Cl} + \underset{\text{Sodium thiosulfate}}{Na_2S_2O_3} + 5H_2O \rightarrow \underset{\text{Sodium bisulfate}}{2NaHSO_4} + \underset{\text{Ammonia}}{4NH_3} + \underset{\text{Hydrochloric acid}}{4HCl}$$

$$\underset{\text{Monochloramine}}{NH_2Cl} + \underset{\text{Sodium thiosulfate}}{Na_2S_2O_3} + H_2O \rightarrow \underset{\text{Sodium sulfate}}{Na_2SO_4} + S + \underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrochloric acid}}{HCl}$$

$$\underset{\text{Monochloramine}}{NH_2Cl} + \underset{\text{Sodium thiosulfate}}{2Na_2S_2O_3} + 2H_2O \rightarrow \underset{\text{Sodium tetrathionate}}{Na_2S_4O_6} + \underset{\text{Sodium hydroxide}}{2NaOH} + \underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrochloric acid}}{HCl}$$

The amount of thiosulfate required is independent of the form of chlorine (free or combined chlorine) present. However, the amount of thiosulfate required for dechlorination may vary with solution pH (15). Approximately 2.23 parts of thiosulfate are required to neutralize one part of chlorine at pH 6.5 and nearly 1.6 parts of sodium thiosulfate is sufficient to neutralize one part of chlorine at pH 9.0.

Compared to sulfite-based chemicals sodium thiosulfate reacts slowly with chlorine and requires more time for dechlorination (9). In addition, over-dechlorination with sodium thiosulfate may encourage growth of thiobacillus and some other bacteria in receiving streams, particularly during low-flow conditions. A drop in pH, caused by the production of H_2SO_4 by microorganisms, has been reported under such conditions. Thiosulfate is an oxygen scavenger and reducing agent. However, it scavenges less oxygen than sodium sulfite, bisulfite or metabisulfite.

Sodium thiosulfate is a skin, eye, nose, and throat irritant. It is moderately toxic by an intravenous route. It has a NFPA rating of 1, 0, and 0 for health, fire, and reactivity, respectively. (Hazard rating is from 0 to 4, with 0 indicating no hazard and 4 indicating extreme hazard.) Results from toxicity studies indicate that sodium thiosulfate is not very toxic to aquatic species (16). For *Ceriodaphnia*, the 24 and 48 h LC_{50} values are 2.5 and 0.85 g/L, respectively. For *Daphnia*, these values are 2.2 and 1.3 g/L, respectively. For fathead minnows, the LC_{50} values for 24, 48, 72, and 96 h are 8.4, 8.4, 7.9, and 7.3 g/L, respectively.

2.2.3. *Sodium Sulfite* (Na_2SO_3)

Sodium sulfite is widely used by utilities for dechlorination. It is generally available in powder, crystalline, and tablet forms. Sodium sulfite undergoes the following reaction with free and combined chlorine (15):

$$\underset{\text{Sodium sulfite}}{Na_2SO_3} + \underset{\text{Hypochlorous acid}}{HOCl} \rightarrow \underset{\text{Sodium sulfate}}{Na_2SO_4} + \underset{\text{Hydrochloric acid}}{HCl}$$

$$\underset{\text{Sodium sulfite}}{Na_2SO_3} + \underset{\text{Monochloramine}}{NH_2Cl} + H_2O \rightarrow \underset{\text{Sodium sulfate}}{Na_2SO_4} + \underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrochloric acid}}{HCl}$$

$$2\,\underset{\text{Sodium sulfite}}{Na_2SO_3} + \underset{\text{Dichloramine}}{NHCl_2} + 2\,H_2O \rightarrow 2\,\underset{\text{Sodium sulfate}}{Na_2SO_4} + \underset{\text{Ammonia}}{NH_3} + 2\,\underset{\text{Hydrochloric acid}}{HCl}$$

On a weight-to-weight basis, approx 1.775 parts of sodium sulfite are required to remove one part of chlorine (17). Sodium sulfite produces sodium sulfate and hydrochloric acid with free and combined chlorine. Ammonia may be present as NH_3 or NH_4^+, depending on pH. Although it produces HCl, field studies (18,19) indicated that the reaction does not appreciably decrease solution pH during dechlorination.

Sodium sulfite is a reducing agent and is reported to scavenge more oxygen than sodium thiosulfate does. About eight parts of sodium sulfite are required to neutralize one part of oxygen. However, field studies performed using sodium sulfite tablets indicated that less than 10% of dissolved oxygen was removed from waters containing approx 1 mg/L of residual chlorine (18).

The hazard rating (NFPA) for sodium sulfite is 2, 0, and 0, for health, fire and reactivity, respectively. It is an eye, skin, mucous membrane, and respiratory tract irritant. Excessive exposure to sodium sulfite may affect the brain, respiratory system, and skin. Crystalline sodium sulfite is a stable compound. However, sodium sulfite solution will decompose upon reaction with air to form SO_2 gas. It is a strong reducing agent and reacts with oxidants and decomposes on heating to produce SO_2.

The major advantage of using sodium sulfite is that, currently, it is readily available in tablet form. Many utilities find dechlorination tablets easier to store, handle, and apply as compared to dechlorination solutions or powders.

2.2.4. *Sodium Bisulfite* ($NaHSO_3$)

Sodium bisulfite is available as a white powder, granule, or clear liquid solution. It is highly soluble in water (39%), and it undergoes the following reactions with free and combined chlorine:

$$\underset{\text{Sodium bisulfite}}{NaHSO_3} + \underset{\text{Hypochlorous acid}}{HOCl} \rightarrow \underset{\text{Sodium bisulfate}}{NaHSO_4} + \underset{\text{Hydrochloric acid}}{HCl}$$

$$\underset{\text{Sodium bisulfite}}{NaHSO_3} + \underset{\text{Monochloramine}}{NH_2Cl} + H_2O \rightarrow \underset{\text{Sodium bisulfate}}{NaHSO_4} + \underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydrochloric acid}}{HCl}$$

$$\underset{\text{Sodium bisulfite}}{2\ \mathrm{NaHSO_3}} + \underset{\text{Dichloramine}}{\mathrm{NHCl_2}} + 2\ \mathrm{H_2O} \rightarrow \underset{\text{Sodium bisulfate}}{2\ \mathrm{NaHSO_4}} + \underset{\text{Ammonia}}{\mathrm{NH_3}} + \underset{\text{Hydrochloric acid}}{2\ \mathrm{HCl}}$$

On a weight-to-weight basis, approx 1.45 parts of sodium bisulfite are required to dechlorinate one part of chlorine. The production of HCl during chlorine neutralization may marginally decrease pH. Sodium bisulfite is a substantial oxygen scavenger. Accidental release of slug loads has been reported to have caused injury and death to aquatic species.

Sodium bisulfite is not carcinogenic or mutagenic and is used in food and drugs as a preservative. The US Food and Drug Administration (USFDA) recognizes sodium bisulfite as safe when used in accordance with good manufacturing practices or feeding practices. However, sodium bisulfite can cause skin, eye, and respiratory tract irritation. It is harmful if swallowed or inhaled. Hypersensitivity reactions occur more frequently with asthmatics and bronchial constrictions may also occur. The Occupational Safety and Health Administration (OSHA) Time Weighted Average (TWA) is 5 mg/m^3. Sodium bisulfite solution may crystallize at room temperatures. It is highly viscous and sometimes difficult to handle. In addition, sodium bisulfite is highly corrosive and caution must be exercised in safely handling this chemical. The strength of sodium bisulfite solutions diminishes somewhat with age. Sodium bisulfite gradually decomposes in air, producing SO_2. It also reacts strongly with acids to produce SO_2.

2.2.5. Sodium Metabisulfite ($Na_2S_2O_5$)

Sodium metabisulfite is available as crystal, powder, or solution. It reacts with chlorine, as well as chloramines, according to the following stoichiometry:

$$\underset{\text{Sodium metabisulfite}}{\mathrm{Na_2S_2O_5}} + \underset{\text{Hypochlorous acid}}{2\ \mathrm{HOCl}} + \mathrm{H_2O} \rightarrow \underset{\text{Sodium bisulfate}}{2\ \mathrm{NaHSO_4}} + \underset{\text{Hydrochloric acid}}{2\ \mathrm{HCl}}$$

$$\underset{\text{Sodium metabisulfite}}{\mathrm{Na_2S_2O_5}} + \underset{\text{Monochloramine}}{2\ \mathrm{NH_2Cl}} + 3\ \mathrm{H_2O} \rightarrow \underset{\text{Sodium bisulfate}}{2\ \mathrm{NaHSO_4}} + \underset{\text{Ammonia}}{2\ \mathrm{NH_3}} + \underset{\text{Hydrochloric acid}}{2\ \mathrm{HCl}}$$

$$\underset{\text{Sodium metabisulfite}}{\mathrm{Na_2S_2O_5}} + \underset{\text{Dichloramine}}{\mathrm{NHCl_2}} + 3\ \mathrm{H_2O} \rightarrow \underset{\text{Sodium bisulfate}}{2\ \mathrm{NaHSO_4}} + \underset{\text{Ammonia}}{\mathrm{NH_3}} + \underset{\text{Hydrochloric acid}}{2\ \mathrm{HCl}}$$

On a weight-to-weight basis, approx 1.34 parts of sodium metabisulfite are required to remove one part of free chlorine. Upon reaction with water, sodium metabisulfite produces sodium bisulfate and hydrochloric acid. Dechloramination using sodium metabisulfite produces NH_3 or NH_4^+, depending on pH. Sodium metabisulfite is a considerable oxygen scavenger. Its scavenging properties are comparable to that of sodium bisulfite.

Sodium metabisulfite is an eye, throat, skin, and lung irritant. Overexposure to sodium metabisulfite can produce highly toxic effects. OSHA Permissible Exposure Limit (PEL) for sodium metabisulfite based on Time Weighted Average (TWA) criteria is 5 mg/m^3. Sodium metabisulfite is a poison if entered through the intravenous route. MSDS warns of adverse reproductive effects due to over exposure. Ingestion may cause mild to moderately severe oral and esophageal burns. Sodium metabisulfite in food can provoke life-threatening asthma. Hazard ratings are 3, 0, 1. The stability of sodium metabisulfite increases with concentration. It is slowly degraded when exposed to oxygen. Solutions of 2%, 10%, and 20% strengths are stable for 1, 3, and 4 wk, respectively.

2.2.6. *Calcium Thiosulfate* (CaS_2O_3)

Calcium thiosulfate is a clear crystalline substance, with a faintly sulfurous odor. It reacts with free as well as combined chlorine. Calcium thiosulfate undergoes the following reactions with chlorine (20):

$$\underset{\text{Calcium thiosulfite}}{\mathrm{CaS_2O_3}} + 2\,\underset{\text{Hypochlorous acid}}{\mathrm{HOCl}} + \mathrm{H_2O} \rightarrow \underset{\text{Calcium bisulfite}}{\mathrm{Ca(HSO_3)_2}} + 2\,\underset{\text{Hydrochloric acid}}{\mathrm{HCl}}$$

$$\underset{\text{Calcium bisulfite}}{\mathrm{Ca(HSO_3)_2}} + 2\,\underset{\text{Hypochlorous acid}}{\mathrm{HOCl}} \rightarrow \underset{\text{Calcium sulfate}}{\mathrm{CaSO_4}} + \underset{\text{Sulfuric acid}}{\mathrm{H_2SO_4}} + 2\,\underset{\text{Hydrochloric acid}}{\mathrm{HCl}}$$

$$\underset{\text{Calcium thiosulfate}}{\mathrm{CaS_2O_3}} + \underset{\text{Hypochlorous acid}}{\mathrm{HOCl}} \rightarrow \underset{\text{Calcium sulfate}}{\mathrm{CaSO_4}} + \underset{\text{Sulfur}}{\mathrm{S}} + \underset{\text{Hydrochloric acid}}{\mathrm{HCl}}$$

Approximately 0.99 mg of calcium thiosulfate is required to neutralize 1 mg of residual chlorine at pH 7.35. At pH 11, 0.45 mg/L of calcium thiosulfate is sufficient to neutralize 1 mg of chlorine residual. On a weight basis, approx 1.30 parts are needed per part of chlorine at pH 6.5. Although calcium thiosulfate is reported to neutralize combined chlorine effectively, the reactions involved are not currently known. Chlorine neutralization produces HCl and H_2SO_4 that may result in lower pH. It does not scavenge oxygen significantly, and does not produce SO_2.

The 96-h LC_{50} of calcium thiosulfate for fathead minnows is greater than 750 mg/L (21). Other toxicity information on calcium thiosulfate is not currently available. Hazardous reporting is not required for calcium thiosulfate. Exposure may cause eye and skin irritation. Hazard rating of calcium thiosulfate is 0, 0, 0, 0 for health, fire, reactivity, and persistence.

Calcium thiosulfate does not off-gas SO_2 as other sodium-based dechlorinating agents. It is less toxic to aquatic species. However, dechlorination reactions using stoichiometric concentrations of calcium thiosulfate require nearly 5 min for complete neutralization when it is added (22). Overdosing of calcium thiosulfate may produce milky colored suspended solids, causing turbidity violations. Also, excess thiosulfate release may promote *Thiobacillus* bacterial growth. However, bacterial growth is promoted mostly in continuous, excess discharge situations (e.g., cooling water and disinfected wastewater dechlorination operations).

2.2.7. *Ascorbic Acid* ($C_5H_5O_5CH_2OH$ — *Vitamin C*)

In recent years more utilities have begun to use ascorbic acid (vitamin C) for dechlorination (23). Vitamin C has long been used in the medical field for dechlorination of tap water prior to use for kidney dialysis treatment. Vitamin C reacts with chlorine to produce chloride and dehydroascorbate. The reactions with chlorine and chloramine are shown below:

$$\underset{\text{Ascorbic acid}}{\mathrm{C_5H_5O_5CH_2OH}} + \underset{\text{Hypochlorous acid}}{\mathrm{HOCl}} \rightarrow \underset{\text{Dehydroascorbic acid}}{\mathrm{C_5H_3O_5CH_2OH}} + \underset{\text{Hydrochloric acid}}{\mathrm{HCl}} + \mathrm{H_2O}$$

$$\underset{\text{Ascorbic acid}}{\mathrm{2C_5H_5O_5CH_2OH}} + \underset{\text{Monochloramine}}{\mathrm{2NH_2Cl}} \rightarrow \underset{\text{Ammonia}}{\mathrm{2NH_4^+}} + \underset{\text{Chloride}}{\mathrm{2Cl^-}} + \underset{\text{Dehydroascorbic acid}}{\mathrm{2C_5H_3O_5CH_2OH}}$$

Ascorbic acid is a non-hazardous compound. The NFPA ratings for health, flammability, and reactivity are 0, 0, and 0, respectively. It may cause minor irritation but is not expected to cause adverse health effects upon inhalation, ingestion, skin/eye contact, or chronic exposure.

Ascorbic acid is reasonably stable in a dry state with a shelf life of about 1–3 yr (23). However, it rapidly oxidizes in solution. A 1% solution may remain at approx 80% potency after 10 d. A 0.02% solution will degrade to 0% within 3 d. Ascorbic acid is also currently available in tablet form for dechlorination applications. Release of ascorbic acid–containing waters under some conditions may reduce the pH of the receiving streams. Use of vitamin C is reported to have other potential benefits as it is an essential vitamin for healthy fish (23). Also, it can easily strip manganese oxide stains from reservoir surfaces and thereby promote better disinfection (once the vitamin C is exhausted). Vitamin C (ascorbic acid) is NSF certified, allowing it to be used in drinking water treatment to remove or reduce chlorine levels.

2.2.8. *Sodium Ascorbate* ($C_5H_5O_5CH_2ONa$)

Sodium ascorbate is the sodium salt of ascorbic acid. Most of sodium ascorbate reactions with chlorinated waters are similar to those of ascorbic acid. However, a key difference in dechlorination using sodium ascorbate is that it does not lower the water pH. Several utilities in the Pacific Northwest have evaluated the use of sodium ascorbate for neutralizing chlorine from potable water releases. The pH of sodium ascorbate is approximately neutral. The expected reaction of sodium ascorbate with chlorine is shown below:

$$\underset{\text{Sodium ascorbate}}{C_5H_5O_5CH_2ONa} + \underset{\text{Hypochlorous acid}}{HOCl} \rightarrow \underset{\text{Dehydroascorbic acid}}{C_5H_3O_5CH_2OH} + \underset{\text{Sodium chloride}}{NaCl} + H_2O$$

Under field conditions approx 3.3 parts of sodium ascorbate were required to neutralize one part of chlorine.

Because sodium ascorbate is more expensive than ascorbic acid, and more sodium ascorbate than ascorbic acid is required to neutralize the same amount of chlorine, treatment using sodium ascorbate is more expensive than treatment using ascorbic acid. However, the utilities favor the use of sodium ascorbate because this chemical does not appreciably alter the pH of the discharge or receiving waters, and the increase in chemical cost is often a minor fraction of the overall dechlorination cost (e.g., labor cost, etc.).

2.2.9. *Hydrogen Peroxide* (H_2O_2)

Hydrogen peroxide is yet another chemical that can potentially neutralize chlorine in solution. It reacts with free available chlorine in solutions with a pH greater than 7 according to the following reaction:

$$\underset{\text{Hypochlorous acid}}{HOCl} + \underset{\text{Hydgrogen peroxide}}{H_2O_2} \rightarrow \underset{\text{Oxygen}}{O_2} + H_2O + \underset{\text{Hydrochloric acid}}{HCl}$$

On a weight-to-weight basis, approx 0.48 mg/L of hydrogen peroxide is required to neutralize 1 mg/L of free chlorine. In most cases, oxygen produced by peroxide will remain dissolved in solution. However, while neutralizing superchlorinated water, in closed environments, the solution may effervesce, and provisions must be made to accommodate the O_2 evolved. The reaction is mildly exothermic, liberating 37 kcal/mole, as

Table 1
Parts of Dechlorination Chemical Required to Neutralize One Part of Free Chlorine in Distilled Water[a]

Chemical	pH 6.6	pH 7.0	pH 9.0
Sodium thiosulfate	2.23	2.13	1.60
Sodium sulfite	1.96	1.96	1.96
Sodium bisulfite	1.61	1.61	1.61
Sodium metabisulfite	1.47	1.47	1.47
Calcium thiosulfate	1.30	1.22	1.08
Ascorbic acid	2.5	2.5	2.5
Sodium ascorbate	2.8	2.8	2.8

[a] Based on information obtained from Best Sulfur Products Company.

opposed to 199 kcal/mole when using SO_2. However, hydrogen peroxide reacts very slowly with combined chlorine and hence, is not recommended for dechlorination of waters containing combined chlorine residuals.

One of the concerns with the use of H_2O_2 is that it is very reactive and rated hazardous when the strength is greater than 52%. At lower concentrations, it is not rated as Hazardous by the Comprehensive Environment Response, Compensation and Liability Act (CERCLA). It does not require a Risk Management Plan (RMP). However, SARA Title III Section 311/312 classifies hydrogen peroxide as an immediate health hazard and a fire hazard. The minimum threshold quantity for reporting is 10,000 lb. Hydrogen peroxide at concentrations of 20% or greater is rated as an “oxidizer and corrosive” by the US Department of Transportation (USDOT) and must be labeled accordingly.

Owing to its US DOT and Sara regulatory requirements, hydrogen peroxide may not be the best dechlorination choice for field applications. It may, however, be a viable alternative to SO_2 for industrial, water and wastewater treatment plant applications.

2.2.10. Dechlorination Chemical Summary

Historically, sodium bisulfite, sodium sulfite, and sodium thiosulfate are most frequently used by water utilities for dechlorination. The use of ascorbic acid/sodium ascorbate is gaining more acceptance worldwide. The choice of a particular dechlorination chemical is dictated by site-specific issues such as the nature of water release, strength of chlorine, volume of water release, and distance from receiving waters. Sodium bisulfite is used by some utilities due to its lower cost and higher rate of dechlorination. Sodium sulfite tablets are chosen by utilities due to ease of storage and handling. Sodium thiosulfate is used for dechlorination because it is less hazardous and consumes less oxygen than sodium bisulfite and sodium sulfite. Ascorbic acid/sodium ascorbate are preferred by some agencies because they are non-hazardous and they do not adversely impact the water quality of the receiving streams.

Tables 1 and 2 summarize information currently available on dechlorination efficiency, water quality impacts and regulatory issues. Table 1 shows the amount of each dechlorination agent required to neutralize one part of chlorine in distilled water at different pHs. Table 2 shows selected regulatory and toxicity information of the dechlorination chemicals.

Table 2
Regulatory Information for Various Dechlorination Chemicals

Activity	Sulfur dioxide	Sodium bisulfite	Sodium metabisulfite	Sodium sulfite	Sodium thiosulfate	Calcium thiosulfate	Ascorbic acid/ sodium ascorbate
USDOT rating	Poison	Corrosive	Corrosive	Not hazardous	Not hazardous	Not hazardous	Not hazardous
NFPA rating[a]	3,0,0	1,0,1	3,0,1	2,0,0	1,0,0	0,0,0	0,0,0
RMP required	Yes	No	No	No	No	No	No
Exposure limits	NA	OSHA TWA 5 mg/m^3	OSHA TWA 5 mg/m^3	NA[b]	NA	NA	NA
Aquatic toxicity	NA	Reported to be toxic	Reported to be toxic	Reported to be toxic	$LC_{50}{}^{c} = 7.3$ g/L	$LC_{50}{}^{d} > 750$ mg/L	NA

[a] National Fire Protection Authority Rating for health, fire and reactivity, respectively. (Ranges from 0 to 4. 0-No hazard, 4-extremely hazardous)

[b] NA, Not available.

[c] US EPA 1988 (19).

[d] 96 h test for fathead minnows.

3. FIELD DECHLORINATION STUDIES

3.1. Background

This section summarizes the field studies performed to compare the efficiencies of dechlorination chemicals under identical conditions to evaluate the chemical of choice for various dechlorination applications (18,19). The field tests were conducted at Tacoma Waters, WA, Portland Bureau of Water Works, OR, and East Bay Municipal Utility District (EBMUD), CA. Six dechlorination chemicals were used in solution, tablet, or powder form in these tests (Table 3). In the Tacoma and Portland studies, a 1% solution of the dechlorination chemicals were introduced into water released from a hydrant. The field studies evaluated the rate of dechlorination, effect of overdosing, and concurrent water quality impacts when stoichiometric or twice the stoichiometric amounts of dechlorination agents were added. In the EBMUD dechlorination studies, bags, or dispensers containing tablets or powders of dechlorination chemicals were placed in the flow path of hydrant water. At all three sites, the water used for the test originated from surface water sources rather than from groundwater sources. Table 3 summarizes the chemicals, forms and dosing rates used in these studies.

3.2. Field Dechlorination Tests at Tacoma Waters

Tacoma Waters uses free chlorine for disinfection. Water from the hydrant was released through a fire hose 50 ft long and 6 in. in diameter. The flow rate was adjusted to 300 gpm. The other end of the fire hose was connected to a diffuser to facilitate mixing of chemicals with the flow. A 1% solution of each chemical was prepared in a polyethylene bucket and introduced into the flow at the upstream side of the diffuser using an adjustable rate metering pump. Dechlorination chemicals were fed either at concentrations just sufficient to neutralize all the chlorine in the water (stoichiometric amount) or at concentrations resulting in 100% overdose for chlorine neutralization (twice the stoichiometric amount). Water released from the hydrant traveled approx 500 ft and discharged into a storm sewer leading to a holding pond. Results from the Tacoma field test are summarized below.

3.2.1. Residual Chlorine Concentrations

Figure 1 shows the chlorine concentrations at sampling points after the addition of stoichiometric concentrations of dechlorination chemicals. Chlorine concentrations during the flow, when no chemicals were added, are also shown.

The field study indicated that, when no chemical was added, free chlorine concentration in the water did not decrease significantly. Chlorine concentrations decreased from 1.2 to approx 1.0 mg/L after a travel of 450 ft (4 min, 10 s) on the semi-paved, asphalt road. When stoichiometric concentrations of dechlorination chemicals were added, most of the chemicals neutralized chlorine instantaneously. Samples analyzed 2 ft (reaction time approx 1 s) downstream of the diffuser contained less than 0.1 mg/L of chlorine. An exception to this trend was calcium thiosulfate. When calcium thiosulfate was added, chlorine concentrations decreased to 0.2 mg/L within 2 ft and residual chlorine was reduced to less than 0.1 mg/L after a travel of 200 ft (reaction time 1 min 40 s).

When twice the stoichiometric concentration of chemicals was added, residual chlorine in all the tests (including calcium thiosulfate) decreased to below 0.1 mg/L immediately (approx 2 s).

Table 3
Summary of Dechlorination Field Test Conditions

Test location	Disinfectant used	Chemicals tested	Form of chemicals used	Chemical feed conditions	Initial chlorine (mg/L)	pH	Source of water	Flow rate (gpm)*
Tacoma Waters, Tacoma, WA	Free chlorine	Sodium metabisulfite Sodium sulfite Sodium thiosulfate Calcium thiosulfate Ascorbic acid Sodium ascorbate	1% solution	Stoichiometric concentrations and twice the stoichiometric concentrations needed for dechlorination	1.2	8.9	Surface water	300
Bureau of Water Works, Portland, OR	Combined chlorine	Sodium bisulfite Sodium sulfite Sodium thiosulfate Calcium thiosulfate Ascorbic acid Sodium ascorbate	1% solution	Stoichiometric concentrations needed for dechlorination	1.1	8.0	Surface water	300
EBMUD, Oakland, CA	Combined chlorine	Sodium sulfite	Tablets from 2 companies	Varied from 1 to 36 tablets	1.2	8.0	Surface water	100–500
		Sodium thiosulfate	Crystals	1 lb in nylon bags placed on the flow path				100
		Ascorbic acid	Powder					100

*1 gpm = 1 gal/min = 3.785 L/min

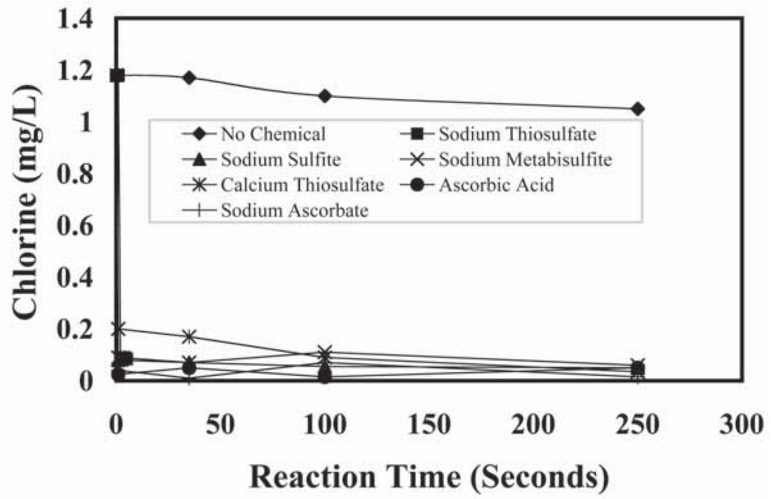

Fig. 1. Chlorine concentrations at Tacoma City Water when stoichiometric concentrations of dechlorination chemicals were added to neutralize chlorine in potable water from a hydrant. The water traveled a distance of about 450 ft after 250 s.

3.2.2. Dissolved Oxygen

When no dechlorination chemical was added, the dissolved oxygen concentration of the released water decreased from an initial concentration of 11 by less than 0.3 mg/L after traveling 450 ft in one test. When stoichiometric amounts of dechlorination chemicals were added, the DO decreased by 1.18, 0.3, 0.55, and 0.5 mg/L in the presence of sodium metabisulfite, sodium sulfite, sodium thiosulfate, and calcium thiosulfate, respectively. When twice the stoichiometric amounts of dechlorination chemicals were added, the dissolved oxygen concentration decreased by 1, 0.9, 0.9, and 0.7 mg/L, respectively, in the presence of these chemicals. With the addition of stoichiometric concentrations of ascorbic acid and sodium ascorbate, the DO of the water increased by 0.3 mg/L, after a travel of 450 ft. When twice the stoichiometric concentrations of these chemicals were used, the DO decreased by 0.2 mg/L.

In summary, results indicated that sodium metabisulfite had a greater impact (1.0–1.18 mg/L depletion) on the DO concentrations of the water tested. Sodium sulfite, sodium thiosulfate, and calcium thiosulfate decreased the DO concentration by 0.3–0.9 mg/L, depending on the amount of dechlorination chemical used. Ascorbic acid and sodium ascorbate had the least impact on the DO of the water tested.

3.2.3. pH

The initial pH of the hydrant water, prior to chemical addition, was between 8.8 and 9.0. Sodium metabisulfite, at either concentration used, decreased the water pH about 0.8 unit after a travel of 450 ft. After a travel of 450 ft, ascorbic acid decreased the pH of the water by 0.3 and 0.6 unit when stoichiometric and twice the stoichiometric amounts, respectively, were used. The pH decreased by less than 0.1 unit when sodium sulfite, calcium thiosulfate, or sodium ascorbate was used at stoichiometric or twice the stoichiometric amounts.

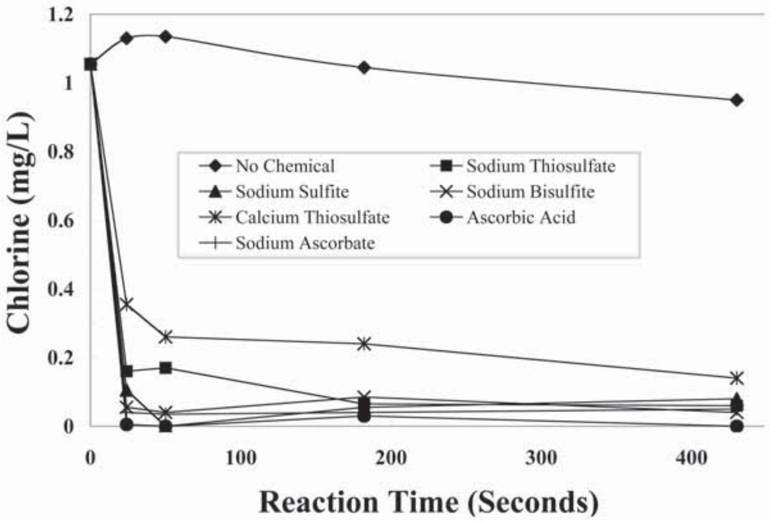

Fig. 2. Chlorine concentrations at Portland City Water when stoichiometric concentrations of dechlorination chemicals were added to neutralize chlorine in potable water from a hydrant. The water traveled a distance of about 1000 ft after 430 s.

3.3. *Field Dechlorination Studies at Bureau of Water Works, Portland*

Portland Bureau of Water Works uses combined chlorine for disinfection. The tests conducted at Portland were similar to those at Tacoma, except in the following aspects: Tests using all the chemicals, except sodium sulfite, were conducted at stoichiometric concentrations only; a 100 ft hose, rather than a diffuser, was provided for mixing of chemicals with the water; the released water traveled along a well-paved surface for 1000 ft prior to discharging into a storm drain leading to a storage pond.

Samples were analyzed for residual chlorine concentrations and pH at the hydrant, and 2, 100, 500, and 1000 ft downstream of the 100-ft-long hose. The travel time for the water to reach the sampling points were 0 min, 24 s (100 ft); 3 min, 2 s (500 ft); and 7 min, 10 s (1000 ft), respectively.

3.3.1. Residual Chlorine Concentrations

When no dechlorination chemical was added, the chlorine concentration decreased from 1.05 to 0.95 mg/L after 1000 feet (Fig. 2). This indicated that only a small amount (0.1 mg/L) of the chloramines dissipated through chlorine demand of paved surfaces. Sodium bisulfite, sodium sulfite, ascorbic acid, and sodium ascorbate neutralized all detectable chlorine to below 0.1 mg/L within 2 ft downstream of the mixing hose (approx 2 s). Sodium thiosulfate neutralized more than 80% of the chlorine within 2 ft. However, chlorine concentrations decreased below 0.1 mg/L (the discharge limit in most states) after about 500 ft (elapsed time 3 min, 2 s). Calcium thiosulfate neutralized 60% of the chlorine within 2 ft and neutralized 90% of the chlorine after 1000 ft (elapsed time 7 min, 10 s).

3.3.2. pH

At concentrations used in this study, none of the chemicals appeared to affect the pH of the Portland Water Bureau water appreciably.

3.4. Dechlorination Field Studies at EBMUD

EBMUD uses combined chlorine for disinfection. The purpose of the field study at EBMUD was to evaluate dechlorination when chemicals were placed either as tablets or as powder within the path of the chlorinated water. The following dechlorination chemicals were evaluated:

- Sodium sulfite (91.5%) tablets
- Ascorbic acid (food grade, free white powder)
- Sodium thiosulfate (photo grade 1/8 in. diameter granules)

Several series of field tests were conducted under different conditions. Flow was discharged from a hydrant on EBMUD's water distribution system, through a fire hose and onto a fairly level paved and curbed street close to the curb. The water flowed down the street, into a drop inlet 160 ft downstream. The drop inlet led to an onsite storm drain system at EBMUD's wastewater treatment plant that flows into the headworks of the plant.

Chlorine residual concentrations of the water upstream and downstream of the dechloramination chemical feed points were measured using a Hach Chlorine Pocket Colorimeter. Temperature, dissolved oxygen (DO), pH, and oxidation–reduction potential (ORP) were also measured during the field study.

3.4.1. Effect of Number of Tablets and Flow Rates

The test procedure consisted of initially placing a single tablet of sodium sulfite, then 2, 4, 16, and 28 tablets of sodium sulfite in the water flow path 10-ft downstream of the flow control valve and meter. The flow rates ranged from 100 up to 500+ gpm. Samples were collected 150 ft downstream of the tablets. As shown in Fig. 3, one tablet effectively reduced the chlorine residual of the flow it came in to contact with, to below 0.1 mg/L for 45 min at a flow rate of 100 gpm. The tablet was not fully consumed, but became ineffective after approx 1 h and the chlorine concentration rose again.

When 12 tablets were placed across the flow of 100 gpm, the chlorine concentration decreased below the detection limit (0.1 mg/L) within 5 min. It remained below the detection limit even after 60 min. In the next test, initially a flow rate of 300 gpm was maintained and 16 tablets were placed across the flow. Within 5 min the chlorine concentration decreased to below detection limit. After 10 min, the flow rate was increased to 450 gpm. At this increased flow rate, the residual chlorine concentration increased to values of 0.6–0.8 mg/L, well above the detection limit of 0.1 mg/L (which is the allowable discharge limit in many locations), within 25 min (Fig. 3). This indicates that the flow rate of chlorinated waters can significantly impact the efficiency of dechlorination operations. Higher flow rates may not provide sufficient contact time for dissolution of tablets into the stream. After approx 40 min, the number of tablets was increased to 20. This decreased the residual concentration to below detection limit within 5 min. The increase in the number of tablets probably provided an enhanced contact area and better dissolution of the tablets into the flow, resulting in a decrease in the residual chlorine concentrations.

No significant impact upon pH was observed in any of the tests. In the test where 1 tablet was placed across the flow, the initial pH was 8.84. The pH after 60 min was 8.80. In the presence of 12, 16, or 28 tablets, the initial pH did not change by more than 0.2 unit. The average alkalinity of EBMUD water is about 26 mg/L as $CaCO_3$.

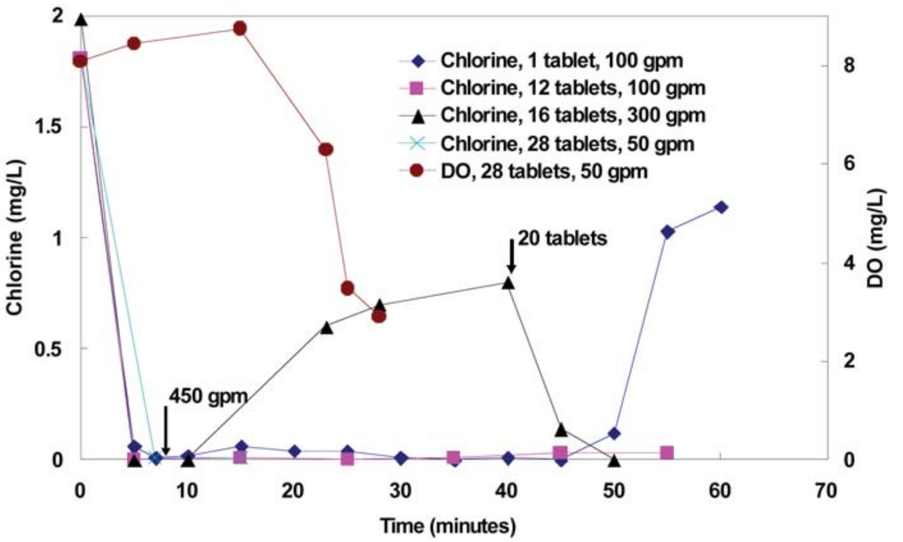

Fig. 3. Chlorine and DO concentrations when sodium sulfite tablets were placed across the floor.

Dissolved oxygen concentrations were not measured when 1 or 12 tablets were placed across the flow. When 16 or 20 tablets were placed across a flow of 300/450 gpm, the initial dissolved oxygen concentration was 8.59 mg/L. No specific trend was observed in the DO profile. When 28 tablets were placed across a flow of 50 gpm, the DO concentration decreased significantly from 8.08 to 2.91 mg/L within 25 min. The larger number of tablets and a lower flow rate maintained in this test as compared to the previous three tests, probably caused for the enhanced depletion of DO in the water.

In summary, results from the test series indicated that, for a flow rate of up to 100 gpm for EBMUD water, one Dechlor tablet maintained the residual chlorine concentration below the detection limit for 45 min. An increase in the number of tablets increased the residual chlorine removal efficiency. However, an increase in flow rate to 450 gpm resulted in an increase in residual chlorine concentrations to above detection (and compliance) limits within 25 min, even in the presence of 16 tablets. Results also indicated that, when the flow rate was decreased (to 50 gpm) and the number of tablets increased (to 28), the DO concentration decreased significantly.

3.4.2. *Chlorine Profile Along the Flow Path*

In this test, water quality was analyzed along the flow path, upon contact with dechlorinating chemical. A flow rate of 100 gpm was maintained, and one or four tablets were placed across the flow. Samples were collected at the point of release and 40, 80, 120, and 160 ft downstream of the tablets. The residual chlorine concentration in the water decreased with distance (Fig. 4). One tablet was sufficient to remove chlorine to below 0.1 mg/L after 120 feet of travel under the test conditions.

The DO concentration decreased from 7.0 to 6.0 mg/L within 80 ft, when one tablet was placed across the flow. The DO subsequently increased to 9.60 mg/L after traveling 160 ft. The pH decreased from 8.95 to 8.70 units within 80 ft and decreased to 6.67 units after 160 ft. The reasons for the increase in DO concentration, and decrease in pH, after

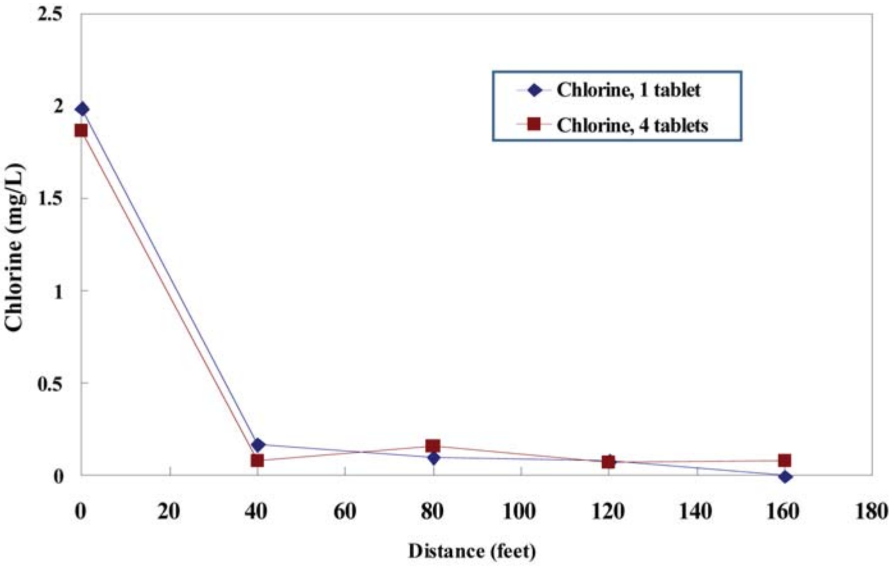

Fig. 4. Chlorine concentrations when one or four tablets were placed along the flow path. The flow rate of EBMUD water was 100 gpm.

a travel distance of 80 ft, are not known. However, the trend was less pronounced when four tablets were placed across the flow path. The DO concentration decreased from 9.26 to 9.05 mg/L after a travel of 80 ft and increased to 9.66 mg/L after 160 ft. The pH decreased from 8.95 to 8.9 units after a travel of 80 ft and decreased to 8.75 units after 160 ft. In general, the initial decrease in DO may be due to the reaction with sodium sulfite. Subsequent increase may have resulted after the exhaustion of the released sodium sulfite in the water.

3.4.3. *Dechlorination Using Ascorbic Acid Powder/Sodium Thiosulfate Crystals*

In these tests, 1 lb of the dry chemical in a nylon bag was placed across a flow of 100 gpm. Both of the chemicals decreased the total residual chlorine to below 0.1 mg/L. However, in both the cases, the chemical dissolved rapidly and escaped the bag. Excessive dissolution of ascorbic acid decreased the water pH from 8.9 to 5.07. Dissolution of sodium thiosulfate did not significantly affect the pH or DO.

3.5. Summary of Field Dechlorination Studies

The field studies indicated that all of the dechlorination chemicals were effective in neutralizing free and combined chlorine to below 0.1 mg/L. In most cases the stoichiometric amount of dechlorination chemicals removed more than 90% of the chlorine. However, the reaction rates and the water quality impacts varied with the type, amount, and form of the chemicals used. In general, the rates of dechlorination using sodium/calcium thiosulfate were slower than those using the other chemicals. However, studies by others indicated that dechlorination of wastewater samples using sodium thiosulfate was more rapid that using ascorbic acid (24).

Sodium metabisulfite, when added in stoichiometric concentrations, reduced the DO by approx 1 mg/L. At elevated concentrations (twice the stoichiometric concentrations) sodium sulfite and sodium thiosulfate also reduced the DO levels by approx 1 mg/L. Ascorbic acid reduced Tacoma water pH by 0.3 and 0.6 unit at stoichiometric and twice the stoichiometric concentrations.

When used in powder or crystal form, dechlorination chemicals (ascorbic acid and sodium thiosulfate) dissolved rapidly causing water-quality concerns, although physical methods (tablets) have been developed since to slow down dissolution rates. Sodium sulfite, when used in tablet form, was very effective in dose control. One tablet was sufficient to dechlorinate 2 mg/L of chloraminated water to below 0.1 mg/L for 45 min when water was released at 100 gpm. Finally, these field tests also indicated that the flow rates of chlorinated waters can significantly impact the efficiency of dechlorination operations.

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14
Advanced Oxidation Processes

**M. B. Ray, J. Paul Chen, Lawrence K. Wang,
and Simo Olavi Pehkonen**

CONTENTS

1. INTRODUCTION

Since the early 1970s, advanced oxidation processes (AOPs) have been used considerably to remove both low and high concentrations of organic compounds from diverse sources such as groundwater, municipal and industrial wastewater, sludge destruction, and volatile organic compound (VOC) control. These processes, although often having high capital and operating costs, are the only viable treatment methods for effluents containing refractory, toxic, and non-biodegradable materials. In the AOP, the organic compounds can be completely mineralized to carbon dioxide and water mostly by hydroxyl radicals, the second most powerful oxidizing agent generated *in situ* in the reaction environment. The rate constant values of oxidation of the organics with hydroxyl radicals range from 10^8 to 10^{11} $M^{-1}s^{-1}$ (1). Depending on the AOP, the hydroxyl radicals can be generated by any one or combination of the following methods: (a) chemical oxidation using hydrogen peroxide, ozone, hydrogen peroxide/ozone, Fenton's agent; (b) radiation methods including ultraviolet (UV) radiation, γ-radiation, electron-beam, and ultrasonic waves; (c) combination of any one of (a) with any of (b), in particular UV radiation or ultrasonication; and (d) photocatalysis using UV and titanium dioxide

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Table 1
Oxidation Potential of Different Oxidants

Name of oxidant	Oxidation protential (eV)
Fluorine	3.0
Hydroxyl radical	2.8
Ozone	2.1
Hydrogen peroxide	1.8
Potassium permanganate	1.7
Chlorine dioxide	1.5
Chlorine	1.4

Table 2
List of Reactions of Hydroxyl Radical

Mechanism	Reaction
Addition	$OH^{\cdot} + C_6H_6 \rightarrow C_6H_6\text{–}OH$
Hydrogen abstraction	$OH^{\cdot} + CHCl_3 \rightarrow CCl_3^{\cdot} + H_2O$
Electron transfer	$OH^{\cdot} + [Fe(CN)_6]^{4-} \rightarrow [Fe(CN)_6]^{3-} + OH^{-}$
Radical combination	$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O_2$

(TiO_2). In Table 1, the oxidation potentials of some important oxidizing agents are listed. The free hydroxyl radical has the second highest oxidizing potential and is the best choice for use in oxidation processes. Hydroxyl radicals ($OH^{\cdot}$) can be generated *in situ*, and compared to fluorine; oxidation products of $OH^{\cdot}$ are less toxic with the possibility of complete mineralization of the organics. Once generated, hydroxyl radical can undergo the following reactions given in Table 2.

The major advantages of AOP include the following: (a) complete mineralization of organics, (b) removal of recalcitrant compounds, and (c) easy combination with biological processes. A wide variety of organic and inorganic contaminants such as halocarbon/hydrocarbon organics and their derivatives, aromatics, organo–N/P/S compounds, TNT, humic substances, heavy metals, and cyanides are susceptible to destruction by AOP.

The viable variant of an AOP depends on the chemical properties of the effluent and the scale of operation. Although, AOP has found wide environmental applications, extensive research is still devoted to the development of large-scale processes and process optimization. In this chapter, fundamentals, design and operations, and economics of different advanced oxidation processes will be presented. In addition, new research development in this area will also be presented.

2. MECHANISMS AND THEORY

2.1. Chemical Oxidation

In chemical oxidation, chemicals with high positive oxidation potential, such as ozone (2.1 V) and hydrogen peroxide (1.8 V), are used to destroy a wide variety of organic and inorganic compounds such as chlorinated VOCs, mercaptans, phenols, and cyanide (NaCN).

2.1.1. Ozone

Ozone is commonly used in water and wastewater applications as a disinfectant because it is a powerful oxidant, and reacts with most toxic organics. Direct ozonation of organic molecules may act in different ways: (a) breaking double bonds to form aldehydes and ketones, (b) insertion of an oxygen atom into a benzene ring, and (c) reacting with alcohol to form organic acids. While direct ozonation is not an effective process in many cases, ozone decomposes in water at high pH (about 10) to create a large number of hydroxyl radicals. Ozone decomposition occurs according to the following equations:

$$O_3 + H_2O \rightarrow HO_3^+ + OH^- \tag{1}$$

$$HO_3^+ + OH^- \rightarrow 2\ HO_2^{\cdot} \tag{2}$$

$$HO^{\cdot}{}_2 + O_3 \rightarrow OH^{\cdot} + 2O_2 \tag{3}$$

2.1.2. Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is one of the most powerful oxidizing agents known and is able to oxidize a wide variety of chemicals such as aldehydes, alcohols, amines, azo-compounds, phenols, cyanides, sulfides, and metals. H_2O_2 also decomposes in the presence of an iron catalyst to create a large number of hydroxyl radicals. This is the widely used Fenton's reaction named after its discoverer J. H. Fenton in 1894. Fenton's reaction is used to treat a large variety of water contaminants such as phenols, formaldehyde, benzene, toluene, ethylbenzene, xylenes, and pesticides. Following equations depict the Fenton's reaction:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{\cdot} + OH^- \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{\cdot} + H^+ \tag{5}$$

Hydrogen peroxide also decomposes in the presence of ozone as

$$2O_3 + H_2O_2 \rightarrow 2\ OH^{\cdot} + 3O_2 \tag{6}$$

2.2. Radiation Methods

Chemical methods using ozone or hydrogen peroxide do not necessarily yield the complete mineralization of many organics. The intermediates formed in some instances are more toxic than the parent compound. Electromagnetic radiation such as UV, γ-radiation, electron-beam, and high-speed sound vibrations such as ultrasonic radiation are commonly used to induce higher rates of hydroxyl radical generation. In addition, some direct degradation of the pollutants may also occur due to bond rupture following the absorption of radiation (in case of UV radiation) or by pyrolysis (in case of ultrasonication).

2.2.1. UV Radiation

UV radiation has been the most widely used radiation method in initiating oxidation processes. The UV wavelengths of importance are UV-A (315–400 nm), UV-B (280–315 nm), and UV-C (200–280 nm) as illustrated in Chapter 10. The radiation energy associated with a photon *(E)* depends on the wavelength of light (λ) according to the equation:

$$E(\text{kJ/mol}) = 12{,}000/\lambda\ (\text{nm}) \tag{7}$$

The extent of absorption of UV radiation and absorption spectra by any compound is related to its molecular/bond structure and the wavelength of radiation. For direct UV radiation, UV-C is most commonly used, while UV-A is used for photocatalytic processes.

The absorption of light energy by organic compounds induces photophysical or photochemical events to occur. While photophysical processes include emission of light or heat, photochemical changes produce new compounds by transformations that include isomerization, bond cleavage, rearrangement, or intermolecular chemical reactions. In the presence of UV-C, organic compounds can undergo photolysis, oxidation, and a combination of oxidation and photolysis. The extent of the individual reaction depends on the type and concentration of the organics, the wavelength of radiation, and the presence of additional oxidants such as ozone, hydrogen peroxide, and hydroxyl radical. UV photolysis is the process by which chemical bonds of the contaminants are ruptured subsequent to the absorption of radiation. Many VOCs such as alkenes like trichloroethylene (TCE), polychromatic erythrocytes (PCE), and aromatics such as benzene, toluene, xylene undergo direct photolysis by UV irradiation (2–4). Greater size and alkyl substitution increase the sensitivity of the aromatic compounds to photolysis.

Direct photolysis often is kinetically simple and easily modeled, especially if the absorption spectrum of the compound and its quantum yield of disappearance are known. The average photoreaction rate in direct photolysis can be expressed as

$$-\frac{dc_A}{dt} = \Phi I_m \tag{8}$$

where c_A = concentration of the organics, Φ = quantum yield of the reaction, I_m = average number of einsteins absorbed by the absorbing species per unit volume and unit time, and t = time.

In situ hydroxyl radicals can be formed with low-pressure UV lamps with 185 nm radiation (ozone producing). Many of the commercial low-pressure UV lamps have a small percentage (typically 5%) of radiation at 185 nm, which produces ozone in the reactor. Hydroxyl radicals can be generated via the UV photolysis of ozone to produce electronically excited singlet oxygen atoms (5):

$$O_3 + hv\ (<310) \rightarrow O\ (^1D) + O_2 \tag{9}$$

A small fraction of O (^{1}D) reacts with a water molecule to yield two OH radicals:

$$O\ (^1D) + H_2O \rightarrow 2OH^{\cdot} \tag{10}$$

Loss of hydroxyl radicals from the active reaction scheme occurs by the following reactions (5):

$$OH^{\cdot} + O_3 \rightarrow HO_2^{\cdot} + O_2 \tag{11}$$

$$OH^{\cdot} + HO_2^{\cdot} \rightarrow H_2O + O_2 \tag{12}$$

$$O + OH^{\cdot} \rightarrow O_2 + H \tag{13}$$

$$OH^{\cdot} + OH^{\cdot} \rightarrow H_2O + O \tag{14}$$

2.2.2. γ and Electron-Beam Radiation

Gamma radiation is very-high-energy ionizing radiation originating in the nucleus of the atom and produced following spontaneous decay of radioactive materials, such as cobalt-60 and cesium-137. Gamma radiation can split water to generate hydroxyl radical. Electron beam (E-beam) radiation is a form of ionizing energy where electrons are concentrated and accelerated to 99% of the speed of light and energies of up to 10 MeV. Because E-beams are generated electrically, they offer certain advantages over gamma radiation: (a) no replenishment of the source such as cobalt-60 is required, and (b) no radioactive waste is generated. However, E-beam technology also has disadvantages such as: (a) shallow depth of penetration, (b) high electric power consumption, and (c) complexity and potentially high maintenance.

2.2.3. Ultrasonication

Sonochemical degradation which combines destruction of the target compounds by free-radical reaction and thermal cleavage is a recent AOP and is proven to be effective for removing low concentration organic pollutants from aqueous streams. The chemical effect of ultrasound is produced through the phenomenon of cavitation, which is caused by the expansion and contraction of cavitation nuclei due to the compression and rarefaction cycles of the ultrasonic waves. Cavitation causes the formation, rapid growth, and finally implosive collapse of the bubbles, resulting in an unusual reaction environment in the vicinity of the bubbles. Compression of gas and vapor in the bubbles generates intense heat and can generate local hot spots. The temperature inside the cavity can reach about 5200 K in the collapsing bubbles and 1900 K in the interfacial region between the solution and the collapsing bubbles. Sonochemical effect takes place either due to the pyrolytic decomposition inside the bubbles or by the reduction and oxidation due to the generation of $H^{\cdot}$ and $OH^{\cdot}$ radicals at the gas–liquid interface, and to lesser extent in bulk solution.

2.3. Combination Processes

2.3.1. UV/H_2O_2

Advanced oxidation based on UV/H_2O_2 is very efficient with a wide range of applications in the treatment of mainly aqueous effluents, and about 200 commercial installations treating contaminated water are found in the literature (6,7). H_2O_2 has a weak molar absorption coefficient, which increases as the wavelength decreases in the 200–300 nm UV range. The photolysis of H_2O_2 produces hydroxyl radicals:

$$H_2O_2 + h\nu \rightarrow 2OH^{\cdot} \tag{15}$$

$$OH^{\cdot} + H_2O_2/HO_2^{-} \rightarrow HO_2^{\cdot}/O_2^{-} + H_2O \tag{16}$$

$$HO_2^{-} + H_2O_2 \rightarrow OH^{\cdot} + H_2O + O_2 \tag{17}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{18}$$

Quantum yield of generated $OH^{\cdot}$ per photon absorbed is 1.0 (7).

2.3.2. UV/Ozone

In the aqueous phase ozone absorbs at 254 nm with a maximum molar absorptivity coefficient 3300 M^{-1} cm^{-1}. Hydroxyl radicals are produced via the ultraviolet photolysis of ozone to produce electronically excited singlet oxygen atoms:

$$O_3 + H_2O + hv\ (<310) \rightarrow H_2O_2 + O_2 \tag{18a}$$

$$H_2O_2 + H_2O \rightarrow H_3O^+ + HO_2^- \tag{19}$$

$$O_3 + HO_2^- \rightarrow O_2 + O_2^{\cdot -} + OH^{\cdot} \tag{20}$$

$$O_3 + O_2^{\cdot -} + H_2O \rightarrow 2O_2 + OH^- + OH^{\cdot} \tag{21}$$

$$O_3 + OH^{\cdot} + H_2O \rightarrow O_2 + H_3O + O_2^{\cdot -} \tag{22}$$

O_3/UV combined technology was used to treat the methyl *tert*-butyl ether (MTBE), a common gasoline additive, which is present in many surface water and groundwater (8). It was found that the technology has a better degradation ability of MTBE with fewer by-products.

2.3.3. UV Photocatalysis

Photocatalytic oxidation (PCO) of the organics using semiconductor catalyst such as TiO_2 possesses great potential, because longer wavelength of UV can be used as the energy source. The ground-level solar spectrum contains approx 1% near-UV photons of sufficient energy to photoexcite TiO_2, thus PCO can be activated in sunlight. TiO_2 exhibited faster rate compared to several semiconductors such as ZnO, ZnS, CdS, Fe_2O_3, and WO_3, and is extremely stable (9). Zinc oxide has a similar band gap (3.2 eV) of that of TiO_2; however ZnO may possess selectivity for complete mineralization of chlorinated wastes (10). The summary of the PCO steps are given as:

$$TiO_2 + hv \rightarrow \text{(holes)}\ h^+_{vb} + e^-_{CB} \tag{23}$$

$$h^+_{\mathrm{vb}} + H_2O\ \text{(ads)} \rightarrow OH^{\cdot} + H^+ \tag{24}$$

$$h^+_{\mathrm{vb}} + OH^-\ \text{(ads)} \rightarrow OH^{\cdot} \tag{25}$$

These holes are very strong oxidizing agents, and the number of electron–hole pairs is dependent on the intensity of the incident light and the electronic properties of the material that prevent them from recombining and releasing the absorbed energy. The energy efficiency (heterogeneous quantum yield) depends on operating conditions such as temperature, reactant and product concentration, pH, oxygen, or air concentrations.

Chen et al. found the H_2O_2 could greatly enhance the degradation of rhodamine 6G in a TiO_2/UV oxidation system (11). Chemical oxygen demand (COD), biochemical oxygen demand (BOD), bacteria, and ammonia nitrogen in the dye and print wastewater were reduced by 93.9%, 87.6%, 99.9%, and 67.5%, respectively, with a contact time of 30 min.

3. REACTION KINETICS

Typically, easily oxidized organic compounds, such as those with double bonds (e.g., TCE, PCE, and vinyl chloride), as well as simple aromatic compounds (e.g., toluene, benzene, xylene, and phenol), are rapidly destroyed in AOP. The reported rate constants of the reactions involving benzene, toluene, ethylbenzene, styrene, and TCE with hydroxyl radicals in water are quite comparable and vary in a narrow range of 3.0×10^9–7.8×10^9 L mol^{-1}s^{-1} (12). The photooxidation rate constants for various volatile organics and their intermediates follow the following order (4,13,14):

Chloro-olefins > Chloro-paraffin > Chloro-acetic acids

Mineralization of chloro-ethylenes decreases with the increase in chlorine atom substitution on the C=C bond and oxidation of nitrogen-containing compounds is slow when compared to the compounds containing phosphorus, sulfur, and chlorine. Photo-oxidation in a mixture of organics is complicated as the rate of one compound may be inhibited or enhanced by the presence of others (4).

Generally first-order kinetics with respect to the concentration of the pollutant is observed for most AOPs in water. The compounds, which exhibit non-first-order kinetics also show quantum yields greater than one. These apparent higher quantum yields are due to sensitized oxidations. The kinetics for photocatalytic oxidation (PCO) can be expressed as one of Langmuir–Hinshelwood type, thus depending on both the degradation rate and the adsorption rate constant of the pollutant.

4. INTERMEDIATES AND BY-PRODUCTS

The intermediates formed in AOPs sometimes are more toxic than the parent compounds and are required to be decomposed completely using either combination of AOPs or combination of AOP and some other treatment methods such as adsorption and biodegradation. Carbonyl compounds, particularly aldehydes, are quite toxic, and some of the secondary compounds formed from aldehydes, especially peroxyacylnitrates are more dangerous than the parent compounds. Organic peroxy radical ($RO_2^{\cdot}$) reactions are of significance because they represent an important class of intermediates formed in the oxidation process of hydrocarbons (15). Intermediates such as ethers and alcohols have enhanced reactivity toward hydroxyl radical. The rate constant of oxidation of these compounds is of similar order of magnitude as of the alkanes.

Isomerization and the formation of addition products with alkenes are the most noted reactions of the benzene ring (16). Alkylbenzenes such as toluene form fairly stable epoxides upon the addition of hydroxyl radical, which are potential toxic and mutagenic compounds (17). The subsequent reactions of the epoxide could lead to the formation of epoxy carbonyls, which can react further with OH radicals or ozone until smaller molecules are formed.

5. PROCESS PARAMETERS

An efficient operation of an AOP depends on both the nature of waste and the type of AOP used. The optimum conditions are determined individually through treatability studies and pilot testing. The process parameters can be broadly divided under the following categories: (a) characteristics of wastewater and (b) operating conditions.

5.1. Characteristics of Wastewater

5.1.1. Chemical Structure and Concentration of Organic Contaminants

As discussed earlier, organic compounds with double bonds, especially with chlorine, react quickly with hydroxyl radical. On the other hand, saturated organic compounds such as 1,1-dichloroethane and chloroform, are better removed by UV photolysis. Depending on the type of organic compound, initial contaminant concentration will affect the performance of the process. For high contaminant level, multiple AOPs can be used. For example, for a COD > 5000 mg/L, sequential treatment using Fenton's reagent followed by UV oxidation may be chosen.

5.1.2. Solution pH

The pH of water is an important factor for AOP application in the water phase as the hydroxyl radical concentration is a function of pH. pH controls the equilibrium of carbonate, bicarbonate, and carbonic acid present in water; carbonate and bicarbonate both scavenge hydroxyl radicals with rate constants of $3.9 \times 10^{8}\ \mathrm{M}^{-1}\mathrm{s}^{-1}$ and $8.5 \times 10^{6}\ \mathrm{M}^{-1}\mathrm{s}^{-1}$, respectively. Thus, acidic pH is better for water with high carbonate and bicarbonate alkalinity (greater than 400 mg/L as $CaCO_3$). However, the effect of pH is system-specific; for example, generally UV/H_2O_2 is more effective at low pH, while UV/O_3 is more effective at slightly basic pH.

5.1.3. Turbidity of Water

The aqueous stream being treated must provide for good transmission of UV light (high turbidity causes interference). This factor can be more critical for UV/H_2O_2 than UV/O_3. Sonodegradation rate also is reported to be affected by turbidity. However, turbidity does not affect direct chemical oxidation of the contaminant by H_2O_2 or ozone. Water with suspended solids above 300 mg/L needs pretreatment to remove the solids for UV oxidation.

5.1.4. Radical Scavenger

Hydroxyl radical scavengers can inhibit contaminant destruction efficiency. Excessive dosages of chemical oxidizers may act as scavenger. Presence of carbonate, bicarbonate, nitrite, sulphite (naturally occurring) and chloride ion (formed as a result of degradation of chlorinated organics) can act as hydroxyl radical scavenger, which result in decreasing degradation rate of the organics. Some other common scavengers available in natural water such as EDTA, humic acid, bromide, and cyanide also act as hydroxyl radical scavenger.

5.1.5. Presence of Metals, Oil, and Grease

The aqueous stream to be treated by UV/oxidation should be relatively free of heavy metal ions (less than 10 mg/L) and insoluble oil or grease to minimize the potential for fouling of the quartz sleeves. In some waters, a small change in pH causes soluble inorganic chemicals such as calcium, iron, and manganese to precipitate. Heavy metals oxidized by hydroxyl radical cause additional concern. For example, Cr^{6+} is more toxic than Cr^{3+}.

5.1.6. Presence of Oil and Grease

Free oil and grease above 50 ppm reduces the efficiency of the process by competing with the target compound for hydroxyl radical. Higher oil and grease content can result in fouling of the quartz sleeves of UV lamps, which reduces the oxidation efficiency.

5.2. *Operating Conditions*

Operating parameters are those varied during laboratory or pilot studies of a contaminant to achieve target treatment efficiency. Depending on the type of AOP used and the target removal, oxidant type and dosage, intensity of radiation, an amount of catalyst are important operating parameters for efficient operation. Although, chemical reaction increases with temperature, primary photochemical processes are temperature independent. Thus, the effect of temperature varies with the type of AOP used, and is usually not an option to vary.

5.2.1. Oxidant Type and Dosage

In AOP such as UV-oxidation, reaction rate with first order with respect to hydroxyl radical increases with the dosage of oxidant such as O_3 and H_2O_2. However, in some systems such as UV/H_2O_2 there exists an optimum dose of H_2O_2 beyond which rate declines as H_2O_2 itself is a scavenger of hydroxyl radical. For UV/ozone system, high ozone concentration in water will result in excess ozone in the off-gas that needs to be disposed.

5.2.2. Radiation Intensity

For any radiation-based AOP such as UV, UV/O_3, UV/H_2O_2, PCO, and sonication, intensity and frequency (for sonication) of irradiation are important parameters. At low intensity, homogeneous photooxidation rate increases with the increase in intensity and the quantum efficiency is independent of intensity. At intermediate intensity, the rate varies as $I^{0.5}$ and the quantum efficiency varies with the inverse of $I^{-0.5}$. However, at high intensity, recombination of hydroxyl radical occurs which reduces the quantum yield of the process.

The rate of degradation of organic compounds increases with the increase in frequency of sonication in the range of 28–100 kHz (12), although the effect of frequency is somewhat system-specific. Frequency of ultrasound has two counteracting effects on the generation of hydroxyl radicals. At very low frequency, although more hydroxyl radicals are generated inside the bubble, chances of recombination of the hydroxyl radicals inside the bubble are higher due to the higher temperature inside the bubble. As the frequency increases, the pulsation and collapse of the bubble occur more rapidly causing more radicals to escape from the bubble. However, at very high frequency, the acoustic period is much shorter, thus decreasing the size of the cavitation bubbles. As a result, the cavitation intensity decreases, subsequently decreasing the amount of hydroxyl radicals in the solution.

5.2.3. Amount of Catalyst

Water-phase PCO studies indicate that there exists an optimum catalyst thickness beyond which no improvement in rate occurs due to mass transfer limitations, once the activation of the catalysts sites by photons is accomplished (18). Rate of diffusion of adsorbates from the interior surface of the adsorbent to the exterior where the reaction takes place limits the overall process. An optimum TiO_2 concentration usually occurs at 0.5–1 g/L of TiO_2 solution. A much lower optimal TiO_2 dosage of 0.1 g/L was achieved in a study where PCO was applied to treat organic–metal wastewater discharged from semiconductor manufacturing facilities (19).

6. REACTOR DESIGN

6. 1. Reactor Models

Reactor designs for AOP depend on the mode of operation: (a) homogeneous or heterogeneous operation, (b) radiation source used, and (c) addition of chemical. AOP reactors are operated in either batch or flow-through mode with or without recycle. For homogeneous AOP, tank type batch reactors are often used. The flow-through mode is used in radiation-based AOP for water with low contaminant concentration (less than 10 ppm).

At low water flow rates, a batch mode of operation can be used for greater treatment efficiency.

The hydraulic residence time can be calculated if the AOP reaction kinetics and reaction rate constants are available. Typically, many AOP exhibit first order kinetics with respect to the contaminant concentration and the hydraulic detention time can be calculated as:

For batch and plug flow flow-through reactors:

$$C = C_0 e^{-k\bar{t}} \tag{26}$$

For flow-through completely mixed reactor:

$$\frac{C}{C_0} = \frac{1}{1 + k\bar{t}} \tag{27}$$

where C is the contaminant concentration in the effluent, ppm or mg/L; C_0 is the contaminant concentration in the influent, ppm or mg/L; k is first-order reaction rate constant, min^{-1} or s^{-1}; and $\bar{t}$ is the average residence time in min or s.

The reaction rate constant, k, strongly depends on the intensity of radiation in a photon-induced AOP. Because the majority of the AOP involve UV radiation, this section deals mostly with the photoreactor design. A significant uncertain aspect of photoreactor design is due to the existence of nonuniform reaction rates in the reactor even if the reactor is well mixed. Such variation occurs due to the absorption of radiation by the reactants, products, and the medium. In addition, divergence of light occurs due to the distance from the source. In heterogeneous reactors, the problem is even more complicated due to the scattering of light by the solid particles. Photoreactor modeling thus should consider the mass, momentum, and energy balance equations. In addition, an equation coupling mass and photon also should be taken into consideration. The quantum yield (efficiency) is related to the local volumetric rate of energy absorption (LVREA). The LVREA represents the amount of photons that are absorbed per unit time and unit reaction volume, which in turn depends on the photon distribution.

Many groups have contributed to the development of light distribution models that describe the light field inside the reactors based on some theoretical assumptions (20). In general, all the existing light distribution models could be basically classified into two different types: line source models and extense source models. In line source models, the light source is assumed to be a line; while in extense source models, dimensions of the light source are considered. Hence, in the extense source model, the characteristics of the lamps could be used as design parameters of the photoreactors. In a recent study, performances of different light emission models, namely, a line source with spherical emission model, a line source with diffuse emission model (LSDE), and an extense source with volumetric emission model, were compared with experimental results obtained from a novel application of chemical actinometry. It was found that the LSDE model was the least computationally intensive, yet sufficiently accurate to be used for reactor scale-up (21).

Radiation model involving multi-lamp reactors is provided by Yokota and Suzuki (22). Based on a diffused line source emission model, the light absorption rate in any geometrical photoreactor with multiple lamps was assessed, and the work reveals the existence of optimum light arrangement.

6.2. *Light Source*

Wavelength region from 175 to 380 nm is beneficial for the photodissociation of a variety of compounds and their intermediates. There are essentially four types of mercury lamps that can deliver significantly between 180 and 300 nm: (a) low-pressure, (b) medium-pressure, (c) pulsed-xenon flashlamps, and (d) excimer lamps. The low-pressure mercury lamps have peak output at 254 nm with a smaller (<15%, usually 5%) emission at 185 nm (ozone producing). Ozone-producing lamps are made of fused silica, which is transparent to this line, and the power output of these lamps is limited due to the self-absorption of produced UV by Hg atoms (23). The rest of the light energy occurs in the visible and infrared regions, which are not useful for organic photolysis. As many organics absorb in the sub-250 nm region, mercury UV lamps rely predominantly on hydroxyl radical processes for organic attack. Thus, these lamps are mostly used in conjunction with the added oxidants in the water phase, as the 254 nm photolyzes ozone or hydrogen peroxide, creating hydroxyl radicals.

Recently, manufacturers of low-pressure mercury lamps have strengthened the direct photolysis capability of the UV lamps by augmenting the 185 nm line by diminishing the overall intensity to some extent. Spangenburg et al. (24) reported a low-pressure 20-W Hg lamp (HNS Osram 20 W/U/Oz) that produced one third of the UV output at 185 nm, which is significantly higher than usual 5% obtained from the available commercial lamps. Most commonly used low-pressure Hg lamps are narrow diameter tubes (1.5–2.0 cm diameter), generally 0.9 and 1.6 m long and the active or the arc portion is 0.75 and 1.47 m long, respectively (25).

New xenon plasma flashlamps, which generate significant light intensity in the deep UV region (<250 nm) are better suited for direct photolysis than conventional mercury-based UV lamps. Spectra of xenon flash lamps are different than those of the mercury arc lamps and in the range of IR to the UV-C region (300–200 nm) (23). The spectral emission of the xenon flash lamps depends on the current density and the plasma temperature.

For PCO, longer-wavelength lamps such as fluorescent UV source with the output wavelength spectrum ranging from 300 to 500 nm, with a maximum intensity near 390 nm is used. Argon ion laser with emission lines at roughly 330 and 360 nm is also used for PCO (26).

6.3. *Reactor Configurations*

6.3.1. *UV Reactors*

Many designs of photoreactors are found in the literature: (a) annular reactors, (b) flat-tray reactors, (c) "merry-go-round" reactors, (d) collimated beam reactors, (e) single lamp multitubular reactor, and (f) multilamp tubular reactor (27–29). Annular photoreactors where the UV lamp is mounted inside the inner annulus of the reactor are more commonly used, and a typical diagram (applied for the gas phase UV-oxidation) is shown in the following figure.

Different photocatalytic reactor configurations are reported in the literature including annular reactor with a small thin film of catalyst coated on the inner surface of the outer annulus, flat-plate fluidized beds, annular packed beds, and catalyst coated on honeycombed monoliths, porous fibrous mesh, and optical fiber bundles (31,32).

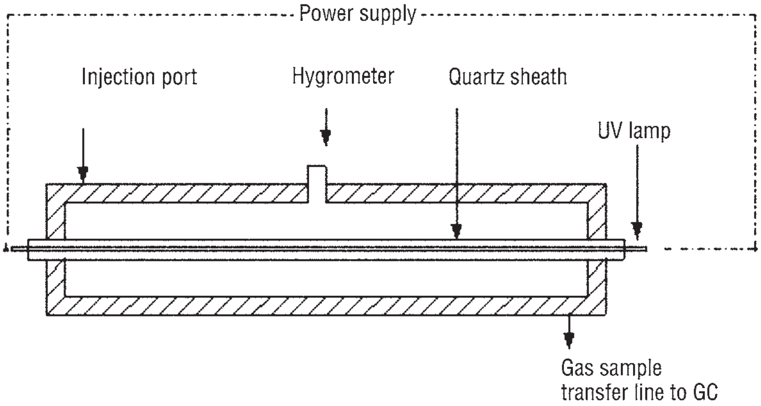


Fig. 1. An annular photoreactor (30).

Although titania catalyst used in the fluidized bed has greater quantum efficiency than the fixed-bed catalyst, the reaction rate is far too low for a viable large-scale operation.

In order to increase the radiative power absorbed within the reactor, and, consequently, the achievable conversion, a reflecting surface is often placed around the lamp–reactor assembly in such a way that at least some of the photons that would otherwise be wasted could be recycled and made available for absorption by the target pollutant. There are several typical reactor and reflector assemblies. One is the flat-plate reactor with a parabolic reflector, which generates a one-dimensional light field with almost "isoactinic" conditions. This assembly can be used for gathering kinetic information and is considered suitable for scale-up, because one can minimize the spatial variations in light intensity. In a second type of reactor, the lamp is mounted along one focal axis of the elliptical reflector, and the reactor is assembled along the other focal axis. This installation is usually employed to generate high intensity of light, particularly in bench-scale studies. In yet other types of reactor and reflector assemblies, a tubular lamp is surrounded by several tubular reactors, and the reactor tubes in turn are surrounded by a reflector with a circular cross section. This reactor is used for operating photochemical reactions under pressure.

In most cases, reflectors are mounted outside the reactor to avoid tarnishment and chemical decomposition of the reflector surfaces, if the reflector directly contacts the chemicals. Other popular designs, where the cylindrical reflector is installed inside the annular photoreactor, were found to be effective in enhancing the pollutant conversion in specific cases. Among all the designs, this is one of the easiest designs for installing and dismantling the reflector. A reactor model is developed and tested for such reactors (33).

For multilamp photo reactors to handle large capacity, about 200–500 lamps can be replaced by one 30 kW medium-pressure high-intensity lamp at the same operating cost, but with much lower volume. However, systems with medium-pressure lamps require an efficient cooling system to maintain the desired reactor temperature. For UV/ozone AOP, ozone dissolution is enhanced by efficient design of the diffusers to improve the mass transfer.

6.3.2. Other Reactors

The sonication reactions are generally carried out in two types of ultrasonic equipment: (a) bath and (b) probe reactors. Ultrasound is mainly generated by immersing the reactor in a sonicating liquid (a reacting vessel in a ultrasonic bath) or by introducing the source directly in the reactor (an ultrasonic probe in the reactor). The cup horn system uses the features of (a) and (b). There is also a third method of generating ultrasound by using a reactor constructed with ultrasonically vibrating walls. The major work on sonochemistry so far has been done in the batch reactor. The high cost of the equipment makes it difficult to carry out the continuous operation. Although higher rate is observed in the probe system as compared to ultrasonic bath, the energy efficiency of both the systems is comparable (12).

Electron irradiation process equipment consists of an electron accelerator that accelerates a beam of electrons to 95–99% of the speed of light. The beam is directed into a thin stream of wastewater or sludge where free radicals are produced to react with the hazardous organics. However, the process is both capital and operating costs intensive and the process performance is impeded by the presence of solids.

6.4. Commercial Applications

A wide range of sizes starting from single-lamp bench-top reactors to pilot and full-scale systems are available to handle higher throughput (3,800–3,800,000 L or 1,000–1,000,000 GPD) of UV/oxidation systems are commercially available. Among many technologies Ultrox® (U.S. Filter/Zimpro, Inc., USA) and Rayox® (Calgon Carbon Oxidation Technologies, USA) can treat a wide range of pollutants. Matrix Photocatalytic Inc. (Ontario, Canada) deals with photocatalytic treatment systems for both air and water. A list of UV and ultrasound based AOP technologies and the process descriptions are available in a report by US Army (34) (1 GPD = 1 gal/d = 3.785 L/d).

6.5. Cost and Energy Efficiency of AOP

In order to evaluate energy efficiency of a radiation-based AOP, a figure of merit (EE/O) for the consumption of electrical energy is calculated according to the following equation (35):

$$\text{EE/O (in KWh per m}^3\text{ per order)} = \frac{P \times 1000 \times t_t}{V \times 60 \times \log(C_i/C_f)} \tag{28}$$

where EE/O is the figure of merit; P is the rated power, kW; V is the volume (L) of water treated; t_t is treatment time, in min; C_i is the initial concentrations (mol L^{-1}) of contaminant in the water; and C_f is the final concentrations (mol L^{-1}) of contaminant in the water.

High EE/O values would correspond to low energy efficiency of a system.

As mentioned earlier, UV/oxidation AOP is more commonly used in environmental applications and, by far, they are the least expensive of all the AOP. Goel et al. (12) compared sonication and UV/oxidation AOP, and concluded that in order to be energy efficient, the present ultrasonic degradation rates need to be improved by at least 10–100 times, especially for the non-volatile compounds (12). UV/oxidation costs generally are between \$0.03 and \$3.00 per 1000 L (\$0.10 and \$10.00 per 1000 gal) of water treated (34). Factors that influence the cost include types and concentration of contaminants, degree of treatment, and requirement for pre- and posttreatment. However, cost only does not determine the selection of an AOP, it is also the type of waste and the degree of treatment that determine the selection of a process.

7. LIMITATIONS AND CHALLENGES OF AOP

There are several limitations of AOP: (a) costs may be higher than competing technologies because of energy requirements, (b) harmful intermediates may form, (c) pretreatment of the aqueous stream may be required to minimize cleaning and maintenance of UV reactor and quartz sleeves, and (d) handling and storage of ozone and hydrogen peroxide require special safety precautions. Ozone is explosive, toxic, and an irritant to the skin, eyes, respiratory tract, and mucous membrane. Ozone is also a significant air pollutant and monitoring must be completed to ensure that ozone levels are not exceeding regulatory concentrations. Hydrogen peroxide is an irritant, and can cause chemical burns. Ultraviolet light can burn unprotected skin and the mercury in UV lamps can damage the central nervous system, along with inflaming the nose and throat area (34).

Major challenges for the photocatalytic process are catalyst deactivation, slow kinetics, low photoefficiency, and unpredictable mechanism (36). Although, photocatalyst can use longer UV wavelength, rate of catalytic degradation is considerably lower than UV-photooxidation at 254 nm. The selective reactivity of the photocatalysts can also be a disadvantage for degradation of a mixture of compounds. The hole–electron recombination rate is a limitation for large-scale application of this technique and the modification of the surface properties of photocatalyst is necessary to decrease the electron-hole recombination (37).

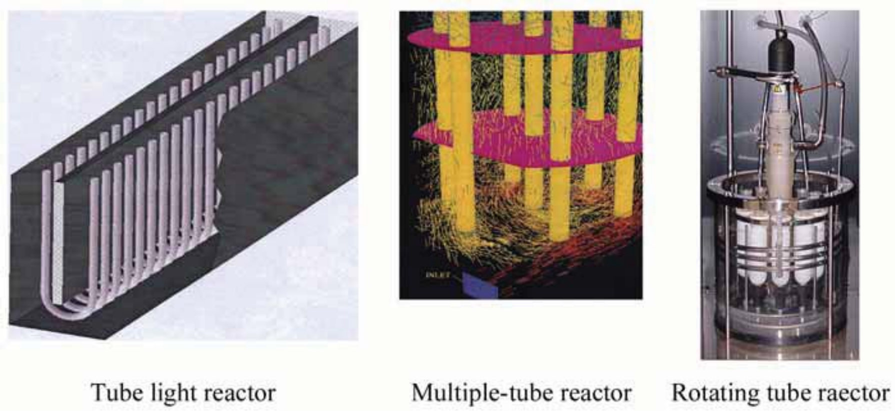
A new challenge reported by Wang (44) is that UV is extremely effective for deozonation, dechlorination, dechloramination, and de-peroxidation when UV is used in conjunction with ozone, chlorine, chloramine, and peroxide, respectively.

8. RECENT R&D

During the last decade or so laboratory and field testing of the AOPs have proved to be useful for the detoxification of a wide variety of harmful chemicals. However, several challenges still need to be met before the full potential of this technology can be realized as shown: (a) complete mineralization of the parent compound, (b) enhancement of quantum yield, (c) higher throughputs, (d) low energy cost, (e) availability of more intense lamps at wavelenghts ≤254 nm, and (f) reliability of the process.

On-going research is focused on various aspects starting from improving the reactor hydrodynamics to the catalyst development. Several new reactor designs (Fig. 2) with possibilty of scale-up are available (38–40). An improved reactor design is recently published where reactor perfromace is improved by inducing Taylor–Couette flow (41).

Performance improvement in TiO_2 is achieved by doping the titania with platinum or vanadium oxide and copper. In order to improve the adsorption characteristics of TiO_2, attempts have been made to support fine TiO_2 on the porous adsorbent materials such as silica, alumina, activated carbon, clay, and zeolites. TiO_2-supported adsorbent provides higher specific surface area and introduces more effective adsorption sites than bare TiO_2. Decomposition rates of the substrates are found to increase due to one or



Tube light reactor Multiple-tube reactor Rotating tube raector

Fig. 2. New designs of photoreactor (38–40).

more reasons such as increased surface area of the catalyst, increased adsorption of the organic substrates, effective separation of photogenerated electron and holes on the supported catalyst, and stabilization of reactive intermediates (42).

Many communities in the United States use the combined UV/chlorine technology for disinfection of drinking water because chlorine is a government-specified secondary disinfectant for the water distribution system. (43). Although the optimum UV radiation have not been determined, researchers at the Lenox Institute of Water Technology, Lenox, Massachusetts, USA, has discovered that at UV radiation of 254 nm, UV/chlorine has similar advantages of UV/ozone and UV/H_2O_2 technologies for water oxidation and disinfection. More research studies should be conducted along this line to document the real effect of this possible new UV/chlorine process.

9. SUMMARY

UV-based technologies can include UV alone, UV/H_2O_2, and UV/ozone. UV radiation (254 nm) disinfection of bacteria and viruses has several important advantages: (a) it is readily available; (b) it produces no toxic residuals; (c) required contact times are relatively short; and (d) the equipment is easy to operate and maintain, although maintenance must be performed on a regular basis to prevent fouling of certain components. UV radiation disinfection is inappropriate for (a) inactivation of *Giardia lamblia* cysts; (b) water containing high suspended solids concentrations, color, and turbidity; and (c) water with high concentrations of soluble organic matter that can react with or absorb the UV radiation, thus reducing the disinfectant's performance.

Because UV radiation is ineffective against *Giardia* cysts, but effective against viruses and bacteria, it is a good candidate for disinfecting groundwater not directly influenced by surface water. If the amount of radiation received by a target organism is not a lethal dose, however, reconstitution of the organism and reinfection of the water can occur.

Because UV radiation disinfection provides no disinfecting residual, a secondary disinfectant is needed. Very little oxidation of organic materials occurs with typical UV radiation systems used for drinking water disinfection; consequently, if oxidation is required (for iron, manganese, sulfide, nitrate, etc.), a strong oxidizing agent may be necessary and can serve as a primary disinfectant as well. However, higher-energy intensities and lower UV wavelengths (184.9 nm) can produce oxidation reactions.

UV bulbs that produce radiation at 184.9 nm generate some quantities of ozone, which, in turn, can provide some oxidation of organic materials. The combination of UV radiation and ozone produces the hydroxyl free radical, which is a more powerful oxidizing agent than is ozone itself. The 184.9 nm wavelength radiation is not as effective for UV disinfection as the 254 nm wavelength, except by the amount of ozone generated, which will provide some CT value.

Ozone used in combination with UV radiation or hydrogen peroxide can adequately disinfect and, at the same time, oxidize many refractory organic compounds such as halogenated organics present in raw water. Although contact times for ozone disinfection are relatively short, they are quite long for oxidizing organic compounds. This combination process accelerates the oxidation reactions.

AOPs involve combining ozonation with UV radiation (UV 254 bulbs submerged in the ozone contactor) with hydrogen peroxide (added prior to ozonation) or simply by conducting the ozonation process at elevated pH levels (between 8 and 10). Under any of these conditions, ozone decomposes to produce the hydroxyl free radical, which has an oxidation potential of 2.80 V compared with 2.07 V for molecular ozone. However, hydroxyl free radicals have very short half-lives, on the order of microseconds, compared with much longer half-lives for the ozone molecule.

In summation, AOPs represent the newest development in oxidation and disinfection technology, and are loosely defined as processes that generate highly reactive oxygen radicals without the addition of metal catalysts. Typically, this means combining H_2O_2 or ozone with ultraviolet light. The result is the on-site total destruction of even refractory organics without the generation of sludges or residues. This technology is being widely applied to treat contaminated groundwaters, to purify and disinfect drinking waters and process waters, and to destroy trace organics in industrial effluents. Many organic compounds that normally are stable under direct reaction with the ozone molecule alone or H_2O_2 alone can be oxidized rapidly by the hydroxyl free radical. Chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE) can be destroyed rapidly and cost effectively by hydroxyl free radicals.

Finally the effect of UV on deozonation, dechlorination, dechloramination, and deperoxidation must be considered in the AOP engineering design when ozone, chlorine, chloramine, and peroxide, respectively, is to be used (43,44).

NOMENCLATURE

t	Average residence time, min or s
Φ	Quantum yield of the reaction
λ	Wavelength of light
AOPs	Advanced oxidation processes
BOD	Biochemical oxygen demand
C	Contaminant concentration in the effluent, ppm or mg/L
C_0	Contaminant concentration in the influent, ppm or mg/L
c_A	Concentration of the organics
C_f	Final concentrations of contaminant in the water, mol L^{-1}
C_i	Initial concentrations of contaminant in the water, mol L^{-1}

COD	Chemical oxygen demand
E	Radiation energy associated with a photon (kJ/mol)
EE/O	Figure of merit, kWh/m^3/order
I_m	Average number of einsteins absorbed by the absorbing species per unit volume and unit time
k	First-order reaction rate constant, min^{-1} or s^{-1}
LSDE	Line source with diffuse emission model
LVREA	Local volumetric rate of energy absorption
MTBE	Methyl tert-butyl ether
O(^{1}D)	Singlet oxygen atom
P	Rated power, kW
PCE	Polychromatic erythrocytes
PCO	Photocatalytic oxidation
T	Time
TCE	Trichloroethylene
TiO_2	Titanium dioxide
t	Time
t_t	Treatment time, min
UV	Ultraviolet
V	Volume of water treated, L
VOC	Volatile organic compound

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15

Chemical Reduction/Oxidation

Lawrence K. Wang and Yan Li

CONTENTS

1. CHEMICAL REDUCTION

In any chemical reactor, if there are chemical reduction reactions, there must be chemical oxidation reactions occurring at the same time (1–13). In an environmental process system, if the target pollutants/impurities are reduced by a chemical (i.e., a reducing agent), it is a chemical reduction process, in which the reducing agent itself is oxidized when the target pollutants/impurities are reduced. If the reduced pollutants/impurities are further precipitated by a chemical (i.e., a precipitating agent), the overall process system is called "chemical reduction precipitation."

Reduction of soluble chromium(VI) to soluble chromium(III) as insoluble chromium hydroxide is a typical example of the chemical reduction precipitation process.

1.1. Process Description

Reduction in a chemical reaction in which one or more electrons are transferred to the chemical being reduced from the chemical initiating the transfer (the reducing agent). Chemical reduction may be necessary to convert metals from a higher valence state to a lower one to decrease toxicity or to encourage a given chemical reaction. As an example, chromium is a very toxic material when in its hexavalent state (Cr^{6+}). Reducing hexavalent chromium to trivalent chromium (Cr^{3+}) causes a substantial decrease in the metal's toxicity and also enables precipitation of the chromium as the hydroxide in alkaline solution (hexavalent chromium and divalent chromium will not form a precipitate) (2–6). The readers are referred to another chapter for a discussion on chemical precipitation.

The first step of the chemical reduction process is usually the adjustment of the pH of the solution. With sulfur dioxide treatment of hexavalent chromium, for instance, the

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reaction requires a pH in the range of 2–3. The pH adjustment is done with the appropriate acid (e.g., sulfuric acid). This is followed by the addition of a reducing agent. Mixing is provided to improve contact between the reducing agent and the waste. The agent can be in the form of a gas (sulfur dioxide), a solution (sodium bisulfite), or as a finely divided powder if there is adequate mixing. Reaction times vary for different wastes, reducing agents, temperatures, pHs, and concentrations. In commercial-scale operations treating chromium wastes, reaction times are on the order of minutes. Additional time is usually allowed to ensure complete mixing and reduction. Once reacted, the reduced solution is generally subjected to some form of treatment to settle, float or filter the reduced and precipitated material. The pH of the reaction medium is typically increased so that the reduced material will precipitate from the solution. A treatment for the removal of what remains of the reducing agent may be included. This can be unused reducing agent or the reducing agent in its oxidized state. Filters, sedimentation clarifiers, or flotation clarifiers are often used to improve separation of suspended solids from the treated wastewater (10,11,13).

A number of chemicals are used as reducing agents. The most common chemicals used for reduction of chromium are sulfur dioxide, sodium metabisulfite, sodium bisulfite, and ferrous salts. Other reducing agents used or which can be potentially used for water and wastewater treatment include sodium borohydride to reduce ionic mercury to metallic mercury and alkali metal hydride to alter the chemical form of lead so that it can be precipitated and also to recover silver. The common chemicals used as reducing agents are discussed on the following sections.

1.2. Chemical Reduction Process Chemistry

1.2.1. Reduction With Sulfur Dioxide

Gaseous sulfur dioxide is a widely used reducing agent. The reduction occurs when sulfurous acid, produced through the reaction of sulfur dioxide and water, reacts with chromic acid as follows:

$$3SO_2 + 3H_2O \rightarrow 3H_2SO_3 \tag{1}$$

$$3H_2SO_3 + 2H_2CrO_4 \rightarrow Cr_2(SO_4)_3 + 5H_2O \tag{2}$$

The reduction reaction is highly dependent on both pH and temperature. A pH of from 2 to 3 is normal for situations requiring complete reduction. At pH levels above 5, the reduction rate is slow. Oxidizing agents such as dissolved oxygen and ferric iron interfere with the reduction process by consuming the reducing agent.

A typical treatment consists of mixing sulfur dioxide with water or wastewater in a reaction tank and providing a retention time of about 45 min to ensure complete mixing and reduction. The reaction tank has an electronic recorder–controller device to control process conditions with respect to pH and oxidation–reduction potential (ORP). Gaseous sulfur dioxide is metered to the reaction tank to maintain the ORP within the range of 250–300 mV. Sulfuric acid is added to maintain a pH level of 1.8–2.0. The reaction tank is equipped with a propeller agitator designed to provide approximately one turnover per minute. A typical wastewater treatment facility for reducing chromate is shown in Fig. 1.

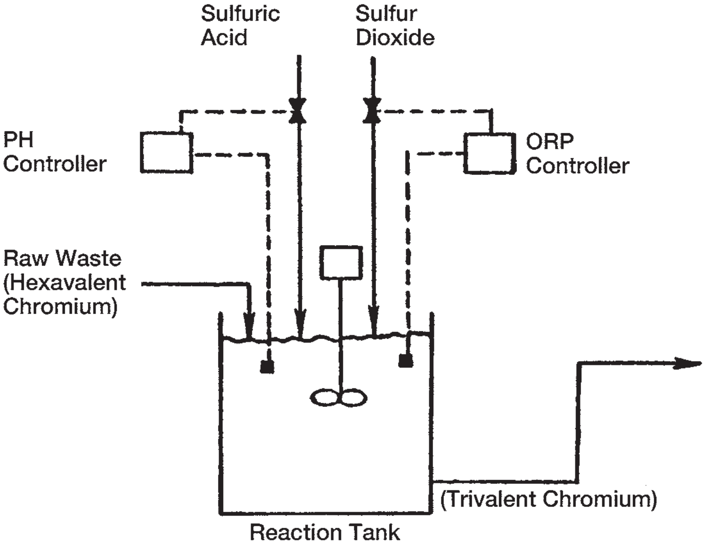


Fig. 1. Hexavalent chromium reduction with sulfur dioxide.

1.2.2. Reduction With Sodium Metabisulfite and Sodium Bisulfite

Metabisulfite and bisulfite are used for reduction of chromium. Metabisulfite hydrolyzes to sodium bisulfite, and bisulfite in turn dissociates to sulfurous acid, which reduces the chromium. The reaction with metabisulfite and bisulfite occurs as follows:

$$3Na_2S_2O_5 + 3H_2O \rightarrow 6NaHSO_3 \tag{3}$$

$$4H_2CrO_4 + 6NaHSO_3 + 6H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 6NaHSO_4 + 10H_2O \tag{4}$$

The reduction reaction is highly dependent on both pH and temperature. The dissociation of sodium bisulfite ($NaHSO_3 + H_2O \rightarrow H_2SO_3 + NaOH$) produces sodium hydroxide (NaOH), thereby requiring acid addition for pH control during the reaction.

A common batch system for chromium reduction with sodium bisulfite consists of a collection tank and a reaction tank with a 4-h retention time. Sodium bisulfite solution is metered into the reaction tank and the pH is controlled by sulfuric acid addition.

1.2.3. Reduction With Ferrous Sulfate

Ferrous ion (Fe^{2+}) reacts with hexavalent chromium, reducing the chromium to a trivalent state and oxidizing the ferrous ion to the ferric state. The reaction occurs as follows:

$$2H_2CrO_4 + 6FeSO_4 + 7H_2O + 6H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 15H_2O \tag{5}$$

The above reaction occurs rapidly at pH levels below 3. Because the acidic properties of ferrous sulfate are low at high dilutions, acid must be added for pH adjustment. The ferrous sulfate reducing process generates large volumes of sludge and thus its use is rare in large-scale treatment facilities. In addition, the use of ferrous sulfate to treat chromate wastes containing cyanide results in the formation of very stable ferrocyanide complexes, which prevent subsequent effective cyanide treatment.

1.2.4. Reduction With Sodium Borohydride.

Sodium borohydride is a mild but effective reducing agent and is used to reduce soluble mercury ion to metallic mercury, which can then be removed from solution. The reaction occurs as follows:

$$4Hg^{2+} + BH^{4-} + 8(OH^{-}) \rightarrow 4Hg + B(OH)^{4-} + 4H_2O \qquad (6)$$

If the mercury solution is in the form of an organic complex, the driving force of the reduction reaction may not be sufficient to break the complex. In that case, the wastewater must be chlorinated prior to the reduction step in order to break down the metal–organic bond.

Sodium borohydride is also reported to be effective in removing silver, gold, lead, and cadmium. However, this technology is only being applied in limited cases because of the high cost of chemicals.

1.3. Process Applications

Technology for large-scale application of chemical reduction is well developed. The reduction of residual chlorine in a chlorination or superchlorination process system is termed dechlorination, which is the most common process in municipal water and wastewater treatment. The reduction of chromium waste by sulfur dioxide is another classic process and is in use by numerous plants employing chromium compounds in operations such as electroplating.

Dechlorination process is discussed in detailed in Section 1.5.4. In wastewater treatment, the major application of chemical reduction is for treatment of chromium wastes. Numerous industrial plants employing chromium in their manufacturing operations use the process to reduce hexavalent chromium to its trivalent form. The chromium reduction process is widely used in the following industries: (a) metal finishing, (b) inorganic chemicals manufacturing, (c) coil coating, and (d) battery manufacturing. The following industries use chemical reduction on a limited basis: (a) iron and steel manufacturing; (b) aluminum forming, (c) electronic and electronic components, (d) porcelain enameling, and (e) pharmaceutical manufacturing.

Wastewaters from metal plating and finishing operations contain chromium in rinse waters and spent baths. Chromium-containing waste streams are usually first treated for chromium reduction and then mixed with other waste streams for subsequent treatment. Chromium reduction is used in the aluminum forming and coil coating industries for treating rinses of chromic acid etching solutions. In the battery manufacturing industry, chromium reduction is used for treating chromium-containing cell wash solutions and heat paper production subcategory wastewater.

The chemical reduction process is also being used on a limited basis to remove mercury and lead from wastewater. Sodium borohydride is currently used in some chlor-alkali plants (inorganic chemicals manufacturing) to reduce the soluble mercury ion to metallic mercury, which is then removed from solution by granular activated carbon adsorption, or solid–water separation process.

The major advantage of chemical reduction when used to reduce hexavalent chromium, or residual chlorine, is that it is a fully proven technology based on many years of experience. Operation at ambient conditions results in minimal energy consumption, and the process is well suited to automatic control especially when using sulfur dioxide. Furthermore, the equipment is readily obtainable from many suppliers, and operation is straightforward.

One limitation of chemical reduction of hexavalent chromium, residual chlorine, and others, is that for high concentrations of chromium the cost of treatment chemicals may be prohibitive. When this situation occurs, other treatment processes are likely to be more economical. Chemical interference by oxidizing agents is possible in the treatment of mixed wastes, and the treatment itself may introduce pollutants if not properly controlled. Storage and handling of sulfur dioxide is somewhat hazardous.

1.4. Chemical Reduction Design Considerations

The chemical reduction process is highly reliable for chrome reduction. The process, however, requires proper monitoring and control and proper pretreatment to control interfering substances.

1.4.1. Chemicals Required

The most common chemicals used for chromium reduction and other chemical reduction applications are sulfur dioxide (SO_2), sodium metabisulfite ($Na_2S_2O_5$), sodium bisulfite ($NaHSO_3$), and sulfuric acid (H_2SO_4).

1.4.2. Residuals Generated

The chemical reduction process normally generates only small amounts of sludge due to minor shifts in the solubility of the contaminants. In a chromium reduction process, the reduced chromium and other metal ions are precipitated and removed in the subsequent precipitation–sedimentation process. An exception would be hexavalent chromium reduction with ferrous sulfate, where sludge generation may be significant. In a dechlorination process, there will be no chlorine residue, nor reducing agent residue, if the dechlorination process is operated properly.

1.4.3. Design Criteria

The chromium reduction process can be employed as batch treatment or continuous treatment. For small daily volumes of water or wastewater that are less than 150,000 L (40,000 gal), the most economical system is batch treatment in which two tanks are provided, each with a capacity of one day’s flow. Reduction, precipitation, and sedimentation are carried out in one tank, while the other is used to collect the waste. In a typical batch system, the required dosage of acid and sodium metabisulfite is added to the tank and the contents are mixed for 15 min to ensure complete reduction of the chromium.

Continuous chromium reduction treatment requires a tank for acidification and reduction with separate tanks for precipitation and sedimentation. The retention time in the reduction tank is dependent on the pH employed but should be at least four times the theoretical time for complete reduction. In cases where the chromium content of the wastewater varies markedly, equalization should be provided prior to the reduction tank to minimize fluctuations in the chemical feed system. Successful operation of a continuous chrome reduction process requires instrumentation and automatic control. Redox and pH control should also be provided.

Another common chemical reduction process, dechlorination, is fully covered in Section 1.5.4.

The chemical reducing agent dosages will vary with the specific waste as a result of the reducing potential or other characteristics of the chemicals, and therefore, the dosages should be determined experimentally.

1.5. Design and Application Examples

1.5.1. Example 1

Chemical reduction alone will only convert metals from a higher valence start to a lower one to either decrease toxicity or to encourage a given chemical reaction. Explain how a combination of chemical reduction and chemical precipitation together (i.e., chemical reduction precipitation process) can remove highly toxic hexavalent chromium ions from an industrial effluent.

Solution:

Chromium in wastewaters is usually present in its most oxidized form, hexavalent chromium(VI). This is the form that is most toxic to humans. It is usually present as the chromate ion, $HCrO_4^-$, at pH between 1.5 and 4, and CrO_4^{2-} above pH 4.0, or it may be present as dichromate, $Cr_2O_7^{2-}$. The dichromate is also in equilibrium with singly dissociated chromate. These salts are highly soluble.

The hexavalent chromium is usually chemically reduced by the addition of sulfur dioxide gas, sodium bisulfite, or sodium metabisulfite. These all form sulfurous acid with water. The undissociated form of sulfurous acid enters into the reduction reaction. Accordingly, the reaction is strongly pH dependent, and is usually carried out at a pH of about 2–3. The pH is controlled by the addition of sulfuric acid.

Chromium(III) is easily precipitated as chromic hydroxide by adjusting the pH with lime or sodium hydroxide.

$$Cr_2(SO_4)_3 + 3Ca(OH)_2 \rightarrow 2Cr(OH)_3 + 3CaSO_4 \qquad (7)$$

The optimum pH for removal of chromium(III) is between 8.5 and 9.0. The amount of base needed is best determined by titration of treated wastewater, although a theoretical contribution to the base demand can be computed for the chromium concentration and for the excess sulfite left over from the reduction step.

1.5.2. Example 2

After the toxic hexavalent chromium(VI) is reduced to less toxic trivalent chromium(III) ion, lime or another base chemical is added to convert soluble chromium(III) to insoluble chromium hydroxide in accordance with Eq. (7). A water–solid separation process unit is needed to remove the insoluble chromium hydroxide from the pretreatment wastewater. What are the feasible water–solid separation processes available?

Solution:

Sedimentation and/or filtration (26,28) will be feasible for separating the insoluble chromium hydroxide precipitates (or chemical flocs) from a wastewater. Other feasible solid–water separation processes for removing the insoluble chromium hydroxide include membrane filtration (such as ultrafiltration and microfiltration), continuous DAF, PC-SBR-sedimentation, PC-SBR-DAF. The following is a summary of the solid–water separation processes feasible for the combined application of chemical reduction and precipitation.

(a) Chemical reduction + continuous dissolved air flotation (DAF) (16,22,23,28)
(b) Chemical reduction + physicochemical sequencing batch reactor (PC-SBR) using sedimentation (18,19,22)
(c) Chemical reduction + PC-SBR using dissolved air flotation (18,19,22)
(d) Chemical reduction + membrane filtration (21,25)

1.5.3. *Example 3*

A study of an operational waste treatment facility that chemically reduces hexavalent chromium has shown that 99.7% reduction efficiency is easily achieved (Appendix A2). Final concentrations of 0.05 mg/L are readily attained, and concentrations of 0.01 mg/L are considered to be attainable by properly maintained and operated equipment. Conduct a literature search, showing how chemical reduction, sedimentation, and/or filtration together can effectively treat the industrial effluents from the industrial operations of metal finishing, aluminum forming, and inorganic chemicals manufacturing.

Solution:

The performance data on the use of chemical reduction and/or filtration have been searched by the U.S. Environmental Protection Agency (US EPA) and summarized in Appendixes A–C as follows:

(a) Appendix A1, Chemical reduction with sedimentation for metal finishing industry
(b) Appendix A2, Chemical reduction with filtration for metal finishing industry
(c) Appendix B, Chemical reduction with sedimentation for aluminum forming industry
(d) Appendix C, Chemical reduction with filtration for inorganic chemicals industry

1.5.4. *Example 4*

Since about 1970, much attention has been focused on the toxic effects of chlorinated effluents. Both free chlorine and chloramine residuals are toxic to fish and other aquatic organisms. Dechlorination involves the addition of sulfur dioxide (or equivalent reducing agent) to the water or wastewater. Please discuss the following:

(a) Dechlorination process description and dechlorination chemical reactions;
(b) Technology status
(c) Dechlorination process equipment
(d) Applications and limitations
(e) Process performance
(f) Chemicals required for dechlorination
(g) Design criteria
(h) Process reliability
(i) Process modifications

Solution:

1. Dechlorination process description and dechlorination chemical reactions: The following reactions occur:

$$SO_2 + HOCl + H_2O \rightarrow SO_4^{2+} + Cl^- + 3H^+ \quad \text{(For free chlorine)} \tag{8}$$

$$SO_2 + NH_2C1 + 2H_2O \rightarrow SO_4^{2+} + Cl^- + 2H^+ + NH_4^+ \quad \text{(For combined chlorine)} \tag{9}$$

   Small amounts of sulfuric and hydrochloric acids are formed; however, they are generally neutralized by the buffering capacity of the water or wastewater. Dechlorination can also be used in conjunction with superchlorination. Because superchlorination involves the addition of excess chlorine, dechlorination is required to eliminate this residual. Sulfur dioxide is the most common chemical used. It is fed as a gas, using the same equipment as chlorine systems. Because the reaction of sulfur dioxide with free or combined chlorine is practically instantaneous, the design of contact systems are less critical than that of chlorine contact systems. Detention time of less than 5 min is quite adequate, and in-line feed arrangements may also be acceptable under certain conditions.

2. Technology status: The technology of dechlorination with sulfur dioxide is established. Many plants in California and New York are known to be practicing effluent dechlorination with SO_2 on either a continuous or intermittent basis.

3. Process equipment: Typical process equipment will include (a) chemical feeders, (b) mixers, and (c) automatic controls.
4. Process applications and limitations: Dechlorination process can be used whenever a chlorine residual is undesirable. This usually occurs when the receiving water contains aquatic life sensitive to free chlorine. It is generally required when super-chlorinatiom is practiced or stringent effluent chlorine residuals are dictated. Dechlorination will not destroy chlorinated hydrocarbons already formed in the water or wastewater. It has been reported that about 1% of the chlorine ends up in a variety of stable organic compound when municipal wastes are chlorinated.
5. Process performance: Available chlorine residuals can be reduced to essentially zero by sulfur dioxide dechlorination. Dechlorination process, if control properly, generates no residuals.
6. Chemicals required for dechlorination: Sulfur dioxide (SO_2) and sulfite salts are the most common chemicals used. Sodium metabisulfite ($Na_2S_2O_5$) can also be used, but is much less common. In fact, any reducing agent can be considered, depending on cost and availability.
7. Design criteria: The required contact time = 1–5 min; sulfur dioxide feed rate = 1.1 lb per lb of residual chlorine; sodium sulfite feed rate = 0.57 lb per lb of chlorine; sodium bisulfite feed rate = 0.68 lb per lb of chlorine; sodium thiosulfate feed rate = 1.43 lb per lb of chlorine.
8. Process reliability: Sulfur dioxide addition for dechlorination purposes is reasonably reliable from a mechanical standpoint. The greatest problems are experienced with analytical control which may lower the process reliability.
9. Process modifications and alternatives: Metabisulfite, bisulfite, or sulfite salts can also be used. Automatic or manually fed systems can also be used. If chlorine is used at the site, sulfur dioxide is preferred, since identical equipment can be used for the addition of both chemicals. Alternative dechlorination systems include activated carbon, and ponds (sunlight and aeration). UV is also an effective dechlorination technology (60,61).

2. CHEMICAL OXIDATION

In an environmental process system, if the target pollutants/impurities are oxidized by a chemical (i.e., oxidizing agent), it is a chemical oxidation process, in which the oxidizing agent itself is reduced when the target pollutants/impurities are oxidized.

If the oxidized pollutants/impurities are further precipitated by a chemical (i.e., a precipitating agent), the overall process system is called "chemical oxidation precipitation."

Removal of iron and manganese from water involves both oxidation and precipitation, and is thus, a typical example of chemical oxidation precipitation.

2.1. Process Description

Oxidation is a chemical reaction process in which one or more electrons are transferred from the chemical being oxidized to the chemical initiating the transfer (the oxidizing agent). In a typical oxidation–reaction shown below, the oxidation state of the cyanide ion is raised from –1 to +1; the cyanide is oxidized as it combines with the atom of oxygen to form cyanate. The oxidation state of the permanganate decreases from –1 to –2 (permanganate is reduced to manganate):

$$\underset{\text{Permanganate}}{2MnO_4^-} + \underset{\text{Cyanide}}{CN^-} + \underset{\text{Hydroxyl ion}}{2OH^-} \rightarrow \underset{\text{Manganate}}{2MnO_4^{2-}} + \underset{\text{Cyanate}}{CNO^-} + \underset{\text{Water}}{H_2O} \quad (10)$$

The change in oxidation state implies that an electron was transferred from the cyanide ion to the permanganate. The increase in the positive valence or decrease in the negative valence with oxidation takes place simultaneously with reduction in chemically equivalent ratios. Some oxidation reactions proceed readily to carbon dioxide (CO_2). In other cases, the oxidation is not carried as far, perhaps because of the dosage of the oxidant, the pH of the reaction medium, the oxidation potential of the oxidant, or the formation of stable intermediates. The primary function performed by oxidation in the treatment of hazardous wastes is essentially detoxification. For instance, oxidants are used to convert cyanide to the less toxic cyanate or completely to carbon dioxide and nitrogen. A secondary function is to ensure complete precipitation, as in the oxidation of Fe^{2+} to Fe^{3+} and similar reactions, where the more oxidized material has a lower solubility under the precipitation reaction conditions (1–3,6,7).

A combination of chemical oxidation and precipitation (i.e., chemical oxidation precipitation) is widely used by the water industry for iron and manganese removals. The readers are referred to Section 2.3.4 for more detailed information on theory and principles.

2.2. *Process Chemicals*

There are many oxidizing agents; however, their application in water and wastewater treatment requires that a specific determination be made of their effectiveness in removing the pollutants, and in particular, to determine if the reaction products are innocuous. The oxidizing agents commonly used in water and waste treatment are described below (8,9,11,12).

2.2.1. Oxidation by Chlorine

Chlorine in elemental or hypochlorite salt form is a strong oxidizing agent in aqueous solution and is used in water treatment for disinfection, and in industrial waste treatment facilities primarily to oxidize cyanide. Chlorine and hypochlorites can also be used to oxidize phenol-based chemicals, but their use is limited because of the formation of toxic chlorophenols if the process is not properly controlled.

2.2.2. Oxidation by Sodium Hypochlorite

An alternative chlorination technique involves the use of sodium hypochlorite (NaOCl) as the oxidant. Reactions with sodium hypochlorite are similar to those of chlorine except that there is no caustic requirement for destruction of free cyanide in the oxidation stages. However, alkali is required to precipitate metal-cyanide complexes as hydroxides. A typical oxidation system using chlorine and caustic is shown in Fig. 2.

2.2.3. Oxidation by Ozone

Ozone, an unstable molecule (O_3), is a highly reactive oxidizing agent that is approx 10 times more soluble than oxygen on a weight basis. Ozone is used in water treatment for disinfection and in industrial waste treatment to oxidize cyanide to cyanate and to oxidize phenols and dyes to a variety of colorless nontoxic compounds. Ozonation is best suited for waters and wastewaters that contain low levels of oxidizable material. There are no inherent restrictions on levels of dissolved or suspended solids in the water and wastewater, so long an they do not contain oxidizable material that can compete

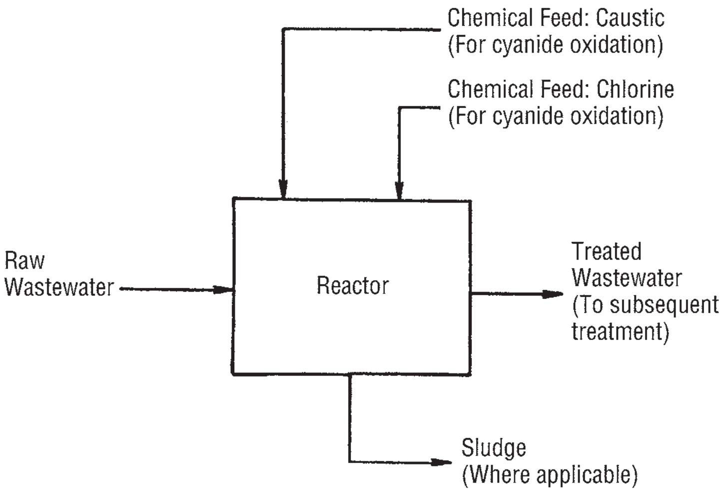


Fig. 2. Process flow sheet—chemical oxidation.

for ozone with the pollutant component to be removed (31–41). Ozone is also used for chemical conditioning and stablilzation of municipal biosolids (38–44).

2.2.4. Oxidation by Ozone With Ultraviolet (UV) Radiation

One of the modifications of the ozonation process is the simultaneous application of ultraviolet light and ozone for oxidation of cyanides, phenolic chemicals, and halogenated organics. Some compounds that are highly resistant to ozone alone can be ozonated in the presence of UV light. UV radiation catalyzes the ozonation process and the mode of action seems to be activation of ozone itself. Application of ultraviolet light reduces the amount of ozone required compared with a system using ozone alone. Another chapter of this handbook series, Advanced Oxidation Process, introduces this UV/O_3 process (60,61).

2.2.5. Oxidation by Hydrogen Peroxide

Hydrogen peroxide (H_2O_2) is a powerful oxidizing agent and has been used in oxidize phenols, cyanides, sulfur compounds, TCE, and metal ions. Hydrogen peroxide in the presence of a metal catalyst (e.g., Fe^{2+}, Fe^{3+}, Al^{3+}, Cu^{2+}, and Cr^{2+}) effectively oxidizes phenols over a wide range of temperature and concentrations. The process is sensitive to pH, with an optimum pH range of 3–4 and efficiency decreasing rapidly at both higher and lower pH values. A combined application of UV and hydrogen peroxide is also termed “advanced oxidation process” (60,61).

2.2.6. Oxidation by Potassium Permanganate ($KMnO_4$)

Potassium permanganate has been used for destruction of organic residues in wastewater and in potable water. Potassium permanganate reacts with aldehydes, mercaptans, phenols, and unsaturated acids. It is considered a relatively powerful oxidizing agent. The reduced form of permanganate is manganese dioxide (MnO_2), which can be removed by filtration.

2.3. *Process Applications*

Chemical oxidation and precipitation together can be used to treat both organic and inorganic pollutants/impurities. The main applications of the process are as follows.

2.3.1. Oxidation of Cyanide Effluent and Precipitation of Heavy Metals

Numerous plating and metal finishing plants use chemical oxidation methods to treat their cyanide wastes; cyanides and heavy metals are often present together in plating industry waste. Their concentration and their value influence the selection of the treatment process. If the cyanide and heavy metals are not economically recoverable by a method such as ion exchange, the cyanide radical is converted either to the less toxic cyanate or to carbon dioxide and nitrogen by oxidation, while the heavy metals are precipitated and removed as sludge.

2.3.2. Chemical Oxidation of Phenols and Filtration of Manganese Dioxide

Chemical oxidation of phenols has found application to date only on dilute waste streams. Potassium permanganate, one of the oxidants used, is reduced to manganese dioxide (MnO_2), which is a filterable solid. Chlorine gas is not frequently used because of the high potential for chlorophenol formation. An ozonation process for oxidation of phenols is currently practiced in the iron and steel manufacturing industry.

2.3.3. Oxidation of Other Organics

Chemical oxidizing agents have been used for the control of organic residues in wastewaters and in potable water treatment. Among the organics for which oxidative treatment has been reported are aldehydes, mercaptans, benzidine, and unsaturated acids. For these applications, sodium hypochlorite, calcium hypochlorite, potassium permanganate, and hydrogen peroxide have been reported as effective oxidants. In one application nitrous acid was used.

2.3.4. Oxidation/Precipitation of Iron and Manganese from Water

In waters containing oxygen, iron and manganese are predominately in the (III) and (IV) oxidation states, respectively. The solubility of iron(III) is 0.06 ppb over the pH range 7.0–10.0. Manganese(IV) is also quite insoluble. Its solubility is sensitive to the amount of carbonate present in the water. At C_T equal to 2×10^{-3} M its solubility goes as low as 0.002 mg/L at pH 10, but is about 2.75 mg/L at pH 7.

In the reducing environment of anaerobic groundwater, iron and manganese both favor the (II) state. Both of these species have solubility minimum at a pH near 12, which is very low, comparable to the more oxidized states. But at lower pH, the solubility increases rapidly. At pH 7, the solubility of ferrous iron(II) hydroxide is approx 1400 mg/L, and manganese(II) hydroxide is greater than 55,000 mg/L. High levels of these minerals in water create problems by affecting taste in drinking water and by precipitating on clothes and fixtures producing red or black stains. Secondary drinking water standards for iron and manganese are 0.3 and 0.05 mg/L, respectively.

Iron and manganese can both be oxidized by oxygen alone, but the rate is relatively slow and is sensitive to pH. For iron, the rate law is second order with respect to hydroxide concentration, and varies greatly in the neutral pH range. At a pH of about 6.56, very little conversion was observed in a 50 min period. At pH 7.24 approx 95% conversion was obtained in 10 min.

Manganese oxidation is an autocatalytic because the precipitated product hastens the reaction. The pH must nevertheless be above 9.5 for appreciable reaction rates to occur. Manganese oxidation is often followed by sand filtration to remove precipitate. When this is done, the precipitate may adhere to the sand particles, which then provides a catalytic surface for the reaction. Thus, a "ripening" effect may be observed in which a new sand bed gradually improves its ability to remove manganese.

Higher rates of reaction can be obtained by using stronger oxidizing agents, such as chlorine or potassium permanganate.

If the concentration of iron and manganese is less than about 10 mg/L, it may not be necessary to use a sedimentation basin before filtration. Iron(II) and manganese(II) are also removed by lime/soda-ash softening, described in another section.

2.4. Chemical Oxidation Design Considerations

2.4.1. Cyanide Alkaline Chlorination Process Design

To illustrate how a chemical oxidation process works, design features of a chemical oxidation process is presented below assuming an industrial effluent containing cyanide is to be treated.

Chemical oxidation equipment often consists of an equalization tank followed by two reaction tanks, although the reaction can be carried out in a single tank. Each tank has an electronic recorder–controller to maintain required conditions with respect to pH and oxidation reduction potential (ORP). In the first reaction tank, conditions are adjusted to oxidize the target pollutants/impurities (such as cyanides) to an intermediate product (such as cyanates). To effect the reaction, chlorine is metered to the reaction tank as required to maintain the ORP in the range of 350 to 400 mV, and 50% aqueous caustic soda is added to maintain a pH range of 9.5–10. In the second reaction tank, process conditions are maintained to oxidize the intermediate product (such as cyanates) to carbon dioxide and nitrogen. The desirable ORP and pH for this reaction are 600 mV and a pH of 8. Each of the reaction tanks is equipped with a propeller–agitator designed to provide approximately one turnover or minute. Treatment by the batch process is accomplished by using two tanks, one for collection of water over a specified time period and one for the treatment of an accumulated batch. If dumps of concentrated wastes are frequent, another tank may be required to equalize the flow to the treatment tank. When the holding tank is full, the liquid is transferred to the reaction tank for treatment. After treatment, the supernatant is discharged and the sludges are collected for removal and ultimate disposal.

Either batch or continuous operations may be employed for oxidation. Batch treatment is preferred for flows less than 190,000–380,000 Lpd (50,000–100,000 GPD). Oxidizing reagent consumption and choice of reagent will depend on process efficiency, presence of competing oxidizable material, and temperature, and should be determined by pilot-scale testing. Very simple equipment is required for chemical oxidation. This includes storage vessels for the oxidizing agents and perhaps for the wastes, metering equipment for both streams, and vessels with agitators to provide suitable contact of oxidant and waste. Some instrumentation is required to determine the concentrations of pollutants, pH of the water, and the degree of completion of the oxidation reaction. The process may be monitored by an ORP electrode. This electrode is generally a piece of noble metal (often platinum), which is exposed to the reaction medium. The electrode produces an electromotive force (EMF) output that is empirically related to the ratio of oxidized to reduced constituents in the solution. (1 GPD = 1 gal/d = 3.785 L/d.)

2.4.2. Ozonation Process Design

Because ozone is unstable, it must be generated on site. Ozone generators utilize a corona discharge that occurs when a high-voltage alternating current is imposed across a discharge gap. Ozone is generated either from air or from oxygen. Two to two and a half times as much ozone will be produced from a stream of 100% oxygen as from an air stream. The ozonized air from the generator is introduced into a contact chamber designed to ensure good mixing with the water or waste streams. The two ozone/water mixing systems in most widespread use are Venturi mixers and porous diffusers. With the Venturi mixer, ozonized gas and liquid (water or waste) flow co-currently, and ozonized gas flow is limited to 30–60% of the liquid volume flow. In a porous diffuser system, a countercurrent flow is usual, and gas flow may be up to 20 times the liquid flow. In some systems the contact column is a packed bed. This increases surface area and increases the rate of mass transfer of ozone into solution. One equipment manufacturer has been using ultrasonic in conjunction with ozonation, which also increases the surface area available for mass transfer. Depending on the extent of treatment required, it may be necessary to incorporate two or more contact stages, which can be of different types. If oxygen is used as the feed gas instead of air, the closed-loop ozonation method is utilized. In this system off-gas from the contactor in recycled back to the ozone generator and enriched with ozone.

Modern ozone systems are completely automated. An ozone monitor provides continuous on-line monitoring of the ozone concentration in the gaseous effluent from the contactor. If the concentration of ozone exceeds a preset level (usually 0.05 ppm), the voltage or frequency of the ozone generator is reduced.

2.5. Design and Application Examples

2.5.1. Example 1

What will be the expected performance of chemical oxidation process? Introduce the performance data of chemical oxidation process in the following industries:

- inorganic chemical manufacturing
- ore mining and dressing
- organic and inorganic substances
- textile mills
- organic chemicals
- adhesives and sealant

Solution:

Chemical oxidation is very effective in destroying free cyanide as well as cadmium, copper, and zinc cyanide complexes. However, nickel cyanide is incompletely destroyed, and iron cyanide complexes are apparently unaffected by chlorine or ozone. The ozone–UV radiation process (i.e., advanced oxidation process) is effective for treatment of complexed cyanide, such an ferric cyanide, copper cyanide, and nickel cyanide. Performance data of oxidation processes from the following industries are presented in the appendixes:

(a) Appendix D1, Chemical oxidation with chlorine for inorganic (sodium bisulfite) manufacturing industry.

(b) Appendix D2, Chemical oxidation with chlorine for inorganic (hydrogen cyanide) manufacturing industry.
(c) Appendix E1, Chemical oxidation with chlorine for ore mining and dressing (lead/zinc) industry.
(d) Appendix E2, Chemical oxidation with chlorine for ore mining and dressing (ferroalloy) industry.
(e) Appendix F, Chemical oxidation with chlorine for organic and inorganic wastes.
(f) Appendix G, Chemical oxidation with ozone for textile mills (woven fabric finishing).
(g) Appendix H, Chemical oxidation with ozone for adhesive and sealants industry.

2.5.2. *Example 2*

Introduce the "cyanide alkaline chlorination," "excess chlorination (superchlorination)," and "acid hydrolysis" processes, which treat industrial effluents containing cyanide.

Solution:

The cyanide alkaline chlorination process uses chlorine and caustic to oxidize cyanides to cyanates and ultimately to carbon dioxide and nitrogen. The oxidation reaction between chlorine and cyanide is believed to proceed in two steps as follows, according to Eqs. (11) and (12):

$$\underset{\text{Cyanide ion}}{CN^-} + \underset{\text{Chlorine}}{Cl_2} \rightarrow \underset{\text{Cyanogen chloride}}{CNCl} + \underset{\text{Chloride ion}}{Cl^-} \tag{11}$$

$$\underset{\text{Cyanogen chloride}}{CNCl} + \underset{\text{Hydroxyl ion}}{2OH^-} \rightarrow \underset{\text{Cyanate ion}}{CNO^-} + \underset{\text{Chloride ion}}{Cl^-} + \underset{\text{Water}}{H_2O} \tag{12}$$

The formation of cyanogen chloride (CNCl) in Eq. (11) is essentially instantaneous. The second reaction in Eq. (12), the formation of cyanate, is accomplished most rapidly and completely at a pH of 10 or higher. A detention time of 30 min to 2 h is usually allowed. The cyanates can be further decomposed into nitrogen and carbon dioxide by excess chlorination, or superchlorination:

$$\underset{\text{Cyanate}}{2CNO^-} + \underset{\text{Hydroxyl ion}}{4OH^-} + \underset{\text{Chlorine}}{3Cl_2} \rightarrow \underset{\text{Chloride ion}}{6Cl^-} + \underset{\text{Carbon dioxide}}{2CO_2} + \underset{\text{Nitrogen}}{N_2} + \underset{\text{Water}}{2H_2O} \tag{13}$$

An alternate approach uses acid hydrolysis:

$$\underset{\text{Cyanate ion}}{CNO^-} + \underset{\text{Water}}{2H_2O} \rightarrow \underset{\text{Carbon dioxide}}{CO_2} + \underset{\text{Ammonia}}{NH_3} + \underset{\text{Hydroxyl ion}}{OH^-} \tag{14}$$

Decomposition by excess chlorination can be accomplished in about 1 h if the pH is adjusted to 8.0–8.5. Acid hydrolysis usually takes place at pH 2–3. Because care must be taken to avoid the liberation of the toxic cyanogen chloride as a gas, hydrolysis in not usually the chosen option.

Section 2.4 and Fig. 2 present the process equipment and monitoring instrument, Appendix D2 shows the typical process performance data. Over 99% cyanide removal can be achieved by this process.

An alternative chlorination process involves the use of sodium hypochlorite (NaOCl) as the oxidant. Reactions with sodium hypochlorite are similar to those of chlorine, except that there is no caustic requirement for destruction of free cyanide in the oxidation stages. Alkali, however, is required to precipitate metal–cyanide complexes as hydroxides. The entire oxidation–precipitation process is a typical chemical oxidation precipitation process system. All chlorination equipment, chlorine compounds, etc., are commercially available (27).

A typical reaction condition for the alkaline chlorination of 1 kg (2.2 lb) of cyanide to cyanate requires 6 kg (13.2 lb) each of sodium hydroxide and chlorine. The reaction is carried out at pH 10, and at least 15 min contact time is required to drive the reaction to completion. If metal cyanide complexes are present, extended chlorination for longer periods may be necessary. Complete destruction of cyanate requires a second oxidation stage with approx 45 min retention at a pH below 8.5. The theoretical reagent requirement for this second stage is 4.1 kg (9.0 lb) of chlorine and 1.1 kg (2.4 lb) of caustic per kg (2.2 lb) of cyanide.

2.5.3. *Example 3*

Introduce chemical oxidation process for cyanide removal using ozone.

Solution:

Appendix B3 shows the typical performance data of ozonation process, for cyanide reduction. Percentage removal in the range of 51–97% was reported by the US EPA.

The cyanide oxidation can be illustrated by the following ionic equation:

$$\underset{\text{Cyanide ion}}{\mathrm{CN}^-} + \underset{\text{Ozone}}{\mathrm{O}_3} \rightarrow \underset{\text{Cyanate}}{\mathrm{CNO}^{\cdot}} + \underset{\text{Oxygen}}{\mathrm{O}_2} \tag{15}$$

The reaction indicated by the above equation represents the oxidation of cyanides to cyanates. Continued exposure to ozone will convert the cyanate to carbon dioxide; however, this is not economically practical. Thus, further breakdown to the cyanate waste is dependent on processes such as hydrolysis and biooxidation.

Ozone is also effective in the treatment of phenols. It is about twice as powerful as hydrogen peroxide and is not as selective; thus, it oxidizes a wide range of materials. For low concentration phenolic wastes, the usual practice is to oxidize the phenolic compound to intermediate organic compounds that are toxic but readily biodegradable. For concentrated or intermediate-level phenolic wastes, oxidation by ozone may not be as economical as compared to biological oxidation; however, it is useful as a polishing process following a biological system.

Ozone is more soluble and more stable in acidic solutions than in basic solutions. However, the rate of ozonation reaction is relatively insensitive to pH. Therefore, it is rarely worthwhile to adjust pH prior to ozonation, because the cost of the neutralization process will frequently offset any gains in ozonation efficiency. One exception to this generalization is cyanide ozonation. The cyanate formed initially hydrolyzes more rapidly in alkaline media. If complete conversion of cyanide to carbon dioxide is required, acidic streams should be adjusted to a pH of about 9 before ozonation.

Oxidation of cyanide to cyanate with ozone requires approx 2 kg (4.4 lb) of ozone per kg (2.2 lb) of cyanide, and complete oxidation requires 5 kg (11 lb) of ozone per kg (2.2 lb) of cyanide. Cyanide oxidation to cyanate is very rapid (10–15 min) at pH 9–12 and practically instantaneous in the presence of trace amounts of copper.

Ozone requirements for partial destruction of phenols range from one to five parts per part of phenol. The actual ozone demand will be a function of phenol concentration, pH, and retention time.

2.5.4. *Example 4*

Introduce the applications of chemical oxidation processes for industrial wastewater treatment using (a) hydrogen peroxide and (b) potassium permanganate.

Solution:

1. *Hydrogen peroxide*: The oxidation of cyanide with hydrogen peroxide can be carried out by two processes. The first involves the reaction of hydrogen peroxide with

cyanide at alkaline pH and in the presence of a copper catalyst. The second process, known as the Kastone process, uses a formulation containing 41% hydrogen peroxide, with trace amounts of catalyst and stabilizers, in conjunction with formaldehyde. The cyanide wastes are heated to 120°C (248°F), treated with oxidizing solution and formaldehyde, and then agitated for 1 h. Principal products from the reaction are cyanates, ammonia, and glycolic acid amide. Complete destruction of cyanates requires acid hydrolysis subsequent to this reaction.

Hydrogen peroxide has been used for the separation of metal ions by selective oxidation. In this way, it helps remove iron from combined streams by oxidizing the ferrous ion to ferric, which is then precipitated by the addition of the appropriate base. In dilute solution (<30%), the decomposition of hydrogen peroxide is accelerated by the presence of metal ion contaminants. At higher concentrations of hydrogen peroxide, these contaminants can catalyze violent decomposition. Therefore, hydrogen peroxides should be added slowly to the solution with good mixing. Sulfides, sulfites, and sulfur dioxide can also be readily oxidized with hydrogen peroxide. Under alkaline conditions, sulfates are usually produced.

2. *Potassium permanganate*: Potassium permanganate is mainly used to destroy phenolic compounds in industrial wastewater. It reacts by cleaving the aromatic ring structure of phenol to produce a straight chain aliphatic molecule. The aliphatic is then further oxidized to carbon dioxide and water. The initial reaction takes place almost immediately, and almost 90% of the phenol is oxidized in the first 10 min. A retention time from one to three hours is sufficient to insure complete oxidation of the phenol. The process is affected by pH; the higher the pH (up to 9.5), the faster is the reaction time.

2.5.5. Example 5

Discuss the source and problem of iron and manganese in drinking water. Introduce the application of chemical oxidation precipitation process for iron and manganese removal in a potable water treatment system.

Solution:

1. Groundwater usually contains significant amounts of carbon dioxide, and appreciable amounts of ferrous carbonate in soil and rock may be dissolved by the following reaction:

$$FeCO_3 + CO_2 + H_2O \rightarrow Fe^{2+} + 2HCO_3^- \qquad (16)$$

Manganese exists in the soil mainly as manganese dioxide, which under reducing (anaerobic) conditions, is reduced from an oxidation state of IV to II, and solution occurs.

Both soluble iron and manganese create serious problems in public water supplies, and must be properly removed by the chemical oxidation precipitation process (1,14,15).

Both iron and manganese interfere with laundering operations, import objectionable stains to plumbing fixtures, and cause difficulties in water distributions systems by supporting the growths of iron bacteria.

2. Table 1 summarizes various oxidants for chemical oxidation of iron and manganese. The following are chemical oxidation reactions assuming potassium permanganate is selected as an oxidant:

$$3Fe^{2+} + MnO_4^- + 4H^+ \rightarrow MnO_2 + 3Fe^{3+} + 2H_2O \qquad (17)$$

Potassium permanganate is very effective in oxidizing soluble manganese. In theory, it requires 1 mg/L of $KMnO_4$ to oxidize of 0.52 mg of soluble manganese.

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow 5MnO_2\,(s) + 4H^+ \qquad (18)$$

Table 1
Comparison of Oxidants for Oxidation of Iron and Manganese (14)

Oxidant	Theoretical weight to oxidize 1 mg of Manganese (Mn^{2+}) (mg)	Theoretical weight to oxidize 1 mg of Iron (Fe^{2+}) (mg)
Oxygen, O_2	0.29	0.14
Chlorine, Cl_2	1.30	0.62
Calcium hypochlorite, $Ca(OCl)_2$	1.30	0.64
Sodium hypochlorite, NaOCl	1.36	0.67
Potassium permanganate, $KMnO_4$	1.92	0.91
Chlorine dioxide, ClO_2	2.45	1.21

In a combined chemical oxidation precipitation process system, the soluble Fe^{3+} ions are converted to insoluble $Fe(OH)_3$ precipitates

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3\ (s) \tag{19}$$

Both insoluble MnO_2 and $Fe(OH)_3$ are then removed by one or more solid–water separation processes, such as sedimentation (1,14,28), dissolved air flotation (16,22), filtration (23,26), membrane filtration (20,21,25,26), electroflotation (17), physico-chemical sequencing batch reactor (18,19), or precoat filtration (29,46).

To eliminate residual free chlorine from liquid, granular activated carbon adsorption or chemical reduction (with reducing agents, such as sulfur dioxide, sodium bisulfite, and sodium metabisulfite) are the most common processes for dechlorination. Ultraviolet (UV) irradiation process is gaining wider acceptance as a dechlorination process (30,45,46, 60,61).

2.5.6. *Example 6*

Introduce the chemical oxidation process, its applicability, limitations, and performance for site remediation involving both soil cleaning and groundwater decontamination.

Solution:

The readers are referred to new references (46–49) and US governmental reports (50–59) for modern site remediation technologies. For completion of a successful site remediation project, all aspects of environmental pollution control (air, noise, water, and soil) must be considered. Oxidation chemically converts hazardous contaminants to non-hazardous or less toxic compounds that are more stable, less mobile, and/or inert. The oxidizing agents most commonly used are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide (46,47). Figure 3 shows a typical chemical oxidation system for site remediation.

The chemical oxidants most commonly employed to date for site remediation include peroxide, ozone, and permanganate. These oxidants have been able to cause the rapid and complete chemical destruction of many toxic organic chemicals; other organics are amenable to partial degradation as an aid to subsequent bioremediation. In general, the oxidants have been capable of achieving high treatment efficiencies (e.g., > 90%) for unsaturated aliphatic (e.g., trichloroethylene or TCE) and aromatic compounds (e.g., benzene), with very fast reaction rates (90% destruction in minutes). Field applications have clearly affirmed that matching the oxidant and *in situ* delivery system to the contaminants of concern (COCs) and the site conditions is the key to successful implementation and achieving performance goals.

Ozone gas can oxidize contaminants directly or through the formation of hydroxyl radicals. Like peroxide, ozone reactions are most effective in systems with acidic pH. The oxidation reaction proceeds with extremely fast, pseudo-first-order kinetics. Owing to ozone's

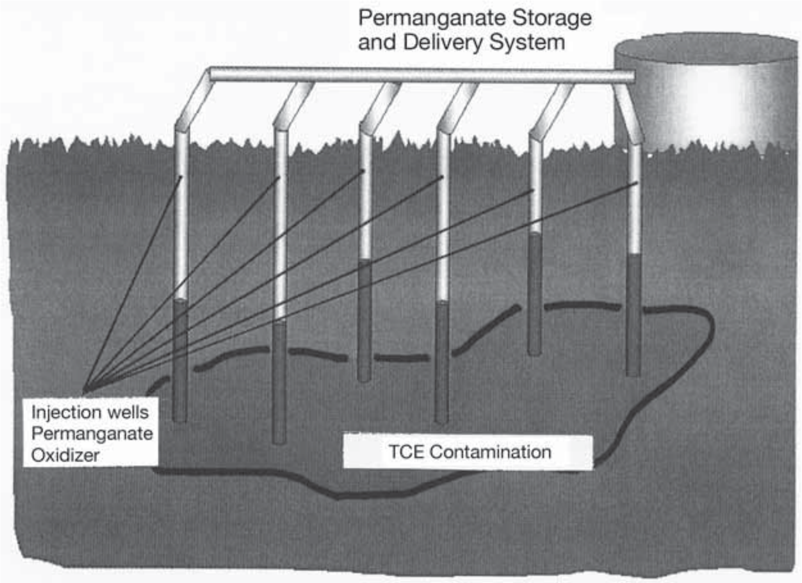


Fig. 3. Chemical oxidation process for site remediation.

high reactivity and instability, O_3 is produced onsite, and it requires closely spaced delivery points (e.g., air sparging wells). *In situ* decomposition of the ozone can lead to beneficial oxygenation and biostimulation.

Oxidation using liquid hydrogen peroxide (H_2O_2) in the presence of native or supplemental ferrous iron (Fe^{2+}) produces Fenton's reagent, which yields free hydroxyl radicals (OH^-). These strong, nonspecific oxidants can rapidly degrade a variety of organic compounds. Fenton's reagent oxidation is most effective under very acidic pH (e.g., pH 2–4) and becomes ineffective under moderate to strongly alkaline conditions. The reactions are extremely rapid and follow second-order kinetics.

The reaction stoichiometry of permanganate (typically provided as liquid or solid $KMnO_4$, but also available in Na, Ca, or Mg salts) in natural systems is complex. Owing to its multiple valence states and mineral forms, Mn can participate in numerous reactions. The reactions proceed at a somewhat slower rate than the previous two reactions, according to second-order kinetics. Depending on pH, the reaction can include destruction by direct electron transfer or free-radical advanced oxidation. Permanganate reactions are effective over a pH range of 3.5–12.

The rate and extent of degradation of a target COC are dictated by the properties of the chemical itself and its susceptibility to oxidative degradation as well as the matrix conditions, most notably, pH, temperature, the concentration of oxidant, and the concentration of other oxidant-consuming substances such as natural organic matter and reduced minerals as well as carbonate and other free-radical scavengers. Given the relatively indiscriminate and rapid rate of reaction of the oxidants with reduced substances, the method of delivery and distribution throughout a subsurface region is of paramount importance. Oxidant delivery systems often employ vertical or horizontal injection wells and sparge points with forced advection to rapidly move the oxidant into the subsurface.

Permanganate is relatively more stable and relatively more persistent in the subsurface; as a result, it can migrate by diffusive processes. Consideration also must be given to the effects of oxidation on the system. All three oxidation reactions can decrease the pH if the system is not buffered effectively. Other potential oxidation-induced effects include colloid genesis leading to reduced permeability; mobilization of redox-sensitive and exchangeable sorbed metals; possible formation of toxic byproducts; evolution of heat and gas; and biological reactions.

The following factors may limit the applicability and effectiveness of chemcial oxidation: (a) requirement for handling large quantities of hazardous oxidizing chemicals due to the oxidant demand of the target organic chemicals and the unproductive oxidant consumption of the formation, (b) some COCs are resistant to oxidation, and (c) there is a potential for process-induced detrimental effects. Further research and development is ongoing to advance the science and engineering of *in situ* chemical oxidation and to increase its overall cost effectiveness.

Engineering of *in situ* chemical oxidation must be done with due attention paid to reaction chemistry and transport processes. It is also critical that close attention be paid to worker training and safe handling of process chemicals as well as proper management of remediation wastes. The design and implementation process should rely on an integrated effort involving screening level characterization tests and reaction transport modeling, combined with treatability studies at the lab and field scale. *In situ* chemical oxidation is a viable remediation technology for mass reduction in source areas as well as for plume treatment. The potential benefits of *in situ* oxidation include the rapid and extensive reactions with various COCs applicable to many bio-recalcitrant organics and subsurface environments. Also, *in situ* chemical oxidation can be tailored to a site and implemented with relatively simple, readily available equipment. Some potential limitations exist including the requirement for handling large quantities of hazardous oxidizing chemicals due to the oxidant demand of the target organic chemicals and the unproductive oxidant consumption of the formation; some COCs are resistant to oxidation; and there is a potential for process-induced detrimental effects. Further research and development is ongoing to advance the science and engineering of in situ chemical oxidation and to increase its overall cost effectiveness (50–59).

3. RECENT DEVELOPMENTS

3.1. Liquid-Phase Chemical/Reduction System for Site Remediation

This section introduces the chemical reduction/oxidation process (Redox), its applicability, limitations, and performance for site remediation involving both soil cleaning and groundwater decontamination. Chemical reduction/oxidation (Redox process) chemically converts hazardous contaminants to nonhazardous or less-toxic compounds that are more stable, less mobile, and/or inert. The oxidizing agents most commonly used are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide (50–59).

Redox reactions involve the transfer of electrons from one compound to another. Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons). The oxidizing agents most commonly used for treatment of hazardous contaminants are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Chemical redox is a full-scale, well-established technology used for disinfection of drinking water and wastewater, and it is a common treatment for cyanide wastes. Enhanced systems are now being used more frequently to treat contaminants in soils. Chemical reduction/oxidation is a short- to medium-term site remediation technology.

The target contaminant group for chemical redox application is inorganics. The technology can be used but may be less effective against nonhalogenated volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs), fuel hydrocarbons, and pesticides, which are defined in detailed elsewhere (48,49).

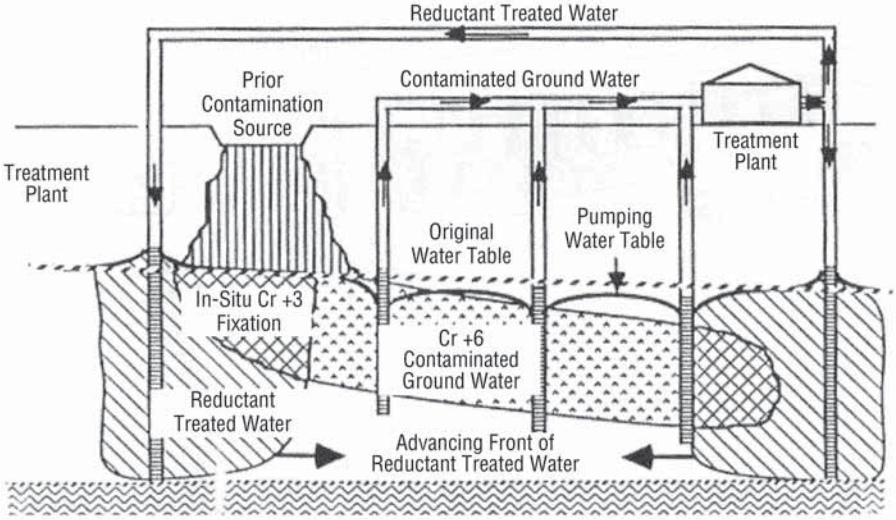


Fig. 4. Chemical reduction/oxidation (Redox) process for site remediation (US EPA).

Factors that may limit the applicability and effectiveness of the redox process include (a) incomplete oxidation or formation of intermediate contaminants may occur depending on the contaminants and oxidizing agents used; (b) the process is not cost-effective for high contaminant concentrations because of the large amounts of oxidizing agent required; and (c) oil and grease in the media should be minimized to optimize process efficiency.

Data for soil, sediment, and sludge are also required for successful project completion. Treatability tests should be conducted to identify parameters such as water, alkaline metals, and humus content in the soils; the presence of multiple phases; and total organic halides that could affect processing time and cost (22).

Chemical redox is a full-scale, well-established technology used for disinfection of drinking water and wastewater, and it is a common treatment for cyanide (oxidation) and chromium [reduction of Cr(VI) to Cr(III) prior to precipitation] wastes. Enhanced systems are now being used more frequently to treat hazardous wastes in soils. Figure 4 shows a typical site remediation project involving the use of chemical redox (chemical reduction/oxidation) for removal of chromium from the environment (22).

3.2. *Gas-Phase Chemical Reduction Process for Site Remediation*

A gas-phase chemical reduction process has been developed for site remediation. This section summarizes the findings of the US Environmental Protection Agency (US EPA) regarding the Gas-Phase Chemical Reduction Process developed by ELI Eco Logic International, Inc. (ECO LOGIC) of Ontario, Canada (47).

Under the auspices of the SITE Program, and in cooperation with the City of Bay City, Michigan; Environment Canada; and the Ontario Ministry of the Environment and Energy; US EPA conducted the demonstration of the gas-phase chemical reduction process at Bay City's Middleground Landfill. The landfill accepted municipal and industrial wastes for approx 40 yr. A 1991 remedial investigation indicated elevated

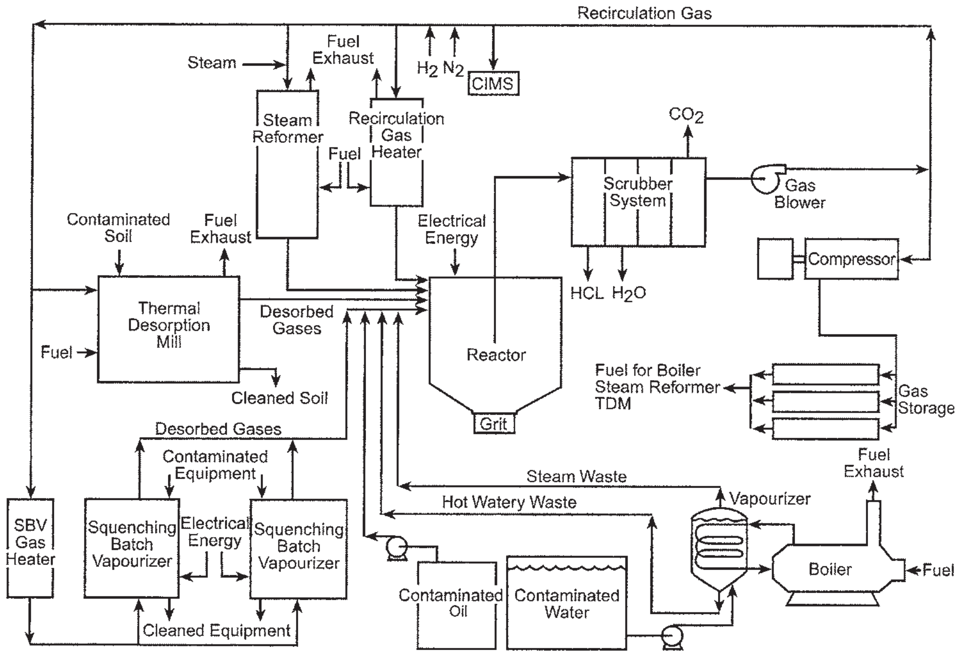


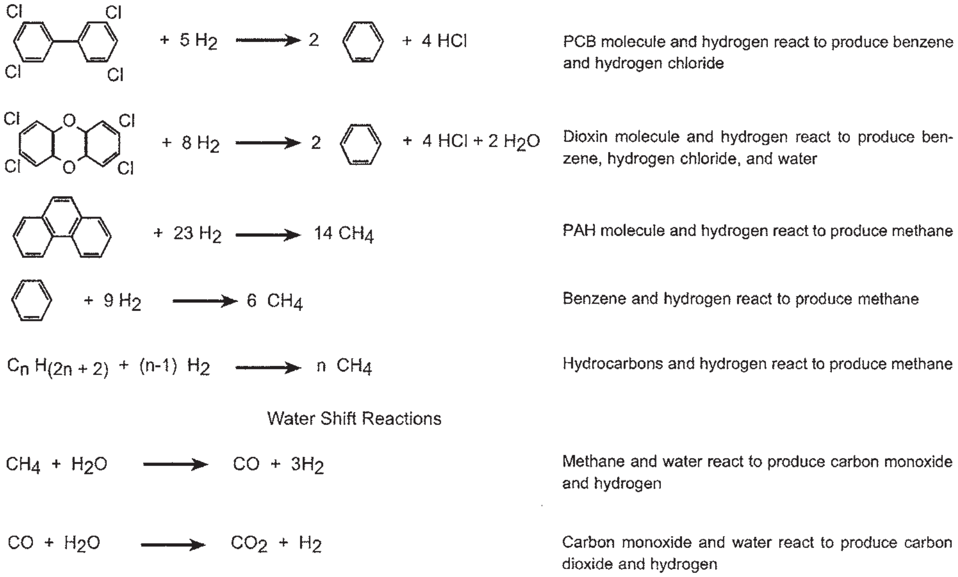
Fig. 5. Flow diagram of a site remediation system involving the use of gas-phase chemical reduction process.

levels in groundwater of trichloroethene, PCBs, 1,2-dichloroethene, methylene chloride, toluene, and ethylbenzene. The groundwater contained lesser concentrations of benzidine, benzene, vinyl chloride, chlorobenzenes, polycyclic aromatic hydrocarbons (PAHs), lindane, dieldrin, chlordane, and DDT metabolites (47).

At a contaminated site, the contaminated soil is preprocessed by a thermal desorption mill (TDM) before going to the patented ECO LOGIC Gas-Phase Chemical Reduction Process unit (i.e., the reactor shown in the center of Fig. 5). The reactor accepts a preprocessed soil, contaminated oil, and contaminated groundwater, if any, for a total treatment. Figure 6 shows the gas-phase chemical reduction process. Briefly speaking, the reactor treats organic hazardous waste in a hydrogen-rich atmosphere at approx 900°C (1650°F) and ambient pressure to produce a reformed gas. The reaction products include hydrogen chloride from the reduction of chlorinated organics, such as PCBs, and lighter hydrocarbons, such as methane and ethylene, from the reduction of straight-chain and aromatic hydrocarbons. The absence of free oxygen in the reactor inhibits dioxin formation. Water acts as a hydrogen donor to enhance the reaction.

A scrubber (46,47) treats the reformed gas to remove hydrogen chloride and particulates. Of this gas, 95% recycles back into the reactor and 5% feeds a propane-fired boiler prior to release to the atmosphere. The recycle stream may be used as a fuel in other system support equipment, such as the boiler that generates steam. The final combustion step in the boiler met the RCRA requirements, making the reformed gas environmentally acceptable for combustion.

The US EPA collected extensive samples at points around the major system components and stored or logged important data on system operation and utility usage. Laboratory



PCB molecule and hydrogen react to produce benzene and hydrogen chloride

Dioxin molecule and hydrogen react to produce benzene, hydrogen chloride, and water

PAH molecule and hydrogen react to produce methane

Benzene and hydrogen react to produce methane

Hydrocarbons and hydrogen react to produce methane

Methane and water react to produce carbon monoxide and hydrogen

Carbon monoxide and water react to produce carbon dioxide and hydrogen

Fig. 6. Chemical reactions of the gas-phase chemical reduction process.

analyses provided information on the principal process streams: reactor grit, scrubber residuals, reformed gas, and boiler stack emissions. The US EPA evaluated these data against established program objectives to determine the capability of the process to treat the designated waste. Based on the program objectives, the demonstration confirmed the feasibility of the gas-phase chemical reduction process for treating PCBs and other chlorinated organic compounds, producing a fuel gas from contaminated liquids and providing environmentally acceptable air emissions.

In general, the gas-phase chemical reduction system effectively destroyed PCBs, reducing them to lighter hydrocarbons. Theoretically, the destruction process could depend on both the reactor system's gas-phase reduction reactions, which produced the reformed gas, and on the propane/reformed gas-fired boiler, a combustion device.

Although the result was not listed as a primary or secondary objective for the demonstration, destruction and removal efficiencies (DREs) for PCBs in the scrubbed reformed gas were essentially equal to the DREs achieved at the boiler stack. This shows that combustion of the reformed gas in the boiler is not required to complete PCB destruction.

The US EPA concluded that the gas-phase chemical reduction system efficiently treated liquid wastes containing oily PCBs, other organics, and water containing PCBs, other organics, and metals. Stack emissions met stringent regulatory levels. The principal residual stream (the scrubber effluent), concentrated metals and some organics (benzene, PCBs, and PAHs), should be monitored for possible further treatment prior to disposal.

As shown in Fig. 6, some of the reduction reactions, including intermediate steps, for the destruction of a variety of contaminants using the gas-phase chemical reduction process. The process primarily involves the gas-phase reduction of organic compounds by hydrogen at temperatures of 850°C or higher. Chlorinated hydrocarbons, such as PCBs and polychlorinated dibenzo-p-dioxins (dioxins), are chemically reduced to methane and

HCl, while nonchlorinated organic contaminants, such as PAHs, are reduced substantially to methane and minor amounts of other light hydrocarbons. The HCl produced can be recovered as acid or scrubbed out in a caustic scrubber downstream of the process reactor. Unlike oxidation reactions, the efficiency of these reduction reactions is enhanced by the presence of water, which acts as a reducing agent and a source of hydrogen. The water shift reactions shown produce hydrogen, carbon monoxide, and carbon dioxide from methane and water. These reactions can be used at higher efficiencies by subjecting scrubbed methane-rich product gas to catalytic steam reforming, reducing the requirements for purchased hydrogen.

A benefit of using an actively reducing hydrogen atmosphere for the destruction of chlorinated organic compounds, such as PCBs, is that no formation of dioxins or furans occurs. Any dioxins or furans in the waste are also destroyed effectively. The reducing hydrogen atmosphere is maintained at more than 50% hydrogen (dry basis) to prevent formation of PAHs. This makes the scrubbed recirculation gas suitable for continuous monitoring using an on-line Chemical Ionization Mass Spectrometer (CIMS). By measuring the concentrations of intermediate reduction products, the CIMS produces a continuous indication of DE.

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Appendix A1

Chemical Reduction and Clarification Used in Metal Finishing Industry (Common and Precious Metals)

TREATMENT TECHNOLOGY: Chemical Reduction With Sedimentation (Lime)

Data source: EGD Combined Data Base
Point source: Metal finishing
Subcategory: Common metals; precious metals; complexed metals; hexavalent chromium; solvents

Data source status:
Not specified ____
Bench scale ____
Pilot scale ____
Full scale x

Pretreatment/treatment: None/Chem. Red., Sed. (tanks), Chem. Ppt. (lime), Coag. Floc. (polyelectrolyte), Filter.

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: 352,000 m^3/day
Chemical dosage (s): Lime: 16,000 kg/yr; coagulating agents: 290 kg/yr
Mix detention time: Unspecified
Flocculation detention time: Unspecified
Unit configuration: Continuous operation (24 hr/day)

REMOVAL DATA

Sampling: 24-hr composite, flow proportion (one hr)

Pollutant/parameter	Concentration Influent	 Effluent	Percent removal	Detection limit
Classical pollutants, mg/L:				
pH, minimum	6.0	6.4		
pH, maximum	7.2	7.5		
Fluorides	11	5.0	54	0.1
Phosphorus	8.6	4.7	45	0.003
TSS	44	10	77	5.0
Iron	0.22	0.046	79	0.005
Tin	1.4	ND	>99	
Oil and grease	BDL	BDL	NM	5.0
Gold	70	40	43	
Toxic pollutants, µg/L:				
Chromium	90	45	50	3.0
Copper	5,900	960	84	1.0
Lead	300	ND	>99	30
Nickel	550	290	47	6.0
Zinc	56	10	82	1.0
Carbon tetrachloride	ND	BDL	NM	1.0
1,1,1-Trichloroethane	1.2	0.3	75	0.1
Chloroform	ND	BDL	NM	1.0
Bis(2-ethylhexyl)phthalate	54	84	NM	10
Butyl benzyl phthalate	BDL	BDL	NM	10
Di-n-butyl phthalate	BDL	BDL	NM	10
Diethyl phthalate	100	75	25	10
Trichloroethylene	ND	0.1*	NM	0.1
Anthracene	BDL	ND	NM	10
Phenanthrene	1.0	ND	NM	10
Methylene chloride	BDL	ND	NM	1.0
Naphthalene	BDL	ND	NM	10

Blanks indicate data not available.
BDL, below detection limit.
ND, not detected.
NM, not meaningful.
*Approximate value.
(a)Original source of data: BAT verification sampling 1978-1979(HS).

Appendix A2
Chemical Reduction and Filtration Used in Metal Finishing Industry (Common Metals and Hexavalent Chromium)

TREATMENT TECHNOLOGY: Chemical Reduction With Filtration (Unspecified)

Data source: EGD Combined Data Base
Point source: Metal finishing
Subcategory: Common metals; hexavalent chromium

Data source status:
Not specified ___
Bench scale ___
Pilot scale ___
Full scale x

Pretreatment/treatment: None/Chem. Red.(Cr), Chem. Ppt., Filter

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: 11,400 m^3/day
Chemical dosage(s): Unspecified
Mix detention time: Unspecified
Media (top to bottom): Unspecified
Unit configuration: Batch chem. red. and chem. ppt., continuous filter

REMOVAL DATA

Sampling: Effluent: 24-hr composite, flow proportion; influent: grab

Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical pollutants, mg/L:				
pH, minimum	1.2			
pH, maximum		8.4		
Fluorides	1.3	1.1	15	0.1
Phosphorus	0.02	8.0	NM	0.003
TSS	1,000	16	98	5.0
TDS	4,200	5,700	NM	5.0
Iron	260	0.17	>99	0.005
Tin	0.14	0.14	0	
Oil and grease	11	6.2	44	5.0
Toxic pollutants, µg/L:				
Cadmium	21	18	14	2.0
Chromium	116,000	18	>99	3.0
Hexavalent chromium	5.0	5.0	0	5.0
Copper	110,000	1,000	99	1.0
Lead	800	68	92	30
Nickel	28,000	120	>99	6.0
Zinc	19,000	18	>99	1.0
Cyanide, total	20	20	0	5.0

Blanks indicate data not available.
NM, not meaningful.

Appendix B
Chemical Reduction and Clarification Used in Aluminum Forming Industry

TREATMENT TECHNOLOGY: Chemical Reduction With Sedimentation (Unspecified)

Data source: Effluent Guidelines
Point source: Aluminum forming
Subcategory: Unspecified

Data source status:
Not specified ____
Bench scale ____
Pilot scale ____
Full scale __x__

Pretreatment/treatment None/Chem. Red. (Cr)

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: Unspecified
Chemical dosage (s): Unspecified
pH in clarifier: See below
Clarifier detention time: Unspecified
Hydraulic loading rate: Unspecified
Unit configuration: Unspecified

REMOVAL DATA

Sampling: Three 24-hour or one 72-hour composite

Pollutant/parameter	Concentration Influent	 Effluent	Percent removal	Detection limit
Classical pollutants, mg/L:				
Oil and grease	5	<95	NM	
Suspended solids	<2	<5	NM	
COD	20	30	NM	
TOC	13	9.7	23	
Phenol	0.003	0.009	NM	
pH, pH units	2.6	9.8	NM	
Toxic pollutants, µg/L:				
Cadmium	2.8	BDL	64*	2
Chromium	100,000	90	>99	5
Copper	40	BDL	89*	9
Lead	30	BDL	67*	20
Mercury	3.4	<5	NM	0.1
Zinc	110	BDL	77*	50
Methylene chloride	30	60	NM	10
Bis(2-ethylhexyl) phthalate	ND	BDL	NM	10

Blanks indicate data not available.
BDL, below detection limit.
ND, not detected.
NM, not meaningful.
*Approximate value.

Appendix C
Chemical Reduction and Filtration Used in Inorganic Chemical Industry (Chrome Pigment)

TREATMENT TECHNOLOGY: Chemical Reduction With Filtration
(Sulfur Dioxide, Acid, Caustic)

Data source: Effluent Guidelines
Point source: Inorganic chemicals
Subcategory: Chrome pigment

Data source status:	
Not specified	
Bench scale	
Pilot scale	
Full scale	x

Pretreatment/treatment: None/Neutral., Chem. Red.

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: 85.6 m^3/Mg
Chemical dosage (s): Unspecified
pH in clarifier: Not applicable
Clarifier detention time: Not applicable
Hydraulic loading rate: Unspecified
Unit configuration: Unspecified

REMOVAL DATA

Sampling: 3 day, 24-hr composite and grab

Pollutant/parameter	Concentration(a) Influent	Concentration(a) Effluent	Percent removal	Detection limit
Toxic pollutants, µg/L:				
Chromium	310,000	130,000	58	
Lead	160,000	120,000	25	
Zinc	54,000	1,500	97	

Blanks indicate data not available.
(a)Concentration is calculated from pollutant flow in m^3/Mg and pollutant loading in kg/Mg.

Appendix D1
Chemical Oxidation (Chlorination) Used in Inorganic Chemical Industry (Sodium Bisulfite Manufacturing Industry)

TREATMENT TECHNOLOGY: Chemical Oxidation (Chlorine)

Data source: Effluent Guidelines
Point source: Inorganic chemicals
Subcategory: Sodium bisulfite

Data source status:
Not specified ___
Bench scale ___
Pilot scale ___
Full scale x

Pretreatment/treatment: None/Chem. Ox.

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: 2.67 m^3/Mg
Chemical dosage(s): NaOCl (unspecified dosage)
Contact time: Unspecified
pH: Unspecified
Type of sedimentation device: Unspecified
Unit configuration: Single reactor tank

REMOVAL DATA

Sampling: 72-hr composite and grab

Pollutant/parameter	Concentration(a) Influent	Concentration(a) Effluent	Percent removal	Detection limit
Classical pollutants, mg/L:				
COD	1,500	980	35	
TSS	89	160	NM	
Toxic pollutants, µg/L:				
Copper	370	320	14	
Lead	2,500	2,500	0	

Blanks indicate data not available.
NM, not meaningful.
(a)Concentration is calculated from pollutant flow in m^3/Mg and pollutant load in kg/Mg.

Appendix D2
Chemical Oxidation (Chlorination) Used in Inorganic Chemical Industry (Hydrogen Cyanide Manufacturing Industry)

TREATMENT TECHNOLOGY: Chemical Oxidation (Chlorine)

Data source: Effluent Guidelines
Point source: Inorganic chemicals
Subcategory: Hydrogen cyanide

Data source status:

Not specified	
Bench scale	
Pilot scale	
Full scale	x

Pretreatment/treatment: Neutral./Chem. Ox.

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: 57 m^3/Mg
Chemical dosage(s): Unspecified
Contact time: Unspecified
pH: Unspecified
Type of sedimentation device: Settling ponds
Unit configuration: Two ponds in parallel where sodium hypochlorite is added, then caustic and chlorine are added in another treatment pond.

REMOVAL DATA

Sampling: 72-hr composite and grab

Pollutant/parameter	Concentration(a) Influent	Concentration(a) Effluent	Percent removal	Detection limit
Classical pollutants, mg/L:				
TSS	980	33	97	
NH_3-N	190	120	37	
Toxic pollutants, µg/L:				
Cyanide	6,800	<2	>99	

Blanks indicate data not available.
(a)Concentration is calculated from the wastewater flow in m^3/Mg of HCN and the pollutant load in kg/Mg. Pollutant load was calculated by apportioning the mass emitted between the two waste streams on the basis of measured flows. This is a very approximate process.

Appendix E1
Chemical Oxidation (Chlorination) Used in Ore Mining and Dressing Industry (Lead/Zinc Industry)

TREATMENT TECHNOLOGY: Chemical Oxidation (Chlorine)

Data source: Effluent Guidelines
Point source: Ore mining and dressing
Subcategory: Lead/zinc mill

Data source status:
Not specified ____
Bench scale ____
Pilot scale ____
Full scale x

Pretreatment/treatment: None/Chem. Ox.

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: Unspecified
Chemical dosage(s): 1,200 - 1,500 16/d Cl_2
Contact time: Unspecified
pH: 11-12 (maintained by lime addition)
Type of sedimentation device: Settling tank
Unit configuration: Three FRP reactor tanks in series plus chlorination and lime slaker

REMOVAL DATA

Sampling: 30 days

Pollutant/parameter	Concentration, µg/L Influent	Concentration, µg/L Effluent	Percent removal	Detection limits
Toxic pollutants:				
Cyanide	68,000	130	>99	

Blanks indicate data not available.

Appendix E2
Chemical Oxidation (Chlorination) Used in Ore Mining and Dressing Industry (Ferroalloy Industry)

TREATMENT TECHNOLOGY: Chemical Oxidation (Chlorine)

Data source: Effluent Guidelines
Point source: Ore mining and dressing
Subcategory: Ferroalloy mine/mill

Data source status:	
Not specified	
Bench scale	
Pilot scale	x
Full scale	

Pretreatment/treatment: Unspecified/Chem. Ox.

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: Unspecified
Chemical dosage(s): 10-20 mg/L NaOCl
Contact time: 30-90 min
pH: 8.8-11.0
Type of sedimentation device: Settling tank
Unit configuration: Unspecified

REMOVAL DATA

Sampling: 4 months

Pollutant/ parameter	Concentration, µg/L Influent	Concentration, µg/L Effluent	Percent removal	NaOCl dosage, mg/L	Contact time, min	pH
Toxic pollutants:						
Cyanide	190	80	58	20	30	8.8
	190	50	74	20	60	8.8
	190	70	63	20	90	8.8
	190	40	79	10	30	10.6
	190	30	84	10	60	10.6
	190	40	79	10	90	10.6
	190	30	84	20	30	10.6
	190	20	89	20	60	10.6
	190	20	89	20	90	10.6
	190	30	84	10	30	11.0
	190	30	84	10	60	11.0
	190	30	84	10	90	11.0
	190	10	95	20	30	11.0
	190	20	89	20	60	11.0
	190	20	89	20	90	11.0

Appendix F
Chemical Oxidation (Chlorination) Used in Organic and Inorganic Chemical Industries

TREATMENT TECHNOLOGY: Chemical Oxidation (Chlorine)

Data source: Government report
Point source: Organic and inorganic wastes
Subcategory: Unspecified

Data source status:
Not specified ___
Bench scale x
Pilot scale ___
Full scale ___

Pretreatment/treatment: Equal., Neutral., Sed. (clarifier)/Act. Sl., Oxidation Column, Sed. (clarifier), Chem. Ox.

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: 1,880 m^3/day
Chemical dosage(s): 5.25% aqueous solution of NaOCl
Contact time: 15 min
pH: Unspecified
Type of sedimentation device: Unspecified
Unit configuration: Unspecified

REMOVAL DATA

Sampling: 24-hour composite

Pollutant/parameter	Concentration Influent	Concentration Effluent	Percent removal	NaOCl dosage, weight %
Classical pollutants, mg/L:				
COD	780	720	7	0.5
COD	780	710	9	1.0
COD(a)	750	560	25	2
COD(a)	750	500	28	3
COD(b)	820	510	38	4
COD	720	440	39	5

(a)Average of 9 samples.
(b)Average of 3 samples.

Appendix G
Chemical Oxidation (Ozonation) Used in Textile Mills (Woven Fabric Finishing)

TREATMENT TECHNOLOGY: Chemical Oxidation (Ozone)

Data source: Effluent Guidelines
Point source: Textile mills
Subcategory: Wool scouring

Data source status:
Not specified ___
Bench scale ___
Pilot scale X
Full scale ___

Pretreatment/treatment: Sed., Filter/Chem. Ox.

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: Unspecified
Chemical dosage(s): Unspecified
Contact time: Unspecified
pH: Unspecified
Type of sedimentation device: Unspecified
Unit configuration: Unspecified

REMOVAL DATA

Sample: 24-hr composite

Pollutant/parameter	Concentration		Percent removal	Detection limit
	Influent	Effluent		
Classical mg/L:				
Aluminum	3.1	7	NM	
Barium	0.11	0.12	NM	
Boron	0.6	1.0	NM	
Calcium	33	30	9	
Cobalt	0.06	0.38	NM	
Iron	2.4	2.3	4	
Magnesium	6.6	6.1	8	
Manganese	0.04	0.09	NM	
Molybdenum	<0.2	<0.4	NM	
Sodium	61	56	8	
Phosphorus	0.1	0.16	NM	
Silicon	2.7	2.6	4	
Strontium	0.16	0.002	99	
Ammonia	2.6	5.5	NM	
Titanium	0.06	0.18	NM	
Vanadium	0.11	0.54	NM	
Phenol	0.02	0.01	50	
Nitrate	6.5	8.8	NM	
Toxic pollutants, µg/L:				
Antimony	<200	1,200	NM	
Arsenic	83	43	48	
Beryllium	<2	<4	NM	
Cadmium	<40	250	NM	
Chromium	<80	<200	NM	
Copper	120	590	NM	
Cyanide	260	<4	>98	
Lead	<400	<900	NM	
Nickel	<700	5,000	NM	
Silver	<100	1,300	NM	
Zinc	400	460	NM	
Di-n-butyl phthalate				
Bis(2-ethylhexyl)phthalate	14	110	NM	0.04
Anthracene	0.2	0.4	NM	0.01
Fluoranthene	0.2	0.1	50	0.02
Benzo(a)pyrene	0.2	BDL	95*	0.02
Pyrene	0.3	0.1	67	0.01
Benzo(k)fluoranthene	0.1	BDL	90*	0.02
Toluene	BDL	1.2	NM	0.1
Ethylbenzene	BDL	BDL	NM	0.2
Methylene chloride	4.8	61	NM	0.4

Blanks indicate data not available.
BDL, below detection limit.
NM, not meaningful.
*Approximate value.

Appendix H
Chemical Oxidation (Ozonation) Used in Adhesive and Sealants Industry

TREATMENT TECHNOLOGY: Chemical Oxidation (Ozone)

Data source: Government report
Point source: Adhesives and sealants
Subcategory: Unspecified

Data source status:
Not specified ___
Bench scale ___
Pilot scale x
Full scale ___

Pretreatment/treatment: Sed., Ultrafiltration/Chem. Ox.

DESIGN OR OPERATING PARAMETERS

Wastewater flow rate: Unspecified
Chemical dosage(s): Unspecified
Contact time: Unspecified
pH: Unspecified
Type of sedimentation device: Unspecified
Unit configuration: Unspecified

REMOVAL DATA

Sampling: Equal volume grab samples collected throughout an 8-hr day; average of 2 days sampling

Pollutant/parameter	Concentration Influent	Concentration Effluent	Percent removal	Detection limit
Classical pollutants, mg/L:				
BOD_5	5,800	5,200	10	
COD	77,000	12,000	84	
TSS	64	140	NM	
Oil and grease	130	4.0	97	
Total phenol	47	0.13	>99	
Toxic pollutants, µg/L:				
Cyanide	560	1,500	NM	
Zinc	2,200	90	96	

Blanks indicate data not available.
NM, not meaningful.

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Oil Water Separation

Puangrat Kajitvichyanukul, Yung-Tse Hung,
and Lawrence K. Wang

CONTENTS

1. INTRODUCTION

Oil and grease (O&G) is a common pollutant frequently found in the effluent of a wide range of industries. Oil and grease concentrations in wastewater, as recommended by the US Environmental Protection Agency, are not determine as the presence of specific compounds but are measured by their extractability using a particular solvent. Hexane and Freon are primary solvents used to extract oily compounds from wastewaters. Therefore, the term "oil and grease" contains a wide range of contaminants, which may include but are not limited to fatty acids, surfactants, petroleum hydrocarbons, phenolic compounds, animal and vegetable oils, etc. Many industries such as steel, aluminum, food, textile, leather, petrochemical, and metal finishing were reported as sources of high concentrations of oil and grease in their wastewaters as shown in Table 1.

Guerin (2) has reported an average annual oily wastewater loadings from mining operation of about 140 kL/d. Clearing of spills, leaks, and overflows with floor wash down accounts for 60% of the operations' oily wastewater. Composition of oily wastewater from mining operation reported by site locations is shown in Table 2.

"Produced water" is also the single largest volume of oily wastewater generated by the oil and gas industry (3). This oily wastewater comes from crude oil and natural gas production, which contain both soluble and insoluble (oil droplets not removed prior to physical separation) petroleum fractions at variable concentrations. The major hydrocarbon groups present in produced water include alkanes, alkenes, alkynes, aromatics, polynuclear aromatics, and complex hydrocarbon compounds containing oxygen, nitrogen,

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Edited by: L. K. Wang, Y.-T. Hung, and N. K. Shammas © The Humana Press Inc., Totowa, NJ

Table 1
Oil and Grease Concentrations in Wastewater of Selected Industries

Type of industry	Oil and grease concentration (mg/L)
Palm oil industry	4000
Food processing	3000–4000
Mining operation	3000–23,000
Metal finishing	100–5,000
Steel-rolling mill	7200
Aluminum rolling	5000–50,000
Oil drilling	7–1300
Crude oil tank ballast	3–72
Petroleum refinery	16–3200
Can production forming	200,000

Adapted from Patterson (1).

Table 2
Oily Wastewater Stream Compositions in Mining Operation From Selected Site Locations

Site locations	Free oil	Emulsified oil	Grease	Diesel or gasoline
Ore crusher houses	√	√	√	—
Plant workshop	√	√	√	—
Drill and shovels	√	√	√	√
Workshop	√	√	√	√
Primary crusher	—	√	√	—

Adapted from Guerin (2).

and sulfur. Produced water from gas production operations generally contains higher levels of benzene, toluene, ethyl-benzene, and xylene (BTEX) than those generated from oil production (4). Chapelle (5) has reported that relatively water soluble light aromatics of BTEX comprise only 2–3% of most crude oils as a whole. Stephenson (6) reported mean concentrations of benzene ranging from 5.8 to 12.2 mg/L and 1.3 to 8.7 mg/L for gas and oil production, respectively.

Another major source, of oily wastewater is food processing industry. Oily and fatty materials are produced mainly from slaughtering, cleaning, and by-product processing (1). The oily vegetable extraction is also the source of oily waste. Ahmad et al. (7) have reported oil and grease concentrations from palm oil processing, which produced as high as 4000 mg/L of oil resulting in high BOD and COD contents.

In general, oily wastewater found in industry comes from many sources including floor wash, machine coolants, alkaline/acid cleaners, and spills from manufacturing process, as shown in Table 3. The nature of oily wastewater is varied due to their production source. Oil from spill is mainly free and emulsified oils, while oil from alkaline and acid cleaning process is normally highly emulsified due to presence of surfactants. Mixtures of various types of oil could be found in wastewater generated from floor wash. These oily wastewaters can be present in both free and emulsified forms stabilized by dirt, debris, and solvents. Oils from petroleum refining or oil from drilling activity

Table 3
Sources of Oily Wastes From Industries

Source	Industries	Nature
Alkaline and acid cleaners	Metal fabrication, iron and steel, metal finishing, industrial laundries	Normally highly emulsified due to surfactants; difficult to treat
Floor washes	All industries	Mixture of various types of oils from spills of hydraulic and cutting fluids, oil mists from spraying/coating, etc.; can be present in both free and emulsified forms stabilized by dirt and debris, and solvents
Machine coolants	Metals manufacturing machining	Normally emulsified and difficult to treat
Vegetable and animal fats splitting, refining, rendering	Edible oil, detergent manufacture, fish processing, textile (wool scouring), leather (hide processing), tank car washing,	Both free and emulsified oils; difficulty of treatment varies
Petroleum oils	Petroleum refining, Petroleum drilling	Both free and emulsified oils; difficulty of treatment varies

Adapted from Cheryan and Rajagopolan (8).

are frequently found in both free and emulsified oils making it more difficult in later oily water separation process.

2. OIL PROPERTIES

Several forms of oil and grease present in wastewater are free, dispersed, or emulsified (9). The droplet size of oils is a major factor for their classification. Free oil has a droplet size larger than 150 μm. Dispersed oil is characterized by droplet sizes ranging from 120 to 150 μm. Oily water, with droplet size less than 20 μm, is classified as emulsified oil.

Tabakin et al. (10), have purposed more specific oil categories based on its physical forms in wastewater:

- Free oil—the rapidly rising oil to the surface of wastewater under quiescent conditions.
- Mechanical dispersions—fine droplets that are stabilized by electrical charges or other forces but not through the influence of surface active agents.
- Chemically stabilized emulsions—oil droplets that are stabilized by the surface active agents at the oil/water interface.
- Dissolved oil—very fine droplets (typically less than 5 μm) that truly soluble species in the chemical sense.
- Oil-wet solids—oil that adhered to the surface of particulate material in the wastewater.

Additionally, oil can be classified by its density. If the ratio of the density of oil to receiving water is larger than 1.0, oil will not float and, with a density less than 1.0, oil will float. Within a few percentage of 1.0, oil is much more likely to become submerged by wave action. The density is also shown in terms of the API (American Petroleum

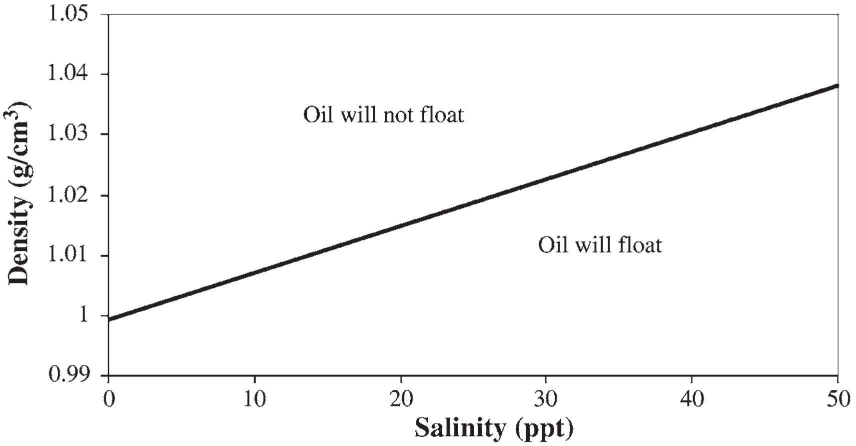

Fig. 1. The relationship between density and salinity at a temperature of 15°C (ppt = parts per trillion). [Adapted from National Academic of Sciences (15).]

Institute) gravity. As shown in Fig. 1, with higher densities than receiving water (above the line), oil sinks; with lower densities (below the line), it initially floats.

In oily wastewater treatment, two types of oil are need to be removed; free and emulsified oils. Free oil has lower specific gravity than water. It can rapidly rise to the surface, thus it is called "floatable oil." It is generally considered to have droplet sizes larger than 250 μm in diameter.

Emulsified oils are often resistant to being separated from water because the droplets are either resistant to rising to the surface or they rise so slowly that they cannot be removed with most oil–water separators.

Oil properties are the crucial factor for separation and removal from water. Compounds in the oil, such as resins, asphaltenes, and waxes, contribute to the formation of stable emulsions (10,11). Nickle porphyrin in seawater is a stabilizing component in oil (13). Changes in density and viscosity, the formation of stable emulsions, and the dispersion of oil and emulsified oil droplets, all play important roles in inhibiting of an effective separation of both oil and emulsion droplets in water and water droplets from an emulsion (14).

Temperature is also one factor that causes changes in oil properties. For example, most crude oils and refined products have specific gravities between 0.80 and 0.98 g/cm^3. The density of both water and oil can be lowered with increasing temperature, as shown in Table 4. Thus, the net effect on the buoyancy force is very restricted for separation of oil droplets from water.

3. TREATMENT TECHNOLOGY

3.1. Process Selection

Oily wastewater treatment can be classified into two categories: primary and secondary treatment systems. The primary treatment is employed to separate floatable oils from water and emulsified oil. This system is suitable for oil or grease that is of lower specific gravity than water. Skimmer and gravity separation are the major treatment systems belonging to this group. A secondary treatment system's goal is to treat or

Table 4
Changes in Density of Oil as a Function of Temperature

Temperature (°C)	Water density	Fuel oil density	Density difference
10	1.024	0.880	0.144
30	1.020	0.870	0.150
50	1.012	0.855	0.157

Adapted from Nordvik et al. (14).

break emulsified oil and, then, remove oil from water. Various techniques used for separation of emulsified oil include chemical treatment, dissolved air flotation, membrane filtration, electrical process, hydrocyclone, and the novel technology of ultrasonic field application.

Generally, the principles used to separate oil and water include gravity, centrifugal separation, and filtration. Although gravity settling and centrifugal separation largely depend on density differences, filtration depends on pressure difference and molecular size and filtration depends on gravitational forces. Viscosity is also an important property of oil, playing a vital role in separation of water from an emulsion. The effectiveness of gravitational separation is enhanced by increasing the droplet diameter and/or buoyancy force, or replacement of gravitational force by centrifugal force, as well as lowering viscosity. As droplet sizes play an important role in gravitational, centrifugal, and filtration separations, possible guidelines for process selection from various oil droplet size categories have been developed (16) as shown in Fig. 2.

To select an appropriate oil–water separation technique, knowledge of droplet size distributions in oily wastewater is the most crucial parameter that has to be identified (17). Three techniques commonly used to determine size distributions are:

- Coulter counter.
- Light microscope.
- Laser particle size analyzer using light-scattering properties of the droplets.

A new method for droplet size measurement, using a bench-top pulsed-field-gradient NMR spectrometer operating in the time domain, has been reported (18). The continuous water phase is successfully suppressed by gradient pulses in order to measure the dispersed oil phase. Simulations show that for most common oil/water food emulsions the influence of droplet diffusion is negligible due to a rather large droplet size or a high viscosity of the continuous water phase.

If the droplet size is not known, or a large range of droplet sized is present, which is frequently a normal situation, it is necessary to make some estimates of droplet sizes to determine the rise rates of the droplets and therefore the separator type and size can be obtained.

3.2. Primary Treatment System

3.2.1. Skimming Process

Primary treatment is necessary to protect the downstream oil–water treatment system from being overloaded. Basic primary treatments include skimming and gravity separators. Skimming is widely used as the fundamental method to remove floatable oil from the surface of wastewater. It is the primary process considered in selecting separation

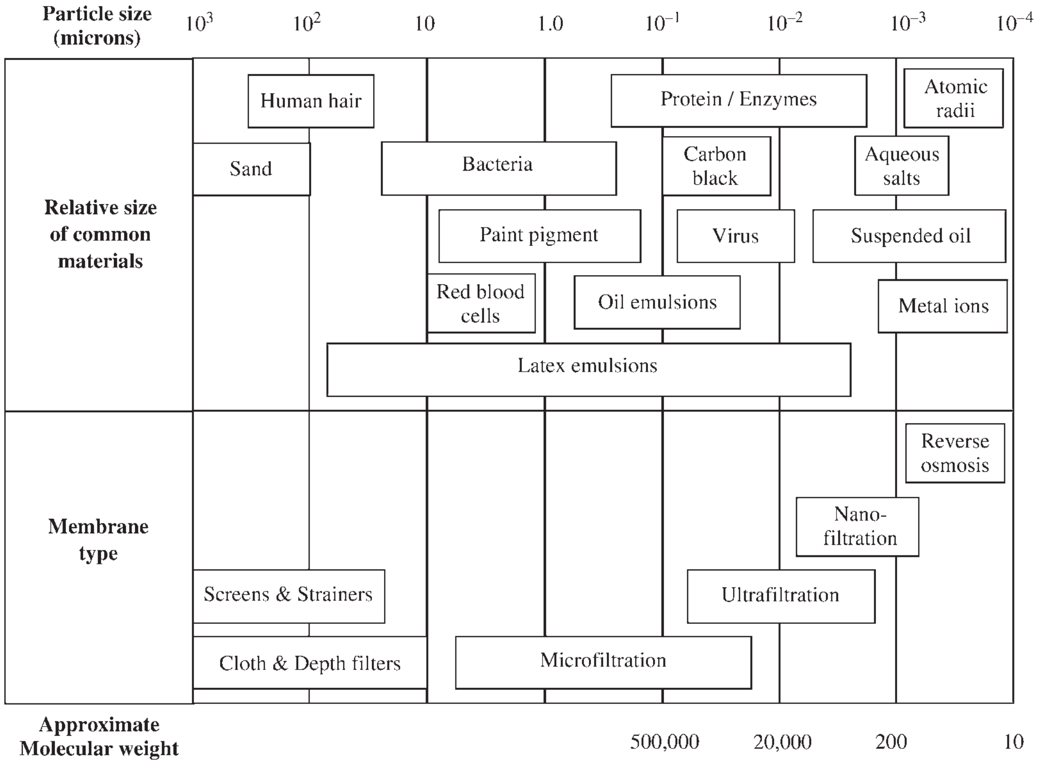

Fig. 2. Separation technologies based on droplet sizes. [Adapted from Nordvik (14).]

technologies for oil removal and recovery. The effectiveness of a skimmer is dependent on oil properties, skimming principle, and oil thickness. A significant potential for improvement of oil recovery capacity by use of this enhanced separation technique has been reported (19). However, the disadvantage of this process is the operation interruption when full storage bladders are unloaded or exchanged for fresh units. In addition, this system is sensitive to adverse weather conditions (14).

Skimmers may equipped in different ways such as free floating, built into a vessel, side mounted on a vessel, or held by crane. Several types of skimmer may be used for oil removal. The rope skimmer is one type that employs polypropylene, PVC, or aluminum as adhesion materials, as shown in Fig. 3. The floating oil can be attached to these moving surfaces and removed out of the water. The belt skimmer (Fig. 4) is used to convey floating oil by moving through the oily waste from water. In a filter skimmer, the water can pass through the belt while the oil is filtrated and adhered on the belt. At the top of the belt the oil is scarped off into a sump or a pump.

The vortex is another technique used in a skimmer with rotating and evacuating water through the bottom of the recovery tank. By using a large propeller pump or paddle wheel, a vortex condition is created in the central part of skimmer resulting in water and oil being dragged toward the skimmer. The centrifuge function is therefore developed, which tends to allow building up of an increased oil layer in the center of the vortex. Finally, oil is pumped or removed by weir at the center of skimmer.

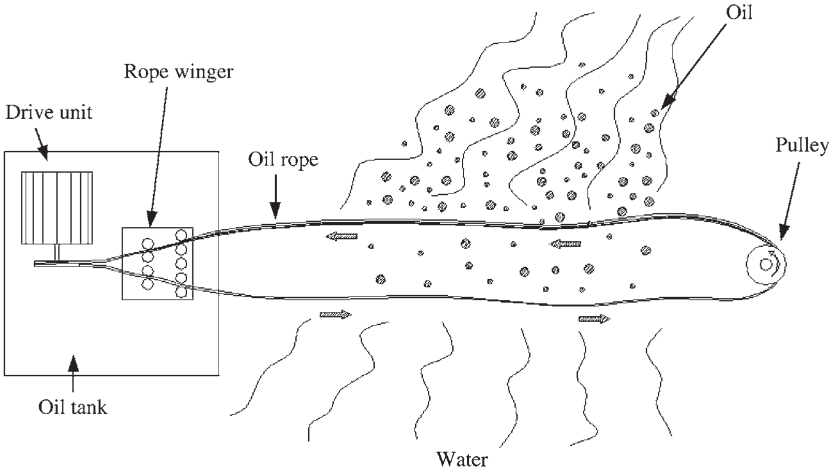

Fig. 3. Rope skimmer using polypropylene as an adhensive material.

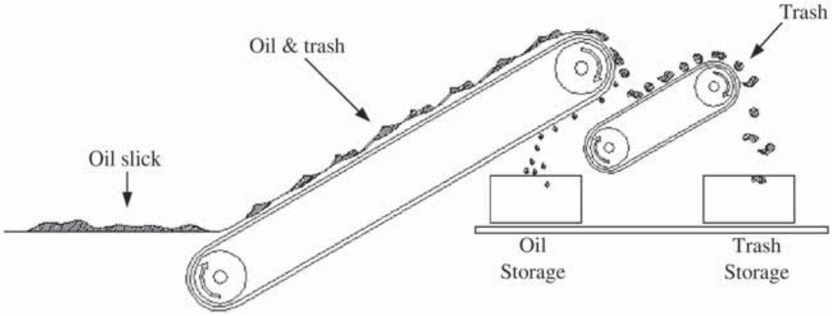

Fig. 4. Schematic of belt skimmer and mechanism of oil removal.

3.2.2. Gravity Separation

Gravity oil–water separators have long been widely used as a pretreatment stage to remove free oil. These systems also perform as a sedimentation basin in capturing settleable solids. The treatment process generally includes holding oily wastewater in a quiescent tank and allowing gravity separation of oily material. The conventional gravity separator is shown in Fig. 5.

Gravity separation is governed by Stokes's law. This law assumes laminar flow, spherical droplets, and ideal droplet distribution. Although these conditions are difficult to achieve in the oily waste, Stokes's law can be used to demonstrate the effect of changes in oil properties on separation of both oil and emulsion droplets in water and for separation of water droplets from an emulsion (14). Turbulence and short-circuiting occurring in a gravity separator are a common operational problem. The effectiveness of a gravity separator depends on proper hydraulic design and designed periods of wastewater retention (1). A high performance of floatable oils separation from water can be expected with long retention times. However, the gravity separators should not be expected to achieve effluent levels less than 100 mg/L (21).

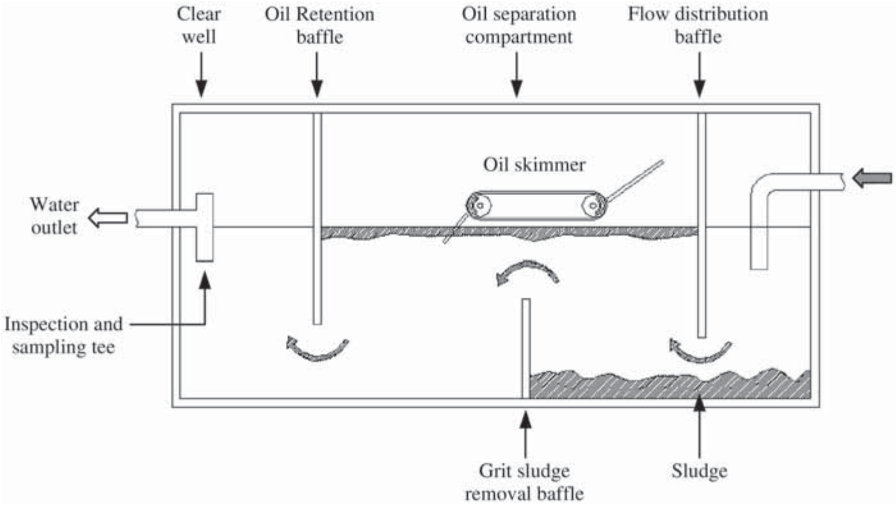

Fig. 5. Schematic diagram of conventional gravity separator. [Adapted from Romano (20).]

This technique is appropriate for large oil droplets with density differences (i.e., light hydrocarbon products such as diesel, gasoline, and kerosene), low water viscosity, and high temperatures. This gravity separator does not effectively separate emulsified oils of small droplet size from the water phase (2). Very small particles such as those of 8 μm and less in diameter do not rise according to Stokes's law because the random motion of the molecules of the water is sufficient to overcome the force of gravity and therefore they move in random directions. This random motion is known as Brownian motion. As the volume of a droplet decreases according to the cube of the diameter, these very small droplets tend to contain very little oil by volume, and unless there are large quantities of very small droplets, they contain negligible amounts of oil.

The coalescent principle becomes the significant principle for small-oil-droplet removal. When the droplets coalesce, they do not form flocs as the solid particles can, but coalesce into larger droplets. Interfacial or surface tension of the liquid tends to make the droplets from spherical shapes, which follows the assumption of Stokes's law mentioned previously. With coalescent principle, the Stokes's law can be applied. The coalescent technique widely used in oil droplet removal is the plate separator.

The plate separator is a major configuration of gravity separators. This equipment uses differences in densities between oils and water as a principle separation technique. The module can be a single plate or three plates or may contain a nest of parallel plates, which is typically 10–20 mm wide. The operational principles of plate separators are to allow oil droplets rise to a plate surface where coalescence can occur and to form larger oil droplets, which are easier to separate. The performance of the plate separator can be enhanced by selecting appropriate plate designs or by the use of a coalescer.

A parallel plate separator is a modified type of plate separator using the same mechanism as the conventional gravity separators. The effectiveness of this separator is increased by installation of parallel plates in the separation chamber, without requiring

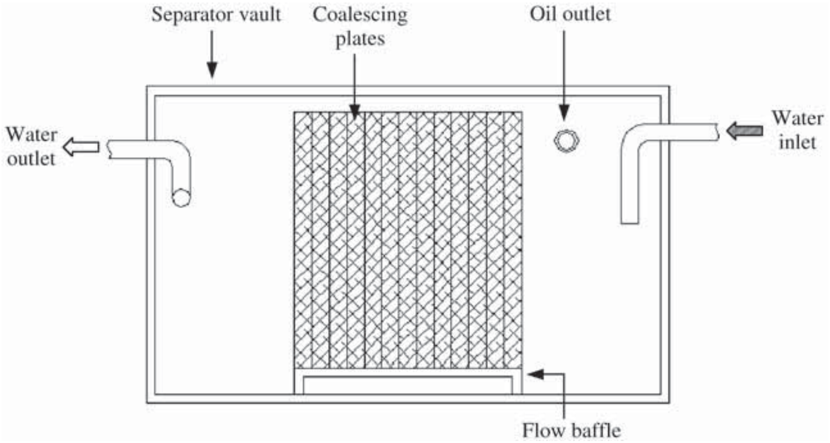

Fig. 6. Schematic diagram of corrugated plate interceptor separator (CPI). [Adapted from Romano (20).]

an increase in separator basin size. Advantages of parallel plate over plate separator are (2).

- decreasing in space requirement for each unit
- increasing in flow through the unit (by two to three times)
- reduction of nonuniform, turbulent flow characteristics, which provides more preferable conditions for oil water separation
- increasing removal efficiency of smaller oil droplets of free oil

The standard unit of gravity separation in floating oil treatment is the API separator. This type of separator is based on design standards published by the American Petroleum Institute. Two other gravity separators are parallel plate interceptor (PPI) and corrugated plate interceptor (CPI). In comparison, the PPI and CPI units provide an advantage over API in requiring a smaller area for installation and having minor cost advantages.

The PPI was designed to improve the performance of existing horizontal–rectangular API separator by installing a series of parallel flat plates at a 45° angle to the direction of water flow. This separator is used for separation of larger oil globules and larger suspended particles as well as finer oil globules. Parallel plates provide a large surface area for oily waste to flow over and provide enough opportunities for coagulation of finer oil globules into larger oil globules.

The CPI system contains closely spaced plates, which enhances the removal efficiency. A schematic diagram of corrugated plate interceptor or CPI is shown in Fig. 6. The angle of the plates to the horizontal ranges from 0° to 60°, with 45°–60° being the most common. The perpendicular distance between the plates typically ranges from 0.75 to 1 in. Figure 7 shows a schematic illustration of modified CPI. In this module the oily wastes first pass through the coalescence section where small oil droplets coalesce into larger ones. The larger oil droplets subsequently flow with the water into the separation section where the oil–water–sludge is separated (22). Generally, conventional separators are capable of removing oil droplets with diameters equal to or larger than 150 μm. A CPI separator should be used if smaller droplets need to be removed.

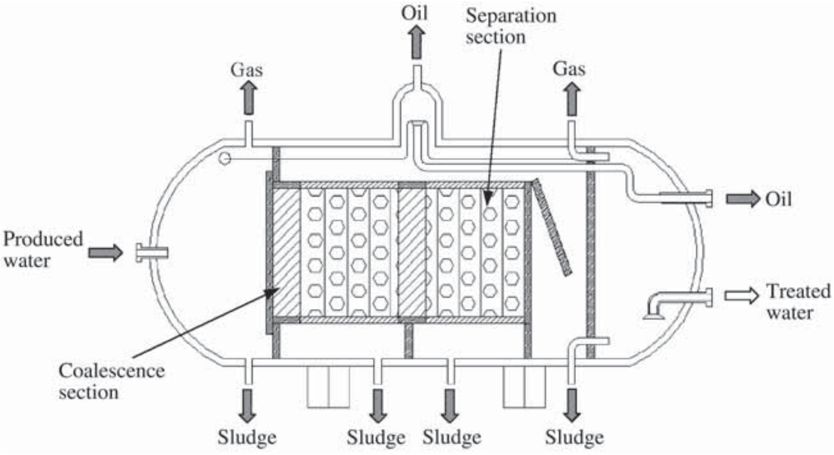

Fig. 7. Modified corrugated plate interceptor separator. [Adapted from Deng et al. (22).]

Mechanical sludge removal equipment may be necessary for sludge handling for gravity separators. Special care for clogging problems, which frequently occur, is required. Many reasons cause clogging problems such as plate inclination is too shallow or to narrow. The mechanical cleaning or flushing with water or air may be required to clear blockages. Clean parallel plate separators are needed to achieve high efficient systems.

3.3. *Secondary Treatment System*

The secondary treatment's goal is to remove emulsified oils or emulsions, which have passed through the primary separator out into water. Emulsions are defined as a colloidal suspension of a liquid within another liquid with droplet sizes typically less than 20 μm. Thus, emulsified oils are the oil droplets that are reduced in size to such a degree that the oil's normal electrical repulsion of the water molecule is overcome due to its minute size. Emulsion can form in several ways as follows (21):

- Energy: pumping, mixing, and other activities of adding energy to a wastewater may, accidentally or purposefully, mechanically emulsify oil.
- Emulsifiers: certain organic chemicals such as soaps and detergents can lower specific gravity of oil causing separating oil from water by gravity to be more difficult. This process widely used in industrial application to dilute oil with water without stratification.
- Heat: some organic chemicals can become emulsified at high or low temperatures.

Emulsion can be broken by many methods such as chemical, electrical, or physical methods. The common methods for emulsion breaking are:

- Chemical treatment method: two methods usually applied for breaking emulsion include acidification and coagulation. The combination of pH adjustment and coagulant addition is also widely used.
- Flotation system: this process is functioned by increased differences in specific gravity between the oil and water by blowing fine air bubbles through the oily wastewater. The most common floatation system is dissolved air flotation (DAF) process.
- Filtration: membrane filtration is a common process that is widely used in many industries. The examples of membrane filtration include microfiltration, ultrafiltration, nanofiltration, reverse osmosis, and the newly developed technology such as hydrophobic membrane.

- Hydrocyclone: hydrocyclone is a physical method used to break emulsion and remove oil from water. This method increases the force for phase separation, which also can handle solids in the influent.
- Electrical process: electrofloatation and electrocoagulation are oil destabilization techniques that utilizes electricity as the major unit for oil and water separation.

Each method is described in details in the following section.

3.3.1. *Chemical Treatment*

The chemical treatment method is the most effective method to break very stable emulsions. This process usually destabilizes dispersed oil or emulsified oil as the first stage, followed by the removal of the separated oil as the second stage. Acidification and coagulation are the common processes for chemical treatment.

Acidification or acid breaking is a process in which the pH of the wastewater is controlled in the acidic range during mixing, which is followed by gravity flotation. However, the pH required for acid breaking largely depends on the nature of the waste. For example, pH as low as 2 was used for oily waste from aluminum can forming process, while a pH in a range of 5.0–5.5 was used for destabilization of oil from steel manufacturing (1). Various acid solutions such as sulfuric, nitric, and hydrochloric acids can be used. This method is more often combined with DAF.

Coagulation can result in the formation of larger droplets, called coalescence or precipitation. Coalescence process the enhances the volume of free oil removed, while precipitation increases the volume of solids generated by the process. A metal salt such as alum [$Al_2(SO_4)_3$], ferrous sulfate ($FeSO_4$), ferric sulfate [$Fe_2(SO_4)_3$], or ferric chloride ($FeCl_3$) or a cationic, anionic, or non-ionic polymer can be applied for emulsion breaking. The surface charge of emulsion as anionic, neutral, or cationic is a key consideration for chemical selection. The gravity sedimentation or air flotation unit is commonly employed as an alternative to separate the oil and water. To minimize amount of coagulants, the addition of chemicals to the wastewater should apply as far as upstream of the following separation unit before the oily waste is greatly diluted.

3.3.2. *Dissolved Air Flotation*

Dissolved air flotation (DAF) is the process of removing suspended solid, oils, and other contaminants via the use of air bubble flotation. Air is dissolved into water, mixed with the waste stream prior to being released from the solution and is in intimate contact with the contaminants. The small bubbles will attach to the floatable oils, increase their buoyancy, and reduce their specific gravity. In this system, a side stream of the oily waste is supersaturated under pressure with dissolved air so that the movement of the air bubbles will carry the floatables upward where they can be removed (46,51).

To achieve efficient clarification by using DAF, coagulation and flocculation is required prior to the introduction of the air bubbles to form the bubble-floc aggregates. A good coagulation pretreatment will enhance the oily removal efficiency. The chemicals used as coagulants have a role in producing the floc particles that are hydrophobic leading the ease of oil–water separation in DAF process. Trivalent metallic salts of iron, such as $FeCl_3$ or $FeSO_4$, or aluminum are the chemical agents most helpful in improving the effectiveness of DAF process (1). Organic and inorganic polymers (cationic or anionic) are often used to enhance the DAF process. Chemical concentrations used normally range from

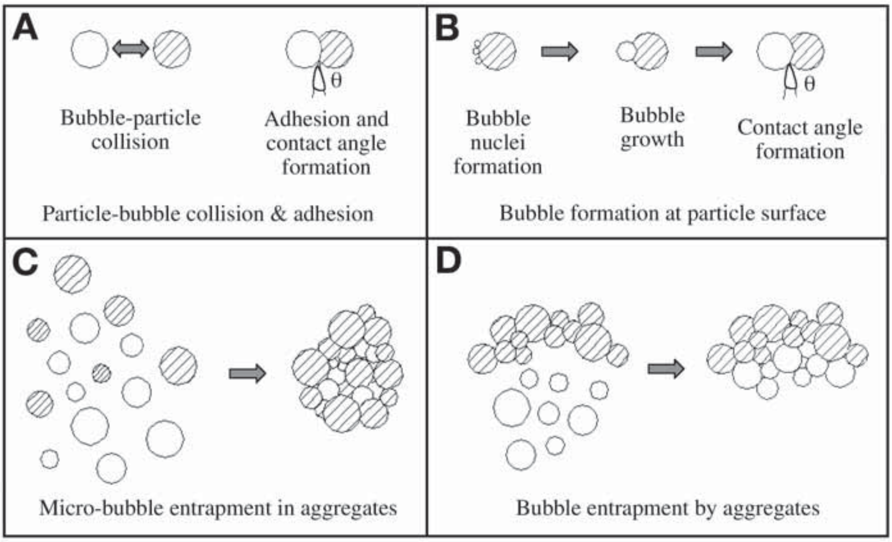

Fig. 8. Bubble–particle mechanisms in DAF: (A) particle–bubble collision and adhesion; (B) bubble formation at particle surface; (C) microbubble entrapment in aggregates; (D) bubbles entrainment by aggregates. [Adapted from Rubio et al. (24).]

100 to 500 mg/L. The pH of wastewater should be adjusted to between 4.5 and 5.5 for coagulation using ferric compounds or between 5.5 and 6.5 for aluminum compounds. The pH adjustment can be done by sulfuric acid or sodium hydroxide addition.

Mechanisms forming the agglomeration of floatable bubble–floc in DAF process are shown in Fig. 8 (24). The beginning of agglomeration is started with particle/bubble collision and adhesion. Apart from that, in DAF, part of the dissolved air in water, which does not convert into bubbles in the nozzle, remains in solution and nucleates at the particle surface (25). This mechanism is independent on surface hydrophobicity and allows flotation of hydrophilic particles. Moreover, bubble entrapment into flocs or coagula and aggregate entrainment by the rising bubbles are mechanisms that make separation easier. However, a major disadvantage is that rapid air bubble levitation speed is not attainable and hydraulic loadings are low reducing and limiting process capacity.

The quantity of air supplied to the flotation tanks is also the important factor affecting the oily waster separation. The air bubbles may be generated in several ways including:

- Vacuum-activated release of dissolved gases—In this system, the oily suspension is saturated with air at atmospheric pressure. Then the air is released from solution when the suspension is subjected to vacuum conditions in a floatation unit. The available amount of air is a limitation of this technique.
- Air injection through submerged diffusers—This technique provides the finely dispersed air bubbles to the oily stream.
- Dissolution of air at high pressure in part of the stream, with its subsequent release in fine bubble form on reduction of the pressure to atmospheric level—This method is widely used in DAF process. In this process, a clean water stream is partly saturated with air at an elevated pressure at 4–6 atm gauge. The high-pressure stream is mixed with the influent at the flotation tank inlet. The tiny bubbles are formed and released from the excess air originating from the pressure reduction of the stream.

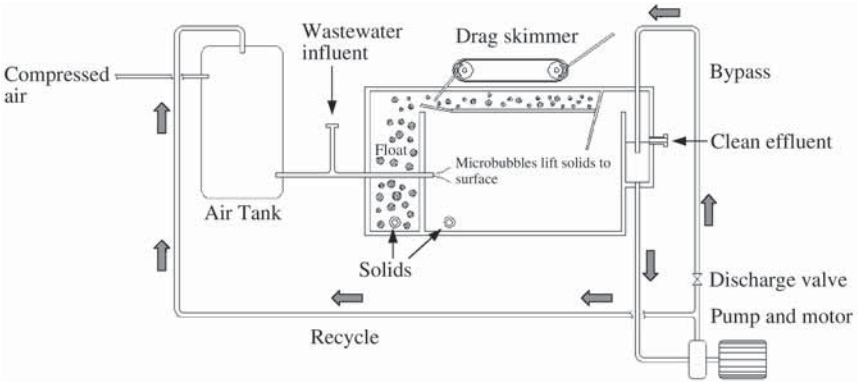

Fig. 9. A schematic of conventional dissolved air flotation unit.

A schematic of conventional DAF unit is shown in Fig. 9. In this unit a recycle pump combined with a saturation vessel and air compressor are used to dissolve air into the water. The dissolved air comes out of solution, producing microscopic bubbles. These bubbles attach to the solids and float them to the surface where they are mechanically skimmed and removed from the tank. This application can be modified and used for various oily industrial wastewaters (51).

Air flotation process might be inefficient when treating high-volume effluents and high flow rates due to the long retention time requirement (24). Removal of very fine oil droplets in range of 2–30 μm is difficult and very limited. Fine bubbles, quiescent hydrodynamic conditions in the cell separation zone, or emulsion breakers prior to flotation are required (17). This is due to collection and adhesion factors, which makes the process very slow when treating with high flow rates.

3.3.3. *Membrane Filtration*

Membrane processes are widely used in oil water separation. In general, a membrane is classified into two groups: pressure-driven membrane and electrical membrane, known as electrodialysis. The most applicable process for oily wastewater removal is the former type. The pressure-driven membrane applications include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). All of them are categorized by the molecular weight or particle size cut-off of the membrane as shown in Table 5.

Membranes are useful for stable emulsion removal particularly water-soluble oily wastes (8). This process is generally regarded as polishing technologies for emulsified oils. The low effluent concentrations of oil less than 5 mg/L could be achieved by this technique (2). Membrane processes have several advantages as described as follows (8,53):

- Applicable for wide range of industries.
- A barrier to rejected components. The quality of treated water is relatively uniform.
- Extraneous chemicals are not needed.
- It can be used in-process to allow recycling of selected waste streams within a plant.
- Concentrates up to 40–70% oil and solids can be obtained by UF or MF.
- Membrane equipment has a smaller foot print.
- Energy costs are lower compared to thermal treatments.
- The treatment plant can be highly automated and does not require highly skilled operators.

Table 5
Types of Pressure-Driven Membrane Processes as Categorized by Size Cut-Off Range

Membrane processes	Size cut-off range (μm)
Microfiltration (MF)	0.05–1.5
Ultrafiltration (UF)	0.002–0.05
Nanofiltration (NF)	0.0005–0.007
Reverse osmosis (RO)	0.0001–0.003

Adapted from Casey (26).

Among the membrane processes, UF is an attractive alternative for the treatment of emulsions, as no chemical additives are required, high removal efficiencies can be achieved and it has low capital and operating costs (27). However, this technique has two drawbacks: concentration polarization and membrane fouling (28). As a filtration process, membranes used are truly porous and separation is a physical process requiring elevated pressure to achieve passage of fluid through the filter. The water and other low-molecular-weight solutes pass through the membrane pores. The larger molecules or aggregates are rejected. The most successful UF separation performance is obtained when discrete and stable emulsion particles of oil, larger than the membrane pore size, are maintained.

Macrofiltration (MF) membrane, with pore sizes of 0.1 μm, have been used to recover surfactants in the permeate. If the salt content of oily wastewater is too high for direct reuse of the permeate in the plant, it can be treated by RO and NF (8,29). In addition, RO can selectively reject solutes of the same size order as water molecules.

Polymeric compounds such as cellulose acetate, polysulfone, or polyethersulfone or inorganic compounds such as alumina and glass materials are used in hydrophilic membranes. These membranes consist of small pores in which water free of oil or reduced oil content can be recovered as permeate. This membrane type preferentially attracts the water rather than the oil. In hydrophobic membrane, the oil-rich mixture can be obtained as permeate from the filtration process. Hydrophobic membrane is usually in a tubular configuration that allows a high degree of turbulence (cross-flow velocity) to be maintained in order to minimize oil wetting of the membrane (8). Polytetrafluroethylene (PTFE) is a widely used material for hydrophobic membrane. The possible steps governing the permeation of oil through the hydrophobic membrane is shown in Fig. 10 (30). The oil transfer in the membrane process might be explained as, first, oil droplets attach to the membrane due to the hydrophobic surface and the high velocity of the fluid toward the membrane surface. The oil droplets can detach from the membrane surface due to the high fluid velocity parallel to the membrane surface. The capillary force and operating pressure can cause the penetration of the remaining oil into the membrane pores. The last step, oil is released from the membranes by sweeping with an inert gas. Physical properties of the membrane and oil, membrane pore size, operating pressure, and flow velocity of the feed are the crucial factors governing the oil transfer (Fig.10). The crucial limitation of polymeric membranes is fouling and degradation while using. Frequent replacement is needed and thus, not only the capital cost of membrane but also the operating costs can be relatively high for large membrane units compared with other oil and water separation systems.

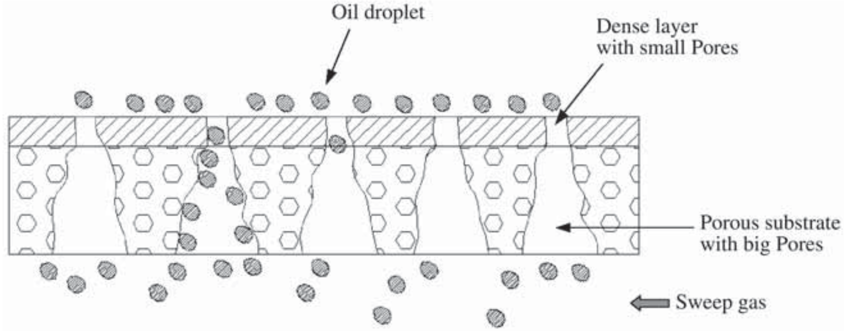

Fig. 10. Schematic diagram of oil transfer in hydrophobic membrane. [Adapted from Kong and Li (30).]

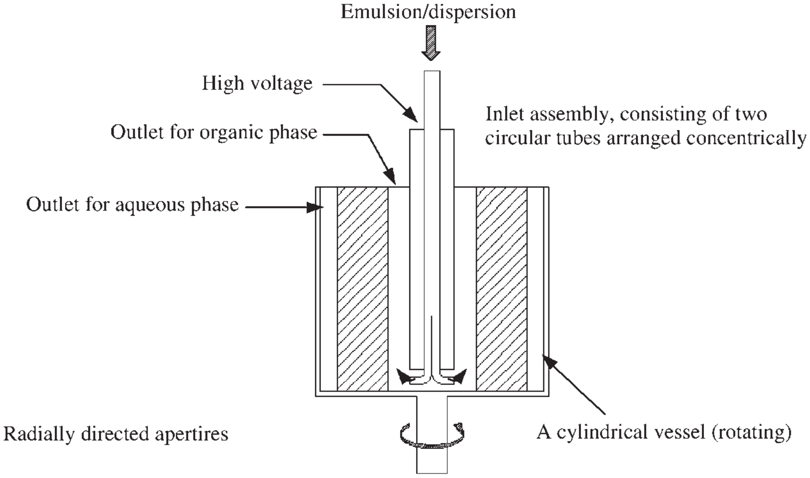

Fig. 11. A schematic of electrostic and centrifugal separation of ily liquid. [Adapted from Bailes and Watson (32).]

3.3.4. *Electrical Process*

3.3.4.1. ELECTROCOALESCENCE

The application of electrocoalescence is largely concentrated and limited in the oil and petroleum industries where high-voltage alternating current (AC) fields and direct current (DC) fields are used for separation of water droplets from crude oil (31).

There are several inventions combining electrostatic coalescence of water with other separate ion technologies such as centrifugal force, mechanical, filtration, heating, and chemical treatment. A schematic of electrostatic and centrifugal separation of oily liquid is shown in Fig. 11 (32). An aqueous electrolyte–oil emulsion is supplied into a rotating cylinder via plastic tubes and a distributor, removing the electrolyte from the edge of the cylinder, and the organic compounds from the adjacent tubes. The emulsion is separated by the application of a radial electric field and a centrifugal force simultaneously to produce a bulk interface perpendicular to the direction of the electric field and centrifugal force (31). The electric field is applied to ensure that coalescence and enlargement of the dispersed aqueous droplets are of sufficient size. It is vital that centrifugal force should be in certain levels that can separate the droplets without producing sufficient shear force to break them up.

Sublette (33) utilized a mechanical coalescence medium, e.g., an inclined surface separator, after a system of charged electrodes. Coalescence of the droplets occurs when it passes the inclined surface separator. The oily droplets encounter each other, then accumulate and agglomerate along the surface. The larger droplets finally leave the surface and separate from the water.

The combination of chemical and electrical treatment has been reported (31). Compounds, used in this application, are chemicals that have a property of liberating free chlorine radicals, such as chlorinated oils, chlorocosane, chloramines, toluene, and hydrochlorites. Effects of chemicals on the breaking of petroleum have been investigated. The most general explanation is that the coalescence of the dispersed phase in emulsion resulted from both chemical reaction and physical effects of the chemicals, change the interfacial properties and facilitating droplet–droplet coalescence.

Advancement of this technology has been applied in many industries. A major potential application of the electrocoalescence technology is in the edible oil production industry such as palm oil processing technology and bioprocesses (51,53).

3.3.4.2. ELECTROFLOTATION

Electroflotation is an alternative to air floatation to induce small gas bubbles or "microbubbles" formation through the electrolysis of water, generating oxygen and hydrogen gases. The basis for the microbubbles generation includes electrolysis of diluted aqueous and conducting solutions with the production of gas bubbles at the surface of the electrodes (24). The anode electrodes frequently are iron or aluminum, which is coupled with an inert cathode. The limitation of this technology is separation efficiency, which is restricted by the oil concentration in emulsion. However, adding flocculating agents in the electrolyte could also overcome this limitation (34). This mixture could promote the separation of the oil from wastewater.

The flotation step starts with adding of solution into electroflotation cell in which gas bubbles produced at the level of the electrodes raise the flocs formed by flocculation to the surface of the cell. The fine bubbles, that necessitate buoyancy to separate oil from emulsions, come from the water electrolysis (H_2, O_2) in accordance with two reactions below (53):

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

$$H_2O \rightarrow 1/2\ O_2 + 2H^+ + 2e^-$$

The gas produced at the level of the electrodes passes through the aqueous phase (35).

Applications of this process at an industrial scale have been in the area of removal of light colloidal systems such as emulsified oil, ions, pigments, ink, and fibers from water (36,37). The advantages of this process are the clarity of the treated wastewater and the disadvantages are the low throughput, the emission of H_2 bubbles, electrode costs and maintenance, and the voluminous sludge produced (24).

3.3.4.3. ELECTROCOAGULATION

Electrocoagulation is a simple and efficient method for oily wastewater treatment. Ideally, this process takes advantage of the combined effect. This method utilizes consumable electrodes such as Fe or scrap iron. Voltage, applied to the system, oxidizes the electrode to release a metallic coagulant such as the ferrous ion. The metallic ions can react with the OH^- ions produced at the cathode during the evolution of H_2 gas to yield insoluble hydroxides. In the meantime, gas bubbles carry oil and grease to the surface of wastewater. The oil and grease will be adsorbed on the insoluble hydroxides. Thus, it is easily collected and removed out of the solution (38).

The electrocoagulation process is characterized by a rapid rate of pollutant removal, compact size of equipment, simplicity in operation, and low capital and operational costs. Moreover, it is particularly more effective in treating oily waste due to accompanying of electroflotation effect. The waste stream of this process requires sufficient conductivity for cell operation and to prevent passivation of the electrode material.

4. ENGINEERING DESIGN

4.1. Gravity Flotation

In general, conventional oil water separator in which gravity is the major reason for this separation method, can be basically designed using Stokes' Law.

As described in Section 3.2.2 (gravity separation), oil and water can be separated using gravity force in conventional a air–water separator, the design of the gravity floatation can be done using Stokes' law. This law developed in 1845 by an English mathematician named George Stokes. The law described the physical relationship that governs the settling of solid particles in a liquid. This same relationship also governs the rising of light liquid droplets within a different, heavier liquid.

Assumptions of this law are:

- Particles are spherical.
- Particles are the same size.
- Flow is laminar, both horizontally and vertically. Laminar flow in this context means flowing gently, smoothly, and without turbulence.

The equation is as follows:

$$\upsilon = \frac{gd^2(d_o - d_w)}{18\mu} \tag{1}$$

where υ = rate of floatation, cm/s; g = acceleration due to gravitiy = 980 cm/s^2, d = particle diameter, cm, d_o = density of oil, g/cm^3, d_w = density of water, g/cm^3, and μ = absolute viscosity of water, poise.

The negative velocity is referred to as the oil droplet rise velocity. The water density and viscosity are shown in Table 6. As those values mainly depend on temperature, the appropriate temperature should be applied to obtain the suitable water density and viscosity for gravity flotation design.

The droplet size of the oil particle should be determined experimentally to apply in Eq. (1). For example, a diameter of petroleum oil globule is typically 0.015 cm (21). The equation reduces to

$$\upsilon = \frac{0.01225\,(d_o - d_w)}{\mu} \tag{2}$$

where υ = rate of flotation, cm/s,

Table 6
Water Density and Viscosity at Different Temperatures

Temperature (°C)	Density, ρ (kg/m^3)	Dynamic viscocity, μ (N-s/m^2) × 10^3
0	999.8	1.781
5	1000.0	1.518
10	999.7	1.307
15	999.1	1.139
20	998.2	1.002
25	997.0	0.890
30	995.7	0.798
40	992.2	0.653
50	988.0	0.547

Adapted from Watts (39).

$$\upsilon = \frac{0.0241\,(d_o - d_w)}{\mu} \tag{3}$$

where υ = rate of flotation, ft/m.

To obtain the horizontal flow velocity, the rate of flotation is applied as follows:

$$\upsilon_L = 15\ \upsilon \tag{4}$$

However, the horizontal flow velocity should not be exceeded 0.0152 m/s. Thus, if the calculated number is larger than this value, the 0.0152 m/s should be applied.

The sizing of gravity separator can be calculated from the minimum vertical cross-sectional area of basin as follows:

$$A_H = \frac{Q}{\upsilon_L} \tag{5}$$

where A_H = vertical cross-sectional area, m^2 or ft^2, Q = wastewater flow, m^3/s or ft^3/s, and υ_L = horizon flow velocity, m/s or ft/s.

To obtain width and depth of the basin, ratio of depth to width of 0.3 is typically used. In certain cases, this ratio can be increased to the absolute maximum of 0.5.

The purpose of the basin depth is for storage and removal without affecting flotation efficiency of floatable and settling particles. The basin efficiency is independent of basin depth. It is recommended that depth of floatation basin should not be less than 0.9 m, preferably 1.2 m. The practical maximum depth is 2.4–3 m (21).

The minimum surface area can be computed as follows:

$$A_S = F\frac{Q}{\upsilon} \tag{6}$$

where A_S = surface area, m^2 and F = turbulence and short circuiting factor. As surface area is the minimum surface area, it provides length and width of the basin. Turbulence and short circuiting are important factors for gravity separation design. This value can be calculated as

$$F = \upsilon_L/\upsilon \tag{7}$$

Thus, the basin length can be calculated from the following equation:

$$L_b = F\frac{\upsilon_L}{\upsilon}d \tag{8}$$

where L_b = basin length, m, F = turbulence and short circuiting factor, υ_L = horizon flow velocity, m/s, υ = rate of flotation, m/s, and d = particle diameter, m.

Other factors to be considered include inlet and outlet designs. Installing inlet baffles with sized opening will enhance flow distribution across entire width and depth of the basin. Underflow baffles following the floatable removal system can also increase the removal efficiency of floatable particles. However, baffles must be deep enough to prevent pulling of the floatable particles under the baffle. It is recommended that flow velocity under the baffle should be limited to 1 ft/min (21).

The outlet of the overflow weir is required to be set at the water level. The weir length should be sufficient to prevent pulling of floatable particles under the baffle, preferably greater than 124 m^3/m-d. The clearance of the baffle and the effluent weir should allow flow velocity to be under 1 ft/min.

4.2. *Coalescing Plate Interceptor (CPI)*

As mentioned earlier, coalescing plate interceptor (CPI) is modified from gravity floatation by adding inclined plates to the conventional unit. The CPI separator contains closely spaced plates that enhance the oil removal efficiency. Required space of this system is significantly less than that of the conventional separator. The angle of plate to horizontal can range from 0° to 60°, commonly from 40° to 60°. The perpendicular distance between plates generally ranges from 0.02 to 0.025 m.

The size of CPI separator is based on the calculation of rise rate of oil droplets, determined as

$$\upsilon_P = 0.54\,(d_o - d_w)\,d_l^2 \times 10^{-8}/n \tag{9}$$

where υ_P = rise rate, m/s, d_1 = diameter of the droplet to be removed, (μm), d_o = density of oil, g/cm^3, d_w = density of water, g/cm^3, n = absolute viscosity of water (poises).

It is believed that the conventional separator is not effective for removal of droplets smaller than 150 μm (21). Theoretically, size of conventional separator that can remove very smaller droplets may be too large that the CPI separator would be more cost-effective.

The size of the CPI separator can be calculated from the expected plate angle, D (as degrees), then identify the required total plate area, A. The degree of plate angle can be determined as follows:

$$A = \frac{Q}{\upsilon_p \cdot \cos D} \tag{10}$$

where A = total plate area, m^2, Q = design flow rate, m^3/s, υ_p = rise rate, m/s, and D = plate angle, degree.

Generally, manufacturers would identify and provide information regarding capacity of various standard CPI units. However, engineers must compare their design criteria to that provided by the manufacturer. Efficiency of CPI separators ranges from 0.35 to 0.95 depending on the plate design. The angle of plate to horizontal can range from 0° to 60°, commonly from 40° to 60°.

The number of plates required can be calculated as:

$$N = \frac{A}{WL_p} \tag{11}$$

where N = number of plate required, W = width of plate, m, and L_p = length of plate, m.

Plate volume can be determined as follows:

$$P_V = \left(\frac{N \cdot S}{100} + L_p \cdot \cos D \right) \left(W L_p \cdot \sin D \right) \tag{12}$$

where P_V = plate volume, m^3, N = number of plates, S = spacing between plates, usually 0.02–0.025 m, W = width of plate, m, L_p = length of plate, m, and D = plate angle, degree.

Routine operational control and maintenance is needed for this type of oil–water separator. Plate cleaning is essential, in order to remove settleable solids, which accumulate on the plates. Moreover, installation of a trash rack or screening with the opening smaller than plate space will prevent this problem.

4.3. Dissolved Air Flotation (DAF)

Dissolved air flotation (DAF) has been widely used over the last 40 yr for removal of oil and grease, suspended solids, and biochemical oxygen demand (BOD) from wastewater and other industrial process stream. The reliability and performance of DAF systems have been improved along with the increasing use of this technology, as shown in Table 7.

The basic concept of DAF is to attach very small bubbles of air to emulsions in order to remove them from water. In this system, a side stream of oil is supersaturated under pressure with dissolved air so that air bubbles will carry the floatable particles vertically upward. A number of advanced DAF designs have contributed to the increased efficiency of this technology, for example:

- Recycle pressurization—Over the years, manufacturers have made a transition from full-flow pressurization to recycle-flow pressurization for the creation of whitewater to induce flotation. Most of the full-flow pressurization systems, which involve pressurizing total influent to flotation cell, operate at low pressure (<50 psig), which limits the amount of air going into solution. In addition, full-flow pressurization exposes the floc to high shear forces and turbulence without destruction prior to entering the flotation cell. The advantages of higher air saturation and undisturbed floc formation outweigh the increased total hydraulic loading to the DAF units.
- Air saturation systems—The advance in dissolving air into water has come primarily from injecting air into pumps capable of handling water with entrained air. The operating pumps work at higher pressure than standard centrifugal pumps, which increases both air saturation and volumetric efficiency.
- Chemical programs—A number of chemical programs for coagulation and flocculation of contaminants have been developed. These chemical programs have improved the destabilization of emulsion through pH control and addition of coagulants, such as metal salts. The resulting floc from these chemical programs can be easier to float and removed by DAF units.

Although DAF has been in use for 40 yr, the design criteria available to engineers are limited in design manuals. The major parameters of concern include hydraulic loading rate, solids loading rate, and air-to solids ratio.

The hydraulic loading rate (HLR) is typically the primary design parameter for most industrial applications. The suggested value range from 11.73 to 234.70 m^3/m^2·min

Table 7
Dissolved Air Flotation Clarifiers–Brief History of Development

Year	Type	Maximum capacity (US gal)	Rate (US gpm/ ft^2)	Retention time (min)	Dissolved air type	Air dissolving tank retention time (s)
1920	SVEEN PETERSON	790 gpm 1.1 MGD	2.0	25	Full	60
1930– 1935	ADKA SAVALLA	600 gpm 0.85 MGD	2.0	20	Vacuum	—
1948	KROFTA Unifloat ADKA Simplex KOMLINE SANDERSON	2500 gpm 3.8 MGD	2.0	20	Full Partial	60
1955	KROFTA Flotator	2800 gpm 4.0 MGD	4.0	20	Full	60
1965	KROFTA Sedifloat ADKA Standard INFILCO Carborundum	4700 gpm 6.6 MGD	2.0	40	Partial	60
1970	PERMUTIT Erpac	4000 gpm 5.8 MGD	3.0	12	Full Partial	60
1975	KROFTA Supracell	8000 gpm 11.5 MGD	3.5	3	Partial Recycle	10
1993	KROFTA Sandfloat BP	20,000 gpm 28.8 MGD	5.0	5	Partial Recycle	10

Adapted from Krofta and Wang (40,41) and Wang, Kurylko, and Wang (42).

(43,44). The HLR of 117.35 m^3/m^2·min without recycle is considered a good starting point in a design (45). Other factors, including pretreatment process and chemical addition, will have an effect on the final design value.

The solid loading rate (SLR) is characterized by dividing mass flow rate of oil stream by available surface area of the floatation unit. The recommended SLR value is ranged from 4 to 10 kg/m^2·h (45). The optimum SLR value is dependent on numbers of other operating conditions.

Air-to-solid ratio is the ratio of mass of dissolved air delivered by the system to mass of solids in influent entering the floatation system. The suggested number is in the wide range from 0.005 to 0.07 mL air/mg solids, with 0.02 as a good design value.

4.4. *Ultrafiltration Membrane*

Ultrafiltration (UF) is a pressure-driven membrane process that can concentrate and fractionate macromolecular solutes and separate suspended species from water. UF provides a nondestructive separation, which can be performed without any phase transition (46). Owing to the osmotic pressure exerted by the high-molecular-weight solutes being negligible, this process is operated at relatively low pressure in range of 0.69–6.91 atm (70–700 kPa) (47,48). The concentrate may contain up to 50% of oil. The oily concentrate can be further separated by centrifugation.

The permeate flux (J) is an important parameter in the design and economic feasibility analysis of the UF separation process. Hydrodynamics of membrane modules have an important effect on the mass transfer, separation, and fouling behavior of membrane systems.

Generally, the pure solvent transporting through porous UF membranes is directly proportional to the applied transmembrane pressure (ΔP). The Kozeny–Carman and Hagen–Poiseuille equations describe the convection flow (J_0) as follows (49):

$$J_0 = \frac{\Delta P}{\eta R_m} \tag{13}$$

where J_0 = initial permeate flux, L/h·m^2, ΔP = applied transmembrane pressure, kPa, η = solvent viscosity, mPa/s, and R_m = intrinsic resistance of clean membrane, 1/m.

A permeate flux declines in the presence of solute due to membrane fouling. A decrease in flux is a result of several phenomenons including adsorption of macromolecules to membrane surface involving pore blocking, concentration polarization, and formation of a gel-like cake layer within the membrane pores (50). Several models have been used to describe solute fouling, among them are hydraulic resistance, osmotic pressure, gel polarization, and film models (51,52).

The permeate flux (J) to the applied pressure is related to the fouling resistance as described by Darcy's law (53):

$$J = \frac{\Delta P}{\eta\left(R'_m + R_p\right)} \tag{14}$$

where J = permeate flux, L/h·m^2, ΔP = applied transmembrane pressure, kPa, η = solvent viscosity, mPa/s, R'_m = intrinsic membrane resistance, 1/m, and R_P = polarization layer resistance, 1/m.

In this equation, R'_m ($=R_m + R_f$) is the intrinsic membrane resistance that includes the fouling layer resistance (R_f) due to specific membrane–solute interactions. The polarization layer resistance, R_P, consists of two resistances: R_g due to gel-polarized layer and R_b due to associate boundary layer. The intrinsic membrane resistance is unaffected by operating parameters, whereas the polarization layer resistance is a function of applied pressure. When R_p is negligible, the filtrate flux is given by (49)

$$J = \frac{\Delta P}{\eta R'_m} = \frac{\Delta P}{\eta\left(R_m + R_f\right)} \tag{15}$$

where J = permeate flux, L/h·m^2, ΔP = applied transmembrane pressure, kPa, η = solvent viscosity, mPa/s, R'_m = intrinsic membrane resistance, 1/m, R_m = intrinsic resistance of the clean membrane, 1/m, and R_f = fouling layer resistance, 1/m.

To determine the relative degree of purification in a given UF process or to estimate the period of UF processing required to achieve a certain degree of separation or purification, the UF process must be mathematically modeled (29). The observed rejection coefficient at any point in the UF process is defined as

$$R = 1 - (Cp/Cr) \tag{16}$$

where R = observed rejection coefficient, Cp = bulk solute concentration in the permeate, mg/L, and Cr = the retained bulk solute concentration, mg/L.

During UF membrane operation, there is a volume rejection. Thus, ultrafiltration data can be presented in terms of volume concentration ratio (VCR) or concentration factor (CF) as shown by the following equation:

$$\mathrm{VCR} = \mathrm{CF} = \frac{V_0}{V_r} = 1 + \frac{V_P}{V_r} \tag{17}$$

where VCR = volume-to-concentration ratio, CF = concentration factor, V_0 = initial feed tank volume, m^3, V_r = retained volume, m^3, and V_p = permeate volume, m^3.

The material balance at any time during UF operation is given by

$$\log(\mathrm{SCR}) = \log\left(\frac{C_r}{C_0}\right) = R\log(\mathrm{CF}) \tag{18}$$

where SCR = solute concentration ratio, R = observed rejection coefficient, CF = concentration factor, C_0 = initial solute concentration in the feed, mg/L, and C_r = retained solute concentration, mg/L.

This equation allows the calculation of rejection using only retentive data.

5. DESIGN EXAMPLES AND QUESTIONS

5.1. *Example 1*

Membrane technology is used to remove oil particles from industrial wastewater. The initial feed tank volume is 8640 m^3/d and after treatment the retained volume is required to be 50% of the initial volume entering to the basin. If the observe rejected coefficient is 0.02, find solute concentration ratio.

Solution:

1. Find concentration factor:

Concentration factor = $\mathrm{CF} = \frac{V_0}{V_r}$

$$\mathrm{CF} = \frac{V_0}{0.5\ V_0} = 2$$

Concentration factor = 2

2. Find solute concentration ratio: The solute concentration ratio, SCR, could be find from

$$\log(\mathrm{SCR}) = R\log(\mathrm{CF})$$
$$\log(\mathrm{SCR}) = 0.02\log(2) = 0.06$$
$$\mathrm{SCR} = 1.15$$

Solute concentration ratio is 1.15

5.2. *Example 2*

CPI separator is used to remove oils and greases from industrial wastewater. The influent concentration of oil is 50 mg/L. The diameter of oil droplet to be removed is 90 μm. Density of water at 10°C is 0.999 g/cm^3 and density of oil is 0.898 g/cm^3. The absolute viscosity of the water is 0.013077 poises. The standard size of plate is 3 × 5 m with spacing 2 cm. Calculate the following items:

(1) Rise rate of oil in cm/s
(2) Total plate area for CPI separator

(3) Number of plate required
(4) Plate volume

Solution:

1. Find the rise rate of oil from Eq. (9):

   Rise rate of oil = $\upsilon_P = 0.54\,(d_o - d_w)\,d_l^2 \times 10^{-8}/n$
   $= 0.54\,(0.898–0.999)\,(90^2) \times 10^{-8}/\,0.013077$
   $= -\,0.00034$ m/s
   $= -\,0.0334$ cm/s

   The rise rate of oil is 0.0011 ft/s or 0.0335 cm/s

2. Find total plate area for CPI separator:

   Total plate area for CPI separator = $A = \dfrac{Q}{\upsilon_P \cos D}$

   $$A = \frac{0.1}{(3.35 \times 10^{-4})\cos 50^\circ}$$

   $$A = 464.4\ \mathrm{m}^2$$

   Total plate area for CPI separator = 464.4 m^2

3. Find the number of plates required:

   Number of plate required = $N = \dfrac{A}{WL}$

   Let width of plate is 3 m and length of plate is 5 m:

   $$N = \frac{A}{WL_p} = \frac{464.4}{3 \times 5} = 30.96$$

   Number of plate required is 31

4. Find plate volume

   Plate volume = $P_V = \left(\dfrac{N \cdot S}{100} + L_p \cdot \cos D\right)\left(WL_p \cdot \sin D\right)$

   $$P_V = \left(\frac{31 \times 2}{100} + 5\cos 50\right)\left(3 \times 5\sin 50\right)$$

   $$P_V = 44.05\ \mathrm{m}^3$$

   Plate volume is 44.05 m^3

5.3. *Example 3*

Gravitational flotation is utilized to remove oil from industrial wastewater of 2.28 MGD. Influent concentration of oil is 50 mg/L. The diameter of petroleum oil to be removed is 150 cm. Density of water at 10°C is 0.999 g/cm^3 and density of oil is 0.90 g/cm^3. The absolute viscosity of the water is 0.013077 poises.

Calculate the following items:

(1) Rate of flotation.
(2) Horizontal flow velocity.
(3) Sizing of a gravitational tank.

Solutions

1. Find rate of flotation:

$$\upsilon = \frac{gd^2(d_o - d_w)}{18}$$

$$\text{Rate of flotation} = \upsilon = \frac{980 \times 0.015^2(0.90 - 0.999)}{18} = -0.022$$

Rate of flotation = 0.022 cm/s

2. Find horizontal flow velocity:

   Horizontal flow velocity = $\upsilon_L = 15\ \upsilon$
   $\upsilon_L = 15 \times 0.022 = 0.33$ cm/s (less than 1.52 cm/s, OK)
   Horizontal flow velocity = 0.33 cm/s

3. Sizing of a gravitational tank:

   Wastewater flow = 2.28 MGD = 0.10 m^3/s
   Horizontal flow velocity = 0.33 cm/s = 0.033 m/s

   Find minimum vertical cross-sectional area of basin as follows:

$$A_H = \frac{Q}{\upsilon_L}$$

$$A_H = \frac{0.10}{0.033} = 30.30$$

Vertical cross-sectional area is 30.30 m^2

Let height (H) to width (W) ratio be 0.3,

$A_H = H \times W = 0.3\ W \times W$ and $A_H = 30.30$
$W = 10.05$
$H = 0.3$ W = 3.013 (used 3 m)

Find minimum surface area, A_S

$$A_S = F\frac{Q}{\upsilon}$$

$$A_S = 15\frac{0.10}{0.022 \times 10^{-2}} = 6818.18$$

Minimum surface area is 6818.18 m^2

NOMENCLATURE

A	Total plate area, m^2
A_S	Surface area, m^2
A_H	Vertical cross-sectional area, m^2 or ft^2
C_0	Initial solute concentration in the feed, mg/L
C_r	Retained solute concentration, mg/L
Cp	Bulk solute concentration in the permeate, mg/L
Cr	The retained bulk solute concentration, mg/L
CF	Concentration factor
d	Particle diameter, cm
d_1	Diameter of the droplet to be removed, μm
d_o	Density of oil, g/cm^3
d_w	Density of water, g/cm^3
D	Plate angle, degree

F	Turbulence and short circuiting factor
g	Acceleration due to gravitiy = 980 cm/s^2
J	Permeate flux, L/h·m^2
J_0	Initial permeate flux, L/h·m^2
L_b	Basin length, m
L_p	Length of plate, m
μ	Absolute viscosity of water, poise
n	Absolute viscosity of water (poises)
N	Number of plate required
η	Solvent viscosity, mPa/s
P_V	Plate volume, m^3
ΔP	Applied transmembrane pressure, kPa
Q	Wastewater flow, m^3/s or ft^3/s
R	Observed rejection coefficient
R_f	Fouling layer resistance, 1/m
R_m	Intrinsic resistance of the clean membrane, 1/m
R'_{m}	Intrinsic membrane resistance, 1/m
R_P	Polarization layer resistance, 1/m
S	Spacing between plates
SCR	Solute concentration ratio
V_0	Initial feed tank volume, m^3
Vr	Retained volume, m^3
Vp	Permeate volume, m^3
VCR	Volume-to-concentration ratio
υ	Rate of flotation, cm/s or ft/min
υ_L	Horizon flow velocity, m/s, or ft/s
υ_P	Rise rate, m/s
W	Width of plate, m

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17
Evaporation Processes

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CONTENTS

1. INTRODUCTION

1.1. *Drying and Evaporation Processes*

Water removal from municipal and industrial effluent streams constitutes an important step in wastewater and sludge treatment. The purpose is to concentrate, separate, dispose, or utilize wastes and pollutants and to regenerate and return clean water to the environment. In this context, the discussion here will be limited only to industrial and municipal sludge dewatering, evaporation, and drying (1–5).

Although sand bed dewatering of sludge has been popular in small communities, heat drying or evaporation have proved feasible in many instances. Water evaporation and heat drying are currently expensive and require fuel consumption to remove the water. They become feasible when the dried sludge can be sold as a fertilizer or used as a vitamin- and protein-enriched animal feedstock. Such possibilities depend not only on the regular market, but also on the attitude of the public to demand recycling of wastes and accept the associated cost. Sludge return to the environment in a dry form and utilization of its nutrient content may be ecologically more attractive than the current trend toward incineration. Although the latter uses the heat content of the sludge to accomplish combustion, the problem of ash disposal remains.

Recent incineration practice usually involves prior removal of excess water and sludge thickening through dewatering and drying steps. Preliminary drying of the sludge may take place either in a separate unit or in the first section of the incinerator. Furthermore, incineration equipment is often designed so as to permit flexibility of operation during either drying or combustion. The significance of water removal steps

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in various sludge and wastewater treatment designs, the associated energy demands and costs, and the possible improvement of the market for dried sludge warrant analysis and further evaluation of drying and evaporation.

A rigid, sharp distinction among evaporation, dewatering, and drying does not exist. All involve water removal to some extent, and also reduction of the weight and volume of the fluid sludge to that of a concentrated sludge or a moist solid. Usually the water content of a dewatered sludge is higher than that of dried sludge. However, sand beds used for physical dewatering are called "sludge drying beds," despite the considerable water content of the remaining cake, in order to distinguish them from other mechanical dewatering systems. In general, water is removed in drying beds and lagoons by natural drainage and evaporation. Drying to low water content requires high-temperature water removal in mechanical dryers. Depending on the drying temperature, simultaneous sludge sterilization can be achieved.

The origin of the effluent stream, the final desirable moisture content, and the end use of the sludge determine whether dewatering is sufficient, or heat drying is necessary. Because, thermal drying is usually more expensive than physical or mechanical water removal, dewatering prior to heat drying is desirable.

Before attempting any theoretical analysis of drying and evaporation processes, the design and operating characteristics of some basic units will be presented. This will familiarize the reader with the operation of physical and mechanical dryers and evaporators and will permit a rational theoretical treatment of these systems. Drying and evaporation consist of a combination of mass and heat transfer processes common to all dryer designs for a given sludge.

1.2. Natural Sludge Evaporation Lagoons and Evaporation Process Reactor

In this chapter, both natural and man-made evaporation processes will be discussed. Evaporation can be defined as the process by which liquid water is converted into a gaseous state. Evaporation can only occur when water is available. It also requires that the humidity of the atmosphere be less than the evaporating surface (at 100% relative humidity there is no more evaporation). The evaporation process requires large amounts of energy. For example, the evaporation of 1 g of water at a temperature of 100°C requires 540 calories of heat energy (600 calories at 0°C) (43).

Because the design and operation of natural sludge evaporation lagoons is presently more of an art than a science, a number of empirical design criteria and variables will be discussed here rather than deferring them to theoretical discussions. Comparison of drying periods, land requirements, and solids loading rates between sand beds and lagoons obviously favor the dewatering technique. However, lagoons are quite commonly used for sludge drying where inexpensive land is available, because of their simple, low-cost operation. Precipitation and evaporation rates are the controlling factors (6,7).

Several large cities have used lagoon drying successfully for several years. Most organic industrial sludges are often dried in lagoons since offensive odors are minimal. Lagooning has been proved to be economical for oil and metal finishing sludges for which vacuum filtration is difficult.

The theory, principles, and design of thermal evaporation process reactors are well established and they are presented in Section 3.

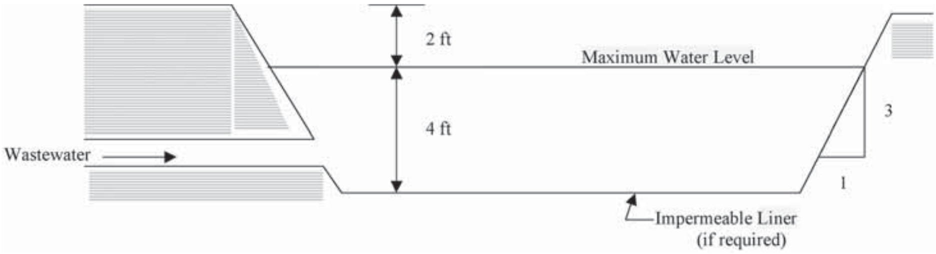

Fig. 1. The sludge evaporation lagoon.

2. SLUDGE EVAPORATION LAGOONS (SLUDGE DRYING LAGOONS)

2.1. *Process Description*

2.1.1. General Process Description

The sludge evaporation lagoon (Fig. 1) may be described as an open holding facility which depends solely on eliminating conditions such as evaporation, precipitation, temperature, humidity, and wind velocity to effect dissipation (evaporation) of on-site wastewater. Individual lagoons may be considered an alternate means of wastewater disposal on individual pieces of property. The basic impetus to consider this system is to allow building and other land uses on properties, which have soil conditions not conducive to the workability and acceptability of the traditional on-site drainfield or leachbed disposal systems (1–3).

Generally if the annual evaporation rate exceeds the annual precipitation, this method of disposal may at least be considered. The deciding factor then becomes the required land area and holding volume. It should be noted that for unlined on-site installation such as homes and small industrial applications, there might also be a certain amount of infiltration or percolation in the initial period of operation. However, after a time, it may be expected that solids deposition will eventually clog the soil surface to the point where infiltration is eliminated. The potential impact of wastewater infiltration to the groundwater, and particularly on-site water supplies, should be evaluated in any event and, if necessary, lagoon lining may be utilized to alleviate the problem.

Lagoons are often preceded by septic tanks or aerobic units in order to provide a more acceptable influent to and minimize sludge removal from the lagoon (5).

2.1.2. Process Operation

Sludge is placed in the lagoon at depths three to four times greater than it would be in a drying bed. Generally, sludge is allowed to dewater and dry to some predetermined solids concentration before removal, a process that might require 1–3 yr. The cycle is then repeated. Sludge should be stabilized prior to addition to the lagoon to minimize odor problems. Large areas of lagoons can produce nuisance odors as they go through a series of wet and dry conditions.

Sludge drying lagoons consist of retaining walls, which are normally earthen dikes 2–4 ft (0.7–1.4 m) high. The earthen dikes normally enclose a rectangular space with a permeable surface. Ancillary equipment includes sludge feed lines and metering pumps, supernatant decant lines, and some type of mechanical sludge removal equipment. The removal equipment may include a bulldozer, dragline, or front-end loader.

In areas where permeable soils are unavailable, underdrains and associated piping may be required.

Operating procedures common to all types of sludge drying lagoons involve:

(a) Pumping liquid sludge, over a period of several months or more, into the lagoon. The pumped sludge is normally stabilized prior to application. The sludge is usually applied until a lagoon depth of 24–48 in. (0.7–1.4 m) is achieved.
(b) Decanting supernatant, either continuously or intermittently, from the lagoon surface and returning it to the wastewater treatment plant.
(c) Filling the lagoon to a desired sludge depth and then permitting it to dewater. Depending on the climate and the depth of applied sludge, the time involved for dewatering to a final solids content of between 20% and 40% solids may be 3–12 mo.
(d) Removing the dewatered sludge with some type of mechanical removal equipment.
(e) Resting (adding no new sludge) the lagoon for three to six months.
(f) Repeating the cycle.

2.2. *Process Applications and Limitations*

2.2.1. *Applications*

The "technology" of evaporation is well developed in terms of scientific understanding and application of climatological and meteorologic data.

The on-site utilization of evaporation lagoons for the disposal of domestic wastewater, from homes and smaller industrial or commercial facilities, may be applicable where access to a municipal sanitary sewer is not available, where subsurface methods are not feasible, and where effluent polishing for surface discharge is not practical.

2.2.2. *Limitations*

The limitations for evaporation lagoons include local health ordinances; potential for odors and health hazard when not properly designed; land area requirements; dependence on meteorological and climatological conditions. Sludge lagoons may require provisions to add makeup water to maintain a minimum depth during dry, hot seasons. Finally, public access restrictions are necessary.

2.2.3. *Advantages and Disadvantages*

The advantages of using sludge evaporation lagoons (or sludge drying lagoons) are

(a) Lagoons are low-energy consumers.
(b) Lagoons consume no chemicals.
(c) Lagoons are not sensitive to sludge variability.
(d) The lagoons can serve as a buffer in the sludge handling flow stream. Shock loadings due to treatment plant upsets can be discharged to the lagoons with minimal impact.
(e) Organic matter is further stabilized.
(f) Of all the dewatering systems available, lagoons require the least amount of operation attention and skill.
(g) If land is available, lagoons have a very low capital cost.

The disadvantages of using sludge evaporation lagoons are

(a) Lagoons may be a source of periodic odor problems, which may be difficult to control.
(b) There is potential for pollution of groundwater or nearby surface water.
(c) Lagoons can create vector problems (for example, flies and mosquitoes).

(d) Lagoons are more visible to the general public.
(e) Lagoons are more land-intensive than fully mechanical methods.
(f) Rational engineering design data are lacking to allow sound engineering economic analysis.

2.3. Design Considerations

2.3.1. Target Process Performance

The performance of evaporation lagoons is necessarily site-specific; therefore, the following data are presented on the basis of net annual evaporation rate that may exist in a certain area:

Net annual evaporation evaporation–precipitation (in.)	Lagoon performance water evaporation (gal/ft^2/yr)
5	3.1
10	6.2
15	9.4
20	12.5
40	24.9
60	37.4

Periodic pump out of accumulated sludge is required from pretreatment unit and/or lagoon.

Lagoon dewatering of sludges does not usually result in fork-liftable sludge. Dewatering from 5% solids to 40–45% solids lasts 2–3 yr, and a 3-yr cycle is usually recommended for lagoon dewatering. Sludge is first dewatered in a lagoon for 1 yr. The lagoon is then allowed to dry for 12–18 mo, followed by a rest period of 6–12 mo.

2.3.2. Design Criteria

Proper design of sludge drying lagoons requires a consideration of the following factors: climate, subsoil permeability, sludge characteristics, lagoon depth, and area management practices. A detailed discussion of these factors follows.

2.3.2.1. CLIMATE

After dewatering by drainage and supernating, drying in a sludge lagoon depends primarily on evaporation. Proper lagoon design, therefore, requires climatic information concerning:

(a) Precipitation rate (annual and seasonal distribution).
(b) Evaporation rate (annual average, range, and seasonal fluctuations).
(c) Temperature extremes.

2.3.2.2. SUBSOIL PERMEABILITY

The subsoil should have a moderate permeability of 1.6×10^{-4} to 5.5×10^{-4} in./s (4.2×10^{-4} to 1.4×10^{-3} cm/s) and the bottom of the lagoon should be a minimum of 18 in. (46 cm) above the maximum groundwater table, unless otherwise directed by local authorities.

2.3.2.3. Sludge Characteristics

The type of sludge to be placed in the lagoon can significantly affect the amount and type of odor and vector problems that may be produced. It is recommended that only those sludges that have been anaerobically digested be used in drying lagoons.

2.3.2.4. Lagoon Depth and Area

The actual depth and area requirements for sludge drying lagoons depend on several factors, such as precipitation, evaporation, type of sludge, volume, and solids concentration. Solids loading criteria have been given as 2.2–2.4 lb of solids/yr/ft^3 (36–39 kg/yr/m^3) of capacity. A minimum of two separate lagoons, or even three lagoons, is provided to ensure availability of storage space during cleaning, maintenance, or emergency conditions.

2.3.2.5. Structure

Lagoons may be of any shape, but a rectangular shape facilitates rapid sludge removal. Lagoon dikes should have a slope of 1:3, vertical to horizontal, and should be of a shape and size to facilitate maintenance, mowing, passage of maintenance vehicles atop the dike, and access for the entry of trucks and front-end loaders into the lagoon. Surrounding areas should be graded to prevent surface water from entering the lagoon. Return must exist for removing the surface liquid and piping to the treatment plant. Provisions must also be made for limiting public access to the sludge lagoons.

2.3.2.6. Hydraulic Loading

The hydraulic loading is the primary sizing criteria for an individual home total-retention lagoon. In order to size the system properly, the following information is needed:

(a) Anticipated flow of wastewater.
(b) Evaporation rates (10-yr minimum of monthly data).
(c) Precipitation rates (10-yr minimum of monthly data).

The rate of wastewater flow is expected to be in the range of 50 gal per capita per day, depending on the individual site location. Precipitation and evaporation data for most areas can be readily found in weather records. A 12-mo mass balance should be utilized to properly determine design sizing. Design criteria include a depth of 2–4 ft, level bottoms, and banks more than 2 ft higher than maximum water level.

2.3.2.7. Monitoring Design

Table 1 summarizes the process variables, measurements, and the monitoring instruments recommended by the US Environmental Protection Agency (US EPA).

Operation of sludge evaporation lagoons is generally slow, proceeding mainly through evaporation. Because of the longer retention of water in lagoons, sludge stabilization is necessary to minimize noxious odors.

Factors discussed in relation to sand bed design, such as climatic conditions, sludge properties, subsoil permeability, sludge load, and so on, also determine the design of lagoons. The design should provide for at least two, or even three, lagoons having a maximum depth of 4 ft. Depending on the climate and the sludge characteristics, 1–4 ft^2/capita are required for sludge drying. A solid loading rate of about 2.4 lb/ft^3/yr (39 kg/m^3/yr) is recommended.

Table 1
Process Variables, Measurements, and Instruments of Sludge Evaporation Lagoons

Process variables	Measurements	Instruments
Feed sludge	Flow	Venturi with diapragm sensors Magnetic Doppler Pump displacement
	Pressure	Bourdon with cylindrical seal
	Density	Nuclear Optical Ultrasonic
Lagoon contents	Moisture content	Portable ohmmeter Lab test
Harvested sludge	Flow (volume)	Transport displacement
	Weight	Static
Supernatant and surface runoff		
Weather	Wind speed [15 ft (4.6 m)] above ground	Anemometer
	Wind direction [15 ft (4.6 m)] above ground	Wind vane
	Temperature [5 and 25 ft (1.5 and 7.6 m)] above ground	
	Relative humidity	RTD with solar shield Thermistor with solar shield
	Rainfall	RTD with lithium chloride cloth (wet bulb temperature)
	Solar radiation	Tipping bucket Thermophile
Atmospheric monitoring	Odors	Portable olfactometer

Source: US EPA.

2.3.3. Environmental Impact and Energy Consumption

Process reliability is good. However, it should be closely controlled to prevent a health hazard. Potential odors, health hazards, and large land area requirements may adversely affect surrounding property value.

Lagoons are usually gravity fed from the source. Where pumping is required and assuming a wire to water efficiency of 60%, using the following expression would approximate energy requirements:

$$\text{kwh/yr} = 0.0019\ (\text{flow in gal/d})\ (\text{discharge head in ft})$$

2.4. Cost

2.4.1. Construction Cost

The US EPA published information on capital cost of constructing sludge lagoons. Using an ENR CC Index equal to 6390.21 (January 2002 Cost), typical excavation and liner costs associated with a two-bedroom residence are as follows:

Item	Unit price	Cost US $
Excavation and hauling (750 yd^3)	\$1.96/yd^3	1472
Liner, 10 mil PVC (21,000 ft^2)	\$0.28/ft^2	5964
Supervision and hand labor	—	2117
Total		9553

To the above must be added costs for land, fencing, septic tank, and ancillary items.

Table 2
Sludge Drying Lagoons, Labor Requirements

Dry solids applied (tons/yr)	Labor (h/yr)		
	Operation	Maintenance	Total
100	30	55	85
1000	55	90	145
10,000	120	300	420
50,000	450	1500	1950

2.4.2. *Operating Costs*

Septic tank pump out is the only energy cost. Pumping of a septic tank is estimated to be about US \$25.82/yr.

Table 2 indicates labor requirements for sludge drying lagoons. The requirements include periodic removal of solids and minor maintenance requirements, such as dike repair and weed control. No information is available on maintenance material costs.

3. EVAPORATORS

3.1. *Process Description*

Detailed discussion of evaporation equipment is beyond the scope of this chapter. However, thermal evaporation precedes sludge drying in several processes. Therefore, a brief description of some basic evaporators will be given here. Standard chemical engineering treatises examine evaporation in further detail (8–10).

Steam-heated evaporators are available in two major types: single-effect and multiple-effect evaporators. Single-effect evaporators are subdivided into short-tube, long-tube, and agitated-film evaporators. Here will be discussed the common, vertical, short-tube evaporator, which also constitutes the basic repeated unit in multiple-effect evaporators.

A vertical, short-tube evaporator is shown in Fig. 2. A bundle of short tubes (A), 4–8 ft long and 2–4 in. in diameter is placed in a vertical shell (B) in which the evaporating liquor is introduced. Steam condenses outside the tubes causing boiling of the liquor. The liquor spouts upward inside the tubes and returns through the downtake. Concentrated liquor is removed from the bottom of the evaporator (C) and liquid vapor is removed at (D). The cross-sectional area of the downtake is 25% of the total cross-sectional area of the tubes.

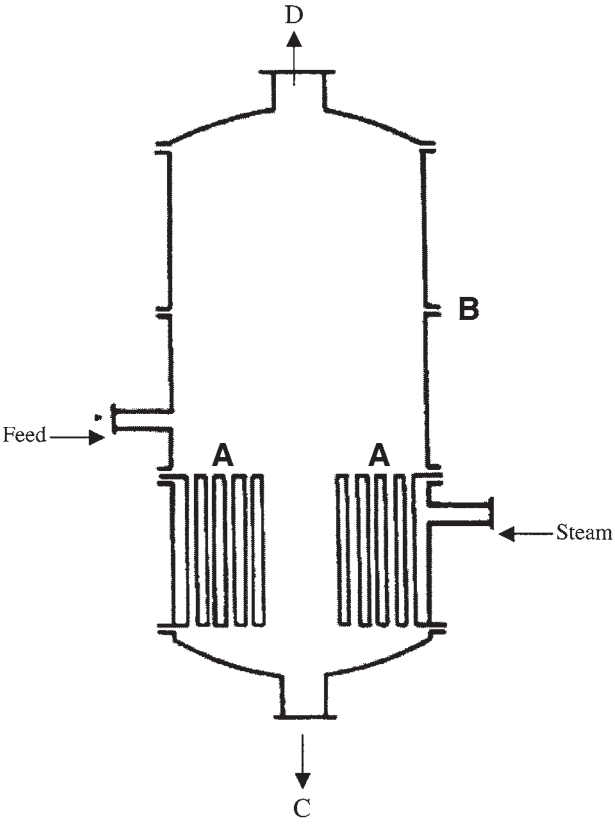

Fig. 2. A vertical short-tube evaporator. (A) Bundle of tubes; (B) shell; (C) exit of concentrated liquor; (D) vapor exit.

Short-tube evaporators are being replaced today by long-tube evaporators to achieve a higher heat transfer coefficient (1).

Single-effect evaporators can be combined in series for multiple-effect operation. Connection is arranged so that the vapor from one evaporator serves as the heating medium for the next one, as shown in Fig. 3. A vacuum is established in the last stage to remove noncondensed vapor from the system. Steam is supplied to the first stage. This arrangement results in the spreading of the pressure difference between inlet steam and final outlet condensate over all stages. The first stage operates at the highest pressure and the last one at the lowest.

Each stage operates as a single-effect evaporator with its own temperature-driving force and heat-transfer coefficient, corresponding to the pressure drop in that stage. At steady-state operation, the temperature, the concentration, and the flow rate of the feed are fixed. The inlet steam pressure and the output condensate pressure are also fixed. Operating conditions within each stage are uniquely established. The composition of the final concentrated liquor can be changed by simply adjusting the flow rate of the feed. By reducing the feed flow rate, the thick liquor concentration is increased and a new steady-state operation is reached eventually.

Evaporators often operate under vacuum to decrease the boiling point of water or solvent. This results in a larger temperature gradient between evaporating liquid and heating

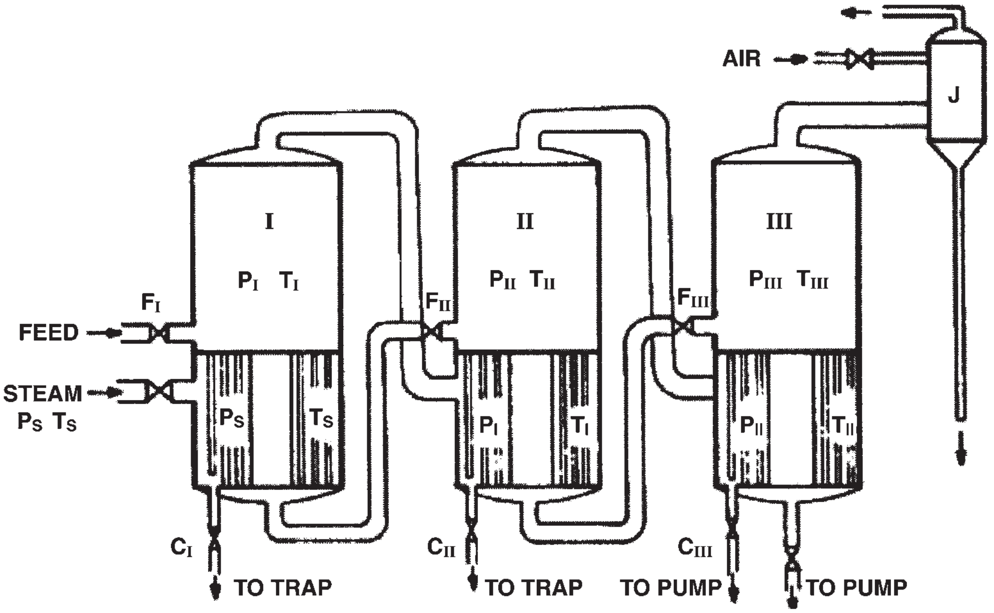

Fig. 3. Triple-effect evaporator. C_I, C_{II}, C_{III}, condensate values; F_I, F_{II}, F_{III}, feed valves; *J*, Air Injector and Condenser; *P* and *T*, pressure and temperature for each effect.

medium and in a smaller heat exchange area than if atmospheric pressure were maintained. Vacuum evaporation is important for heat-sensitive materials not only to achieve better heat transfer, but also to avoid decomposition or alteration of these materials at elevated boiling temperatures. Food and pharmaceutical slurries are, therefore, evaporated under vacuum.

Vacuum evaporation has been used in vitamin B_{12} production from wastewater sludge in Milwaukee (11). The Carver–Greenfield dehydration system uses a triple-effect evaporation step in recovering grease from municipal wastewater and industrial wastes. The Bell–Fons process uses evaporation to precipitate ferrous sulfate monohydrate and to recover sulfuric acid from the pickling liquor of steel mills (12). Similarly, calcium chloride is recovered from the industrial wastes of Columbia-Southern Chemical Company and is marketed for ice making and highway dust control. Celanese Chemical Corporation at Bishop, Texas has developed a solar evaporation process for treatment of its wastes from the production of organic chemicals.

Some typical operating data for the Carver–Greenfield process are given here. Over 65 plants exist worldwide, including an 180,000 gal/d (692 m^3/d) plant for treating 4%-solids activated sludge from the Coors Brewery and a 264,000 gal/d (1000 m^3/d) plant for a 2%-solids wastewater effluent at Hiroshima (13). Mixing sludges with oils (e.g., No. 2 fuel) helps maintain fluidity of the sludge through all stages and minimizes corrosion and scale formation in the equipment. Steam requirements have been estimated at 0.45 lb/lb H_2O at about 50 psig for a four-effect unit. Energy requirements, including steam production, are about 675 BTU/lb water, compared to 1200–2000 BTU/lb water for other dryers (2).

3.2. Process Applications and Limitations

Although the man-made evaporators are technically feasible for water evaporation, they are generally only economically feasible when the dried sludge can be sold as fertilizer or used as vitamin- and protein-enriched animal feedstock. Such possibilities will depend on the market values, as well as the attitude of the public to demand waste recycle and accept the associated environmental costs. More detailed evaporation process applications are discussed in Example 9 (Section 4.9).

Evaporation can greatly reduce the volume of wastewater requiring disposal. The water recovered from evaporation (distillate) is of high purity; therefore, the process can be used to convert waste effluent to pure or process water where other water supplies are inadequate or nonexistent. In the electroplating subcategory of the metal finishing industry, evaporation has the advantage of permitting recovery of a wide variety of plating and other process chemicals.

The evaporation process consumes relatively large amounts of energy. However, the recovery of waste heat from many industrial processes to provide a source of heat can alleviate the costs. Moreover, the equipment is sometimes highly specialized, and thus can be expensive. Another limitation is that, in some cases, pretreatment may be required to remove solids and/or bacteria that tend to cause fouling in the condenser or evaporator.

The build-up of scale on the evaporator plates reduces the heat transfer efficiency and may present a maintenance problem or increase operating cost. However, it has been demonstrated that fouling on the heat transfer surfaces can be avoided or minimized for certain dissolved solids by maintaining a seed slurry, which provides preferential sites for precipitate deposition. In addition, low-temperature differences in the evaporator will eliminate nucleate boiling and supersaturation effects.

Steam distillable impurities in the process stream are carried over with the product water and must be handled by pre- or posttreatment, if they cannot be tolerated.

Evaporator liquids, usually considered the product, must be further treated for recovery or disposal if they are not already in recoverable form. When ponding is used, the solid residues generated must also be disposed of.

3.3. Design Considerations

The evaporation process is designed on the basis of the quantity of water to be evaporated, the quantity of heat required to evaporate water from solution, and the heat-transfer rate. The necessary heat-transfer rate can be calculated on the basis of the required evaporation rate. The evaporator and operating conditions for the evaporator can then be selected to achieve the computed overall heat-transfer rate.

3.3.1. Heat Transfer

The design of evaporators depends on their required capacity and the required steam consumption. Heat is transferred from the steam in the evaporating liquid through a heating surface. The rate of heat transferred Q (BTU/h) is

$$Q = UA\Delta T \tag{1}$$

where U = the overall heat transfer coefficient, BTU/ft^2-h-°F; ΔT = the overall temperature drop between steam and evaporating liquid, °F; and A = heating surface area, ft^2.

The transferred heat raises the temperature of the liquid to its boiling point, corresponding to the absolute pressure in the evaporator, and supplies the latent heat

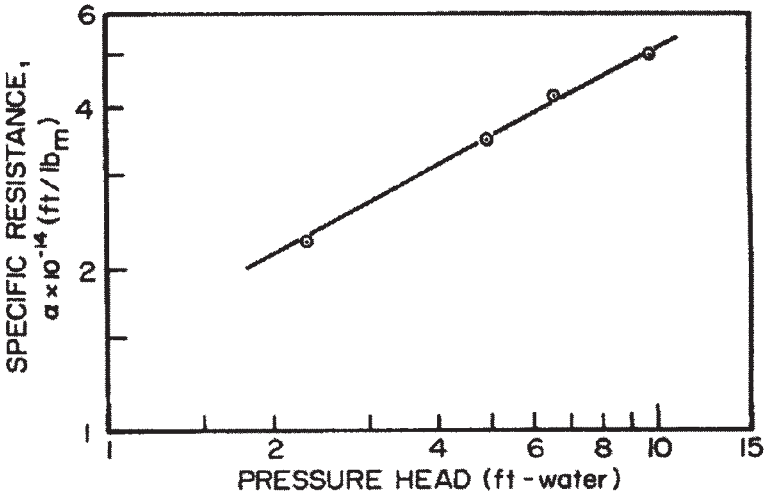

Fig. 4. Dependence of the specific resistance on pressure head.

of vaporization of water. If the feed is at a temperature above the boiling point, flash evaporation occurs.

Dissolved substances in water tend to lower the vapor pressure of water at a given temperature. Conversely, the boiling point of solutions at a given pressure is higher than that of pure water. Boiling point elevation is particularly significant for strong solutions for which Dühring's rule applies (1).

In an evaporator loaded with an appreciable depth of liquid, the boiling point increases with the depth because of the existing liquid head. Therefore, the actual boiling point is higher than that corresponding to the pressure in the evaporator, resulting in decreased capacity (8,9).

The heat-transfer coefficient expresses the facility of heat flow for a particular design and operation. The overall resistance ($1/U$) is the sum of the resistances to heat transfer on the steam side, on the liquid side, and across the tube wall:

$$\frac{1}{U} = \frac{D_s}{D_l h_l} + \frac{\delta}{k_T} \cdot \frac{D_s}{D_{ln}} + \frac{1}{h_{os}} \tag{2}$$

where D_s, D_l, and D_{ln} = the outside (steam), inside (liquid), and mean logarithmic tube diameters, respectively, ft; δ = the tube wall thickness, ft; k_T = the wall thermal conductivity, BTU-ft/ft^2·h·°F; h_l = the heat transfer coefficient on the liquid side, and h_{os} = the heat transfer coefficient on the steam side, BTU/ft^2·h·°F.

If scale forms inside and/or outside the tube walls, additional resistance terms (Fig. 4) should be added to Eq. (2). Some typical values of overall heat-transfer coefficients are given in Table 3 for various evaporator designs.

3.3.2. Heat and Material Balance

A schematic diagram of a single-effect evaporator with all streams and their properties is shown in Fig. 5. A material balance in the evaporator gives

$$F' = L' + V' \tag{3}$$

Table 3
Overall Heat Transfer Coefficients for Evaporators

Evaporator type	U (BTU/ft^2·h·°F)
1. Short tube	
a. Horizontal tube	200–400
b. Calandria type	150–500
2. Long tube, vertical	
a. Natural circulation	200–600
b. Forced circulation	400–2000
3. Coil evaporators	200–400
4. Agitated film, μ = 1cp	400

Adapted from Mc Cabe and Smith (9).

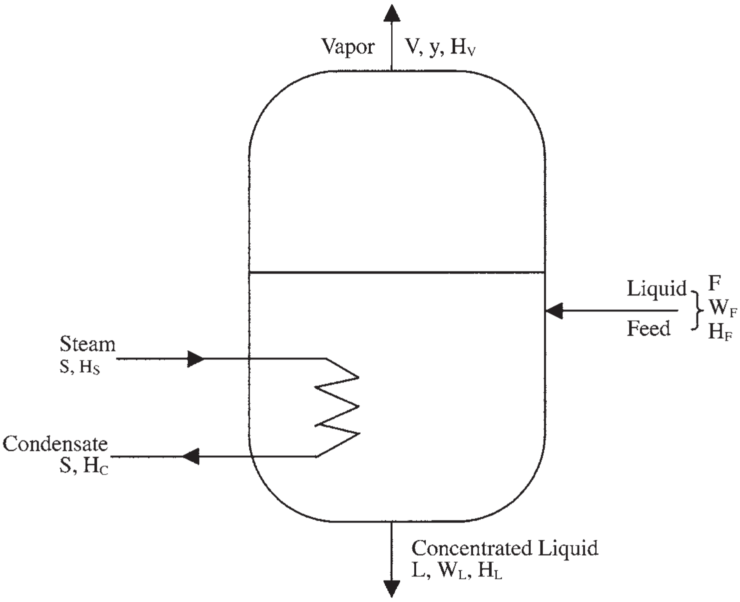

Fig. 5. Schematic diagram of a single-effect evaporator.

where F' = the weight of feed, lb/h; L' = the weight of the resulting thick liquor, lb/h; and V' the weight of the vapor phase, lb/h.

If w_F = the weight fraction of water in the feed, w_L = the weight fraction of water in the concentrated liquid, and y = the weight fraction of evaporated water

A material balance for water yields

$$w_F F' = w_L L' + yV' \tag{4}$$

The heat supplied by the steam is

$$Q_S = S'(H_S - H_C) \tag{5}$$

where Q_s = rate of heat transfer by steam, BTU/h; S' = the weight of steam supplied to the evaporator lb/h; and H_s and H_c = the enthalpies of steam and condensate, respectively, BTU/lb. Complete condensation of saturated steam is assumed with no condensate cooling in the evaporator.

A heat balance for the condensing liquid gives

$$Q_L = (\text{Heat out, in vapor and thick liquid}) - (\text{Heat in, in feed}) \tag{6}$$

$$Q_L = (L'H_L + V'H_V) - F'H_F \tag{7}$$

where Q_L = rate of heat transfer to liquid, BTU/h; H_F = enthalpy of feed, BTU/lb; H_L = enthalpy of thick liquid, BTU/lb; and H_V = enthalpy of vapor, BTU/lb.

At steady state, $Q_L = Q_S$ and using Eq. (3),

$$S'(H_S - H_C) = L'(H_L - H_F) + V'(H_V - H_F) \tag{8}$$

Normally, low-pressure steam is used in evaporation. Although high-pressure steam could provide a larger temperature gradient across the heating surface for given conditions, such steam is usually valuable for energy generation.

3.3.3. Multiple-Effect Evaporators

Equation (1) holds for heat transfer in each stage of a multiple-effect evaporator (Fig. 3). For the first stage (I) then

$$Q_{\mathrm{I}} = U_{\mathrm{I}} A_{\mathrm{I}} \Delta T_{\mathrm{I}} \tag{9}$$

If the feed is at or close to the boiling point corresponding to the conditions in the first stage, essentially all Q_{I} goes into vaporizing water in this stage. At steady state, this water vapor will condense around the tubes of the second stage to vaporize an almost equal amount of water in stage II. The condensate in this stage is at about the same temperature as the vapor of the boiling liquid in the first stage.

The heat exchanged in stage II is

$$Q_{\mathrm{II}} = U_{\mathrm{II}} A_{\mathrm{II}} \Delta T_{\mathrm{II}} \tag{10}$$

From the operation of this stage it follows that the amounts of heat exchanged in effects II and I are almost equal.

$$U_{\mathrm{I}} A_{\mathrm{I}} \Delta T_{\mathrm{I}} = U_{\mathrm{II}} A_{\mathrm{II}} \Delta T_{\mathrm{II}} \tag{11}$$

By similar reasoning, the same amount of heat is exchanged in the third effect, thus

$$U_i A_i \Delta T_i = Q_i = Q \tag{12}$$

where Q = a constant and the subscript denotes the effect.

Usually, the heating surface areas of all effects are equal for construction economy, therefore,

$$U_i \Delta T_i = Q/A = \text{Constant} \tag{13}$$

Equation (13) suggests that the temperature drops are inversely proportional to the overall heat-transfer coefficients in each effect, e.g.,

$$\Delta T_{\mathrm{I}}/\Delta T_{\mathrm{II}} = U_{\mathrm{II}}/U_{\mathrm{I}} \tag{14}$$

It should be emphasized that Eqs. (12)–(14) are only approximate. The total heat exchanged in an N-effect evaporator is the sum of all Q_i:

$$Q_T = \sum_{i=1}^{S} Q_i = \sum_{i=1}^{S} U_i A_i \Delta T_i \tag{15}$$

If all A_i and U_i are equal to a constant value A and U, respectively, then

$$Q_T = UA\sum_{i=1}^{S} \Delta T_i = U_{\mathrm{I}} A_{\mathrm{I}} \Delta T_T \tag{16}$$

where ΔT_T = the total temperature drop across the system.

Equation (15) suggests that the total heat exchanged in the multiple effect evaporators would be the same as the heat exchanged in a single effect evaporator with the same U and A as each effect, operating under a temperature gradient ΔT_T. Therefore, the capacity of a multiple-effect evaporator is no better than that of an equivalent single-effect unit. Here, capacity is defined as the total rate of water vaporization (lb/h). However, significant steam economy is achieved. Each pound of steam supplied to an N-effect evaporator vaporizes approximately N pounds of water. In a single-effect evaporator, each pound of steam vaporizes only about 1 lb of water. To arrive at these approximate relationships, liquid heating and any heat losses have been neglected.

4. DESIGN EXAMPLES

4.1. *Example 1*

Sludge having 8% solids is concentrated in a single-effect evaporator to 35% solids. The evaporator operates at 0.95 psia and uses steam at 10 psig. If the feed rate is 10,000 lb/h at 70°F, and the heat-transfer coefficient is 400 BTU/ft^2·h·°F, calculate: (a) the amount of steam required; (b) the amount of water evaporated per pound of steam (economy); and (c) the heating surface area. Neglect the boiling point elevation and heat of dilution for the sludge. The specific heat capacity of the feed sludge is $C_{P,F}$ = 0.88 BTU/lb·°F.

Solution:

Material Balance:

$$\text{Water in feed: } \frac{92}{8} = 11.50 \text{ lb water/lb solids}$$

$$\text{Water in concentrate: } \frac{65}{35} = 1.85 \text{ lb water/lb solids}$$

Water evaporated: = 9.65 lb water/lb solids

For a feed F' = 10,000 lb sludge/h, then,

$$V' = 10{,}000 \times 0.08 \times 9.65 = 7720 \text{ lb water/h}$$

$$L' = 10{,}000 - 7720 = 2380 \text{ lb liquor/h}$$

Steam Requirements: The steam requirements are estimated from Eqs. (3)–(7) rearranged to give

$$S'\Delta H_v = (F' - L')H_v + L'H_L - F'H_F \tag{17}$$

where ΔH_v is the latent heat of vaporization of steam at 10 psig.

If the temperature of the concentrated liquor, T_L(°F) , is considered as a reference temperature (T_R, °F) Since $T_L = T_R$, then

$$H_L = C_{P,L}\,(T_L - T_R) = 0 \tag{18}$$

and

$$H_F = C_{P,F}\,(T_F - T_R) = C_{P,F}\,(T_F - T_L) \tag{19}$$

where T_F = temperature of feed sludge, °F; $C_{P,L}$ = specific heat capacity of the concentrated liquor, BTU/lb·°F.

The enthalpy of the vapor H_v with respect to the thick liquor now represents the latent heat of vaporization at the operating pressure in the evaporator. Equation (18) then yields

$$S'\Delta H_v = (F' - L')H_v - F'C_{P,F}\,(T_F - T_L) \tag{20}$$

From steam tables (such as Appendix), at 10 psig, the temperature of steam (T_S) can be found:

$$T_s = 239.4°\text{F}$$

$$\Delta H_v = H_s - H_c = 952.6 \text{ BTU/lb}$$

At 0.95 psia,

$$T_L = 100°\text{F}$$

$$H_v = 1037 \text{ BTU/lb}$$

With the feed entering at T_F = 70°F, the steam rate is

$$S' = \frac{(10{,}000 - 2380)1037 + 10000 \times 0.88(100 - 70)}{952.6} = 8572 \text{ lb/h}$$

Steam Economy

$$\frac{V'}{S'} = \frac{7720}{8572} = 0.90 \text{ lb water evaporated / lb steam}$$

Heating Surface Area

$$A = \frac{Q}{U(T_S - T_L)} = \frac{S'\Delta H_v}{U(T_S - T_L)} \tag{21}$$

or

$$A = \frac{8{,}572 \times 952.6}{400(239.4 - 100)} = 146.4\text{ft}^2$$

4.2. Example 2

Sludge is concentrated in a triple-effect evaporator to recover vitamin B_{12}. The first effect operates at 8 psig, whereas the last effect operates at a temperature of 110°F. If the overall heat transfer coefficients are 400, 320, and 240 for the first, second, and third effects, respectively, estimate the liquor boiling temperature in each stage. Neglect any boiling point elevation.

Solution:

Assuming that all effects have the same heating surface area, Eqs. (13) and (14) give

$$\Delta T_{\mathrm{I}} : \Delta T_{\mathrm{II}} : \Delta T_{\mathrm{III}} : (\Delta T_{\mathrm{I}} + \Delta T_{\mathrm{II}} + \Delta T_{\mathrm{III}}) = 1/U_{\mathrm{I}} : 1/U_{\mathrm{II}} : 1/U_{\mathrm{III}} : (1/U_{\mathrm{I}} + 1/U_{\mathrm{II}} + 1/U_{\mathrm{III}}) \quad (22)$$

Thus

$$\Delta T_i = \frac{\Delta T_T}{\sum_{i=1}^{3} \frac{1}{U_i}} \cdot \frac{1}{U_i} \quad (23)$$

where

$$\Delta T_T = \sum_{i=1}^{3} \Delta T_i = T_{\mathrm{I}} - T_{\mathrm{III}}$$

From steam tables, at 8 psig

$$T_{\mathrm{I}} = 235°\mathrm{F}$$

and

$$\Delta T_T = 235 - 110 = 125°\mathrm{F}$$

Thus

$$\Delta T_{\mathrm{I}} = \frac{125}{\left(\frac{1}{400} + \frac{1}{320} + \frac{1}{240}\right)} \left(\frac{1}{400}\right) = 32°\mathrm{F}$$

Similarly,

$$\Delta T_{\mathrm{II}} = \frac{125}{\left(\frac{1}{400} + \frac{1}{320} + \frac{1}{240}\right)} \left(\frac{1}{320}\right) = 39.8°\mathrm{F}$$

and

$$\Delta T_{\mathrm{III}} = \frac{125}{\left(\frac{1}{400} + \frac{1}{320} + \frac{1}{240}\right)} \left(\frac{1}{240}\right) = 53.2°\mathrm{F}$$

from which

$$T_{\mathrm{II}} = T_{\mathrm{I}} - \Delta T_{\mathrm{I}}$$
$$= 235 - 32 = 203°\mathrm{F}$$

and

$$T_{\mathrm{III}} = T_{\mathrm{II}} - \Delta T_{\mathrm{II}} = 203 - 39.8 = 163.2°\mathrm{F}$$

4.3. *Example 3*

Analyze the performance of a 60.5-ft diameter (max. surface area on top) evaporation lagoon in Spokane County, Washington, USA, for treating 5400–5580 gal per month of liquid sludge in April–June, assuming the following data are known:

Month	April	May	June
Average flow, gal	5400	5580	5400
Average evaporation, in.	5.54	7.79	9.26
Average precipitation, in.	1.00	1.00	1.20

Solution:

Based on the above data, the water mass balance analysis has been conducted, and its results are:

Month	April	May	June
Net Evaporation, in.	4.54	6.79	8.06
Net Evaporation, gal/ft^2	2.83	4.23	5.02
Evaporation Area, ft^2	1908	1319	1076
Net Evaporation, gal	5400	5580	5400

(Note: 1 in. = 0.6233 gal/ft^2)

4.4. *Example 4*

Discuss the following for the sludge evaporation lagoon in Example 3:

(a) Structural elements.
(b) Performance expectations.
(c) A cable and scraper system for the sludge evaporation lagoon.
(d) Operation and maintenance.

Solution:

(a) Structural Elements: The retaining walls for drying lagoons are typically earthen dikes 0.7–1.4 m (2–4 ft) high with a side slope of 1:3. Although the lagoon is typically rectangular in shape to facilitate sludge removal, a circular 60.5-ft diameter evaporation lagoon is technically feasible for efficient water evaporation. Figure 1 shows that the required equipment includes sludge feed lines and pumps, supernatant decant lines, and sludge removal equipment. The last may include trucks, front-end loaders, bulldozers, or draglines, depending on the size of the operation.

(b) Performance Expectations: Solids concentrations in the range of 15–40% are expected in the sludge removed from the lagoon, although concentrations can be higher in arid climates. These lagoons share a common problem with other air drying processes in that a surface crust forms early in the evaporative stage, which then restricts further evaporative water losses. This problem is minimized with the paved drying beds that use mechanical equipment to move around the bed to turn and mix the sludge. Similar equipment and procedures can be used in drying lagoons, if the depth of sludge permits. Floating devices can also be used.

(c) Larger scale facilities may use cable and scraper system as shown in Fig. 6.

(d) Operation and Maintenance: The routine operational activities consist of sequential sludge applications and decantations until the lagoon contains the design volume of sludge. The periodic break-up or removal of the surface crust then ensures continued evaporation. Sludge removal is labor intensive but occurs infrequently. Maintenance activities include care of equipment and dikes and control of dike vegetation. Some sludge drying lagoons may require insect and odor control. The labor requirements for sludge drying lagoons are shown in Table 2.

4.5. *Example 5*

Obtain the annual evaporation data for the United States. Discuss its applicability for a sludge evaporation lagoon design.

Solution:

Annual evaporation data for the contiguous United States are presented in Fig. 7, which was compiled by Buonicore and Davis (7). The compiled annual evaporation data will be

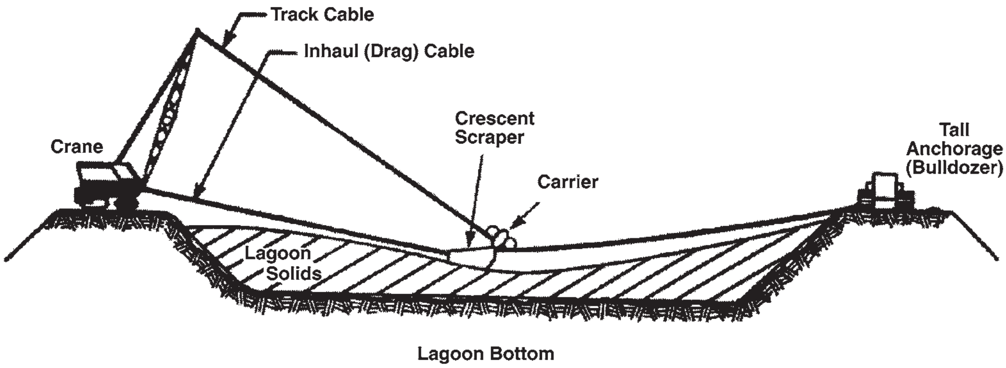

Fig. 6. Cable and scraper system for sludge drying lagoons.

suitable for long-term operation of a sludge evaporation lagoon. For better lagoon design and operation, the environmental engineer in charge of design and operation should obtain the local 10-yr monthly evaporation and precipitation data and perform calculations similar to Example 3.

4.6. *Example 6*

Introduce the manufacturers of commercial prefabricated evaporators.

Solution:

The manufacturers of commercial prefabricated evaporators can be found in refs. 14–18.

4.7. *Example 7*

Briefly define "evaporation process," discuss the process energy source, and explain the difference between "evaporation" and "drying" from technical viewpoints.

Solution:

Although the sludge evaporation lagoon process is also called a sludge drying process, there is a difference between evaporation and drying.

Evaporation is a concentration process involving removal of water from a solution by vaporization to produce a concentrated residual solution. The energy source may be synthetic (steam, hot gases, and electricity) or natural (solar or geothermal). The process offers the possibility of total wastewater elimination with only the remaining concentrated solution requiring disposal and also offers the possibility of recovery and recycle of useful chemicals from wastewater.

Evaporation differs from drying in that the evaporation residue is usually a highly viscous liquid, and the vapor a single component. When the vapor is a mixture, no attempt normally is made in the evaporation step to separate the vapor into different components.

4.8. *Example 8*

There are many types and modifications existing for the evaporation process. The text divides the evaporation process into natural evaporation and man-made evaporation. Please divide the evaporation process into other categories based on energy source and mechanical operation.

Solution:

The evaporation process can be divided into the broad categories of steam evaporation and solar evaporation.

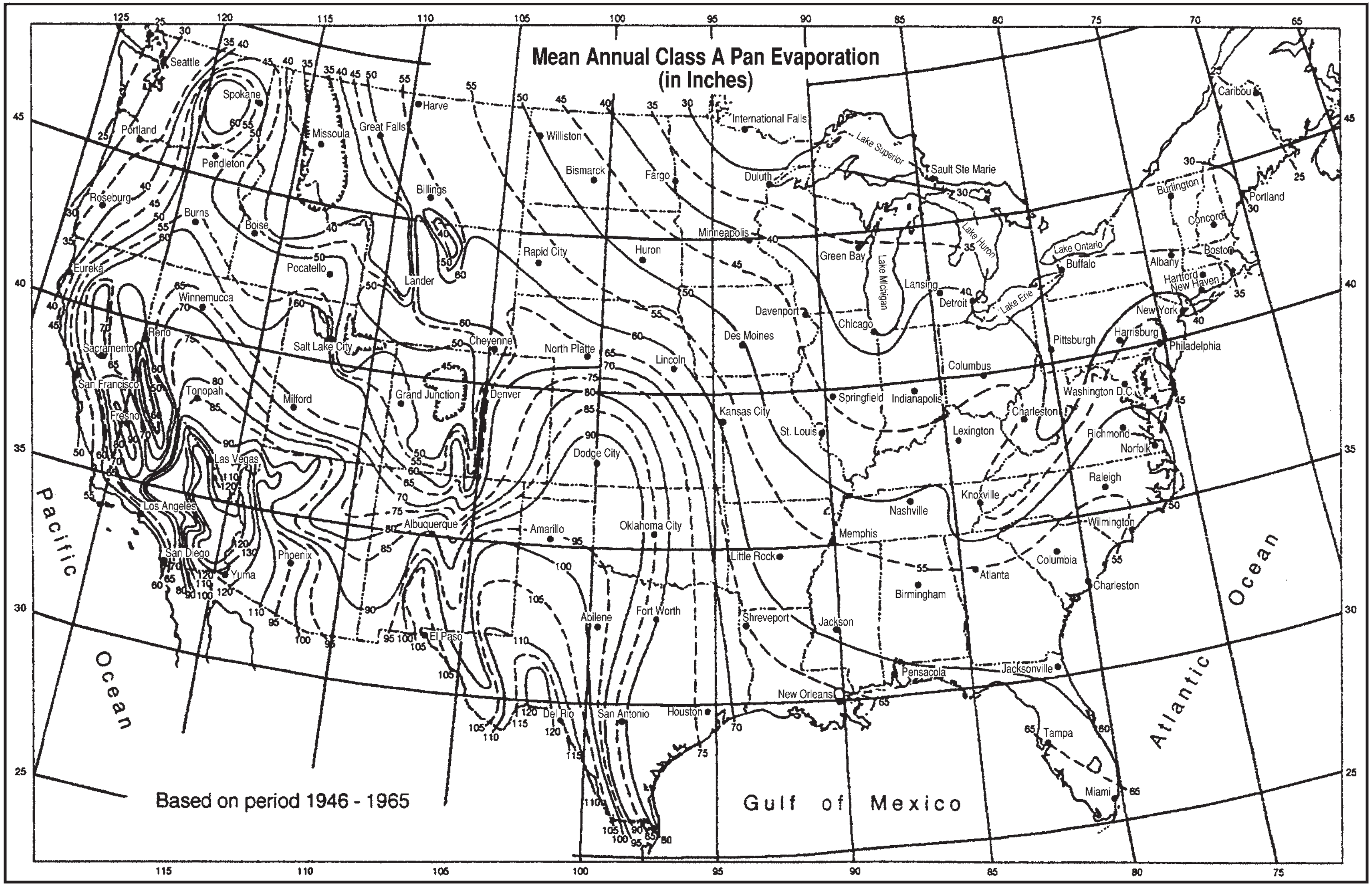

Fig. 7. Annual evaporation data for the contiguous United States.

1. Steam Evaporation: In this process, steam is used to raise the temperature of solution to its boiling point. The process is carried out either at a pressure less than atmospheric (vacuum evaporation) or at atmospheric pressure (atmospheric evaporation).
    (a) Vacuum Evaporation: In this modification, the pressure is lowered to cause the liquid to boil at a reduced temperature and to protect any organic fraction of the evaporating solution from thermal decomposition. All of the water vapor is condensed and, to maintain the vacuum condition, noncondensible gases (air in particular) are removed by a vacuum pump. Vacuum evaporation may be either single or multiple effects. For example, in double-effect evaporation, the water vapor from the first evaporator is used to supply heat to a second evaporator operated at a lower pressure. Roughly equal quantities of wastewater are removed in each evaporator; thus, the double effect system removes twice the water of a single-effect system, at nearly the same cost in energy but with added capital cost and complexity. Thermal or mechanical vapor recompression is another energy-conservation technique available, which enables heat transfer from the condensing water vapor to the evaporating wastewater.
    Vacuum evaporating equipment may be classified as submerged tube or rising (climbing) film. A brief description of the two follows:
        (i) Submerged tube (In most commonly used submerged tube evaporators, the heating and condensing coils are contained in a single vessel to reduce capital cost. The vacuum in the vessel is maintained by an eductor-type pump, which creates the required vacuum by the flow of the condenser cooling water through a Venturi. Wastewater accumulates in the bottom of the vessel and is evaporated by means of submerged steam coils. The resulting water vapor condenses as it contacts the condensing coils in the top of the vessel. The condensate then drips off the condensing coils into a collection trough that carries it out of the vessel. Concentrate is removed from the bottom of the vessel.
        (ii) Rising film (The major elements of the rising film evaporator are the evaporator, the separator, the condenser, and the vacuum pump. Wastewater is "drawn" into the system by the vacuum so that a constant liquid level is maintained in the separator. Liquid from the separator enters the steam-jacketed evaporator tubes and is partially evaporated. A mixture of vapor and liquid returns to the separator, with the liquid removed by mesh entrainment and continuously circulated from the separator back to the evaporator. The vapor entering the separator flows into the condenser where it is condensed as it flows down through the condenser tubes. The condensate, along with any entrained air, is pumped out of the bottom of the condenser by a liquid ring vacuum pump. Thus, the liquid seal provided by the condensate keeps the vacuum in the system from being broken.
    (b) Atmospheric Evaporation: Atmospheric evaporators do not recover the distillate for reuse and do not operate under a vacuum. Wastewater is evaporated by using it to humidify air flowing through a packed tower. The humidified air is exhausted to the atmosphere, eliminating the need for a condenser.
2. Solar Evaporation: Natural evaporation from wastewater impoundments located in arid regions is a technique practiced at many operations to reduce discharges to zero or nearly zero. Successful implementation depends on favorable climatic conditions (not evaporation) and on the availability of land. Land requirements can be significant in areas where the net evaporation value is small, and a large surface area of water must be exposed. In some instances where impoundment is not practical for the total wastewater discharge, impoundment of smaller, highly contaminated wastewaters from specific processes may afford significant advantages.

Solar evaporation can be substantially increased by a variety of techniques that mechanically improve mass transfer rates, such as spraying. The wastewater is sprayed under pressure through nozzles producing fine aerosols, which are evaporated in the atmosphere. The driving force for this evaporation is the difference in relative humidity between the atmosphere and the humidity within the spray area. Temperature, wind speed, spray nozzle height, and pressure are all variables that affect the amount of wastewater that can be evaporated.

4.9. *Example 9*

Evaporation is a well-defined and well-established process. The technology is proven and its application is expanding. Evaporation is very reliable and generally does not require extensive operator attention. This chapter's text places emphasis on sludge evaporation/drying. Please explain other environmental applications of the evaporation process.

Solution:

Evaporation can be used for a variety of purposes including dehydration, recovery, separation, and concentration. Evaporation is especially useful in the treatment and disposal of specific high-strength, low volume process waste streams. The following industries use evaporation methods on a widespread basis for waste treatment and/or recovery of chemicals:

(a) Metal Finishing
(b) Explosives Manufacturing
(c) Timber Products Processing

The following industries use evaporation on a limited basis:

(a) Inorganic Chemicals Manufacturing
(b) Aluminum Forming
(c) Battery Manufacturing
(d) Pharmaceutical Manufacturing
(e) Nonferrous Metals Manufacturing
(f) Organic Chemicals Manufacturing
(g) Paint and Ink Formulation
(h) Petroleum Refining
(i) Rubber Processing
(j) Textile Mills

In the metal finishing industry, evaporation is a common technology for recovery of plating chemicals from rinse water. Evaporation achieves recovery by distilling the wastewater until there is sufficient concentration of plating chemicals to allow reuse in the plating operation. The water vapor is condensed and returned to the rinse tank. In the pulp and paper industry, evaporation is used to concentrate the spent liquor into a viscous mass called "strong black liquor." The strong black liquor is then burned to recover heat and chemicals.

4.10. *Example 10*

An innovative potable filtration plant with a design capacity of 1.2 MGD has been reliably serving 10,000 residents and tourists in the town of Lenox, Massachusetts, USA, since July 1982. Its process system consists of chemical flocculation, dissolved air flotation, and automatic backwash and sand filtration. It substantially improves upon the conventional flocculation, sedimentation, and filtration system in performance, capability, operation, maintenance, and energy use (19–42).

The detention time of the Lenox flotation system including flocculation, flotation, filtration, and clear-well is only 15 min in comparison with the conventional system's 6–9 h of detention time. Because of the Lenox flotation plant's compact design (diameter = 22 ft;

Table 4
Investigation of Sludge Production, Lenox Water Treatment Plant, November, 1982

Date	Influent flow (gpm)	Sludge flow (gpm)	Sludge TSS (mg/L)
11/01/82	429–545	3	3271
11/02/82	390–545	2	1334
11/03/82	390–519	2	2611
11/04/82	519	4	3051
11/05/82	490–519	5	1771
11/06/82	391–519	5	1771
11/07/82	391–519	6	1771
11/08/82	391–535	3	1771
11/09/82	391–535	4	1029
11/10/82	391	5	1029
11/11/82	391–535	2	1440
11/12/82	535–536	2	2555
11/13/82	391–536	4	3180
11/14/82	536	2	1035
11/15/82	391–536	5	3810
11/16/82	391–527	4	948
11/17/82	527	4	488
11/18/82	387–527	4	3000
11/19/82	387–536	3	1303
11/20/82	536	3	1548
11/21/82	387–547	3	1548
11/22/82	547	3	1258
11/23/82	388–547	8	2732
11/24/82	388–595	3	983
11/25/82	477–481	5	1346
11/26/82	476–481	7	4621
11/27/82	471–476	3	7705
11/28/82	471–500	1	12,535
11/29/82	479–500	2	3211
11/30/82	479	2	3211
Range	387–595	1–8	488–12,535
Average		3.63	2596

Adapted from Krofta and Wang (30,31).

depth = 6 ft), its equipment installation cost, housing cost, heating cost, land requirement, etc., are all significantly reduced.

The Lenox Water Treatment Plant has been using a sludge evaporation lagoon (sludge drying lagoon) for thickening its alum sludge. Introduce the plant's sludge generation data and its sludge evaporation lagoon's performance.

Solution

(a) Sludge Generation: An investigation of sludge production at the Lenox flotation plant was conducted in November, 1982, and the results are presented in Tables 4 and 5. Table 6 documents the chemical consumption of the Lenox plant in the

Table 5
Sludge Generation at Lenox Water Treatment Plant

Parameters	Data
Average plant flow	
gpm	521.0
MGD	0.75
Peak plant flow	
gpm	694.4
MGD	1.0
Raw sludge concentration	
mg/L	2600.0
Sludge production rate	
dry lb/d/MGD	150.8
Average sludge production	
dry lb/d/MGD	113.0
Peak sludge production	
dry lb/d/MGD	150.8
Sludge flow rate	
gpm/MGD	4.84
% influent flow	0.70
Average sludge flow	
gpm	3.63
gph	217.8
Peak sludge flow	
gpm	4.84
gph	290.4

Adapted from Krofta and Wang (30,31). 1 gpm = 1 gallon per minute = 3.785 liters per minute; 1 gph = 1 gallon per hour = 3.785 liters per hour; 1 MGD = 1 million gallons per day = 3.785 million liters per day; 1 lb = 454 grams.

Table 6
Chemical Treatment Summary

Month in 1982	Water treated (gal)	Alum dosage (mg/L Al_2O_3)	Alum dosage (lb)	Alum residue (mg/L Al_2O_3)	Polymer dosage (mg/L)	Polymer dosage (lb)	Polymer residue (mg/L)
July	11,622,900	1.99	192.60	0.31	0	0	0
August	31,480,646	2.75	723.27	0.50	0.46	120.25	0.09
September	20,461,473	2.90	491.75	0.43	0.02	4.12	0
October	24,471,287	2.27	463.52	0.37	0.11	22.46	0.004
November	20,351,372	2.40	407.76	0.35	0.84	142.16	0.03
December	21,113,800	3.39	597.33	0.32	0.44	77.17	0.07
Total	129,501,478		2876.23			366.16	
(Average)		(2.66)		(0.38)	(0.34)		(0.03)

Adapted from Krofta and Wang (30,31) and Wang (41,42).
1 gal = 3.785 liters; 1 lb = 454 grams.

Table 7
Analytical Data of Composite Settled Lagoon Sludge*, Lenox Water Treatment Plant, Lenox, Massachusetts

Parameter	Sludge data	US EPA limits for land application
pH, unit	6.9	None
Total suspended solids, mg/L**	30,425	None
Volatile suspended solids, mg/L**	3420	None
Fixed suspended solids, mg/L	27,005	None
Cadmium, mg/kg dry sludge	<0.14	16
Chromium, mg/kg dry sludge	54	140
Lead, mg/kg dry sludge	25	500
Copper, mg/kg dry sludge	64	850
Nickel, mg/kg dry sludge	80	82
Zinc, mg/kg dry sludge	14	1740
Aluminum, mg/kg dry sludge	30,500	None
Iron, mg/kg dry sludge	NA	None
Mercury, mg/kg dry sludge	BD	5

Adapted from Krofta and Wang (30,31) and Wang (41,42).
*The settled lagoon sludge was accumulated in the period from May 21 to Nov. 21, 1982.
**Total suspended solids and volatile suspended solids are average values of eight sludge samples.
NA = Not available.
BD = Below detection limit of AA.

sludge-testing period. It can be seen that the plant's chemical consumption was much lower than that of a comparable conventional water purification plant. However, the sludge production rate was estimated to be 150.8 dry lb/d/MGD, as shown in Table 5.

An engineer's rule of thumb for sludge production rate of a comparable conventional water purification plant is usually set at 75 dry lb/d/MGD. It is believed that the low sludge production rate of a conventional plant is caused by discharge of filter backwash wastewater, without recycle. Thus, the sludges in the discharged wastewater are not included in sludge quantity estimation (30,31,44):

It is understandable that the potable water flotation plant recycles its backwash wastewater for reuse, and in turn, has higher sludge production rate (150.8 instead of 75 dry lb/d/MGD) because almost all sludges are captured by dissolved air flotation. Table 5 further confirms the plant's sludge flow rate is about 0.7% of influent flow rate. The raw sludge concentration of TSS is about 2600 mg/L.

(b) Sludge Evaporation Performance: The data documented in Table 7 are for sludge handling and disposal (30,31,41,42). For freewheeling automatic operation without an operator's attention, the average sludge flow and sludge concentration (TSS) were 3.63 gpm and 2600 mg/L, respectively. By manual operation, with the operator's attention on June 29, 1982, the sludge concentration was as high as 15,800 mg/L, and the sludge flow was as low as 0.3 gpm. The floated sludge was discharged into a sludge lagoon with a built-in slow sand filter for disposal. The analytical data in Table 5 are for the settled lagoon sludge accumulated in the period from May 21 to November 21, 1982. It can be seen that the settled lagoon sludge with a consistency of about 3% meets the US Environmental Protection Agency limits for land application. The lagoon sludge contained mainly inorganic fixed suspended solids (27,005 mg/L),

Table 8
Sludge Evaporation and Monitoring at Lenox Water Treatment Plant

Date	Lagoon flow (gpm)	Lagoon and filter effluent Turbidity (NTU)	TSS (mg/L)	Color (unit)
11/04/82	3.8–4.0	1.4	–	4
11/07/82	5.4–6.0	2.6	2.4	5
11/08/82	3.0–5.6	1.8	0.9	5
11/09/82	4.0–5.3	2.7	–	5
11/20/82	5.0–6.2	3.0	3.9	6

Adapted from Krofta and Wang (30,31). Fresh raw alum sludge (non-dewatered) was discharged directly into the sludge lagoon; 1 gpm = 1 gallon per minute = 3.785 liters per minute.

or, more specifically, the non-toxic aluminum (30,500 mg/kg dry sludge). All heavy metal contents were extremely low. The lagoon overflow passed though a slow sand filter, and eventually reached a small creek. The November 1982 lagoon operational data in Table 8 show that the slow sand filter effluent was as clean as reservoir raw water. When there is a water shortage, the lagoon/filter effluent can be pumped back to the Lower Root Reservoir for reuse, so every drop of water can be conserved.

A Discharge Permit for discharging the lagoon effluent from the Lenox Water Treatment Plant to a nearby stream has been granted by the Commonwealth of Massachusetts, Department of Environmental Quality. All dewatered alum sludge from the Lenox Water Treatment Plant is discharged to the town's Wastewater Treatment Plant.

The following paragraphs introduce the physical structures of the sludge evaporation lagoon system.

The Lenox plant's sludge evaporation lagoon consisting of a sludge lagoon and a slow sand filter was designed for holding and thickening of an average sludge flow of 3.63 gpm.

The lagoon's inlet and outlet are located at opposite ends. Its size is approx 31 ft W × 47.5 ft L at the top and 18.75 ft W × 42.5 ft L at the bottom, with a side slope of 1 1/2 to 1. Its depth is about 6 ft. The lagoon effluent is discharged to the slow sand filter via a spillway on a dividing concrete wall between the lagoon and the filter. The lagoon overflow rate and weir overflow rate are less than 500 gpd/ft^2 and less than 2000 gpd/ft, respectively.

The slow sand filter has a dimension of approx 34 ft L × 20 ft W, and is packed with 2 ft of coarse sand (0.5–0.7 mm effective size), 3 in. of small-diameter gravel under the sand, and 9 in. of graded gravel under the small diameter gravel. Its loading rate is equal to or less than 15 gpd/ft^2. The slow sand filter further polishes the lagoon effluent. The filter effluent is as clean as the reservoir raw water.

The entire sludge evaporation lagoon system has been constructed so as to provide for cleaning without interference with normal operation.

The lowest elevation of the sludge evaporation lagoon has been kept above ground water level to avoid being overflowed with ground water.

A similar but more improved evaporation lagoon system has been used at Feura Bush Filtration Plant of the City of Albany, New York, USA. The City of Albany's evaporation lagoon system involves the use of natural evaporation, freezing, thawing, and sedimentation processes for treatment of combined filter backwash water and sedimentation waste sludge.

NOMENCLATURE

A	Exposed or cross-sectional area, ft^2
$C_{P,F}$	Specific heat capacity of feed sludge, BTU/lb·°F
$C_{P,L}$	Specific heat capacity of thick liquor, BTU/lb·°F
D_i	Inside tube diameter, ft
$D_{\ln}$	Mean logarithmic diameter, ft
D_s	Outside tube diameter, ft
F'	Mass of mixture, lb/h
H_c	Enthalpy of condensate, BTU/lb
H_F	Enthalpy of feed sludge, BTU/lb
H_L	Enthalpy of thick liquor, BTU/lb
H_S	Enthalpy of steam, BTU/lb
H_V	Enthalpy of vapor, BTU/lb
h_i	Heat transfer coefficient, BTU/ft^2·h·°F
h_{os}	Heat transfer coefficient on steam side, BTU/ft^2·h·°F)
ΔH_V	Latent heat of vaporization of steam, BTU/lb
k_T	Thermal conductivity of wall, BTU ft/ft^2·hr·°F
L'	Mass of concentrated liquid, lb/h
Q	Rate of heat transfer, BTU/h
Q_L	Rate of heat transfer to liquid, BTU/h
Q_S	Rate of heat transfer by steam, BTU/h
S'	Mass of steam, lb/h
T_L	Temperature of concentrated liquid, °F
T_R	Reference temperature, °F
T_S	Steam temperature, °F
ΔT	Overall temperature drop, °F
U	Overall heat transfer coefficient, BTU/ft^2·h·°F
V'	Mass of vapor phase as water, lb/h
w_F	Weight fraction of water in the feed
w_{L}	Weight fraction of water in the concentrated liquid
W_s	Weight of solids, lb
y	Weight fraction of evaporated vapor
δ	Tube wall thickness, ft

Subscripts

a	Air
I, II, III	Interface; stage of evaporators
F	Feed
L	Thick liquor
R	Reference
V	Vapor

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Appendix: Steam Tables (45)

Temperature (°F)	Pressure (psia)	ΔH_v (BTU/lb)	H_v (BTU/lb)
100	0.95[1]	1036.98	1105.02
230	20.781	958.81	1157.12
240	24.968[2]	952.27	1160.70

[1] 0.95 psia corresponds to a T_L of 100°F, with $\Delta H_v = 1037$ BTU/lb.

[2] 10 psig corresponds to 24.696 psia. Interpolation yields a T_S of 239.4°F and 952.6 BTU/lb. 8 psig corresponds to 22.696 psia. Interpolation yields a T_L of 235°F.

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Solvent Extraction, Leaching and Supercritical Extraction

Paul Scovazzo, Wei-Yin Chen, Lawrence K. Wang, and Nazih K. Shammas

CONTENTS

1. INTRODUCTION

Solvent extraction, or liquid–liquid extraction, is the separation of impurities (solutes) from a liquid solution by contacting it with another immiscible liquid (solvent) in which the impurities have a high affinity. The high affinity driving the separation can be either physical solubility differences or a chemical reaction. The solvent may be a single component liquid (toluene) or a mixture (isopropyl ether/octanol).

The term “solvent extraction” can apply to the removal of pollutants from soil with a solvent. However, this is properly called “leaching” and will be covered separately toward the end of this chapter along with “supercritical fluid extraction” (SFE). Initially,

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the material will focus on liquid–liquid extraction and then tie its concepts into leaching and supercritical fluid extraction.

2. GENERAL APPLICATIONS

Solvent extraction is used to treat concentrated wastewater streams where solute recovery could offset process costs. Solvent extraction may not produce a treated effluent that can be directly discharged to surface waters. Therefore, some form of final polishing of the effluent is usually needed. Solvent extraction may not compete economically with biological oxidation or adsorption in the treatment of large quantities of very dilute wastes. It will also have difficulty competing with steam stripping in the recovery of volatile solutes present in moderate to low concentrations. However, it does compete with distillation for close-boiling mixtures or separations that would require a large number of distillation trays.

3. PROCESS DESCRIPTION

Figure 1 shows a schematic diagram for a solvent extraction process for the recovery of a solute from a wastewater feed. The extraction process typically includes three basic steps (1,2):

1st. The actual extraction.
2nd. Solvent removal from the treated stream.
3rd. Solute removal from the extracting solvent (solvent recovery) and recycle to first step.

The process may be operated continuously. The end result of the solvent extraction process is to separate the original solution into two streams: a treated stream or "raffinate," and a recovered solute stream, which may contain small amounts of water and solvent. Therefore, solvent extraction is a recovery process, because the solute chemicals are generally recovered for reuse, resale, further treatment, or disposal.

3.1. The Extractor or Extraction Step

In Fig. 1 the actual extraction step occurs in the "Extractor" unit. In practice this unit could have one of three configurations (3):

(a) A single-stage mixer–settler device in which feed and solvent are mixed by agitation, allowed to settle, and separate into two streams.
(b) Several mixers and settlers in series.
(c) A multistage column operating by countercurrent flow in one device (i.e., a column or differential centrifuge). In the column configuration, density differences between the two liquids causes the countercurrent flow.

Regardless of its mechanical configuration, the extractor brings two liquid phases (feed and solvent) into intimate contact to allow transfer of solute from the feed to the solvent. The process yields two streams, the cleaned stream or raffinate and the extract or solute-laden solvent stream. Both streams will contain extraction solvent and may require further processing to remove and/or recover the solvent and solute.

3.2. Solvent Recovery

As Fig. 1 indicates, reuse of the solvent (following solute removal) and recovery of the solvent dissolved in the raffinate phase are usually necessary aspects of the overall

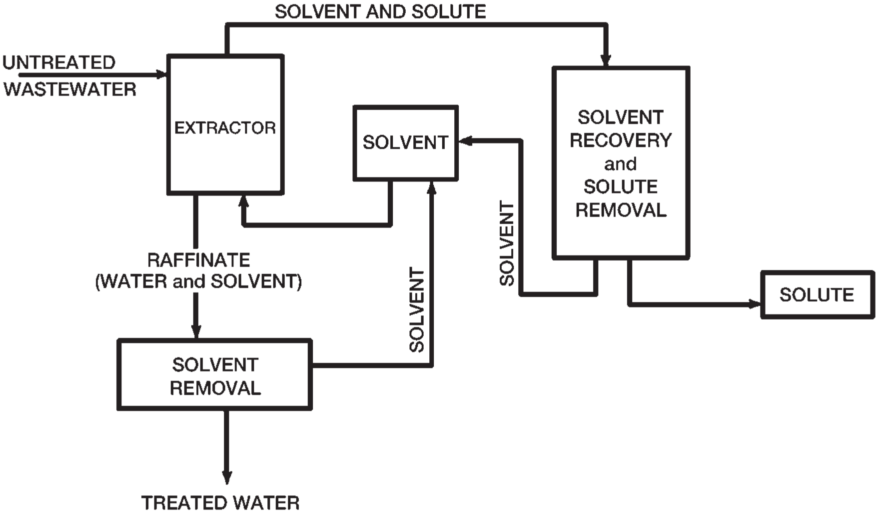

Fig. 1. Schematic of a representative extraction process, showing the extractor, and solvent recovery subsystems (US EPA).

solvent extraction process. Solvent reuse is necessary for economic reasons as the cost of the solvent is generally too high to consider disposal after use. Only in a very few cases may solvent reuse be eliminated. These cases arise where an industrial chemical feed stream can be the solvent and then sent on for normal processing, thus eliminating solute recovery. This is apparently the case at some refineries where crude or light oil can be the solvent for phenol removal from water and later processed with the solute in it. This application is particularly attractive because it eliminates one costly step. Solvent recovery from the raffinate phase (i.e., water) may be eliminated in cases where the solvent concentration in the water to be discharged is not harmful and where the solvent loss does not represent a high cost.

However, in general, solvent recovery is an important step in the overall solvent extraction process. Solvent recovery from the raffinate (i.e., water phase) may be accomplished by stripping, distillation, or adsorption. The extract, or solute-laden solvent stream, may also be processed to recover solvent via removal of the solute. The solute removal and solvent recovery step may include reverse solvent extraction, distillation, or some other process. For example, an extraction with caustic extracts phenol from light oil, which was used as the solvent in dephenolizing coke plant wastewaters (4). The caustic changes the affinity of the solute (phenol) for the solvent (light oil) in comparison to water as will be explained in the equilibrium conditions section. Distillation is more common if there are no azeotropes.

4. TECHNOLOGY STATUS AND RELIABILITY

Solvent extraction is a proven and highly reliable method for the recovery of organics from liquid solutions and may be the process of choice in some cases. For instance, if a distillation process requires an unusually high number of equilibrium stages, the same separation may be achieved with a solvent extraction process using significantly fewer stages. The result would be a significant saving in capital cost.

5. REPRESENTATIVE EQUIPMENT TYPES AND MODIFICATIONS

There are two major categories of equipment for liquid extraction: single-stage and multistage equipment. In single-stage equipment, the fluids are mixed, extraction occurs, and then the insoluble liquids settle and separate. A single-stage unit must provide facilities for mixing the insoluble liquids and for settling and decanting the resulting emulsion or dispersion. In batch operation, mixing together with settling and decanting may take place in the same or in separate vessels.

Multistage equipment could be a cascade of single stages or the equivalent of many stages incorporated into a single device or vertical column with countercurrent flow. The difference in densities of the liquids produces the countercurrent flow. With few exceptions, column equipment takes the form of a vertical tower that may or may not contain internal devices to influence the flow pattern. Other forms include centrifuges, rotating discs, and rotating buckets. Depending on the nature of the internal structure, the equipment may have individual stages or continuous-liquid contact.

6. CHEMICALS REQUIRED

Commonly used solvents include crude oil, light oil, benzene, and toluene. Less common but more selective solvents include chloroform, ethylacetate, isopropyl ether, tricresyl phosphate, methyl isobutyl ketone, methylene chloride, and butyl acetate. The selection of a solvent type for a specific extraction will be discussed under the section dealing with “Equilibrium Considerations.”

7. RESIDUALS GENERATED

Solvent extraction generates no solid wastes. However, when the feed is a mixture of organic liquids that is treated for the recovery of just one component (e.g., halogenated hydrocarbons), economics may make the purification of the other mixture components impractical. The result is a waste stream needing disposal.

8. APPLICATIONS

The major applications of solvent extraction are the recovery of solutes, such as phenolic materials, from wastewater and the recovery of halogenated hydrocarbon solvents from organic solutions. The following industries currently use solvent extraction:

(a) Iron and steel manufacturing.
(b) Organic chemicals manufacturing.
(c) Petroleum refining.

Coke making for iron and steel production utilizes solvent extraction to dephenolize the generated waste streams. In the process, the benzene light oil, or other suitable solvent, extracts phenolic compounds from the wastewater. The phenolized solvent is then separated and extracted with caustic. Sodium phenolates separate out, allowing the reuse of dephenolized solvent (4). Solvent extraction can reduce phenol concentrations from levels of several percent down to levels of a few parts per million. Removal efficiencies of 90–98% are possible in most applications, and with special equipment (e.g. centrifugal and rotating disk contactors) removal efficiencies of about 99% have been achieved.

The following are other representative applications of solvent extraction (5–7):

(a) Extraction of thiazole-based chemicals from rubber processing effluent with benzene.
(b) Extraction of salicylic and other hydroxy-aromatic acids from wastewaters using methyl isobutyl ketone.
(c) Deoiling of quench waters from petroleum operations. In a process developed by Gulf Oil Corporation, a light aromatic oil solvent extracts 6000 mg/L of dissolved and emulsified oil from quench water. The extract solvent then becomes feed for refinery processing. Additional treatment of the water (e.g., via coalescence) is necessary for water reuse.
(d) Recovery of acetic acid from industrial wastewaters that contain acetic acid levels of 0.5% to over 5%. The proposed solvent system is a solution of trioctylphosphine oxide in a carrier solvent.

9. ADVANTAGES AND LIMITATIONS

The main advantage of solvent extraction is the recycling of the “pollutant” or solute. Valuable solutes can be recovered for reuse in the process stream of an industry. There is a wide range of extraction equipment available today and space requirements are not a problem. There are relatively few insurmountable technical problems with solvent extraction. The most difficult problem is usually finding a solvent that best meets a long list of desired qualities including (3–6):

(a) Low cost.
(b) High extraction efficiency.
(c) Low solubility in the raffinate.
(d) Easy separation from the solute.
(e) Adequate density difference with raffinate.
(f) No tendency for emulsion formation.
(g) Nonreactive.
(h) Nonhazardous.

No one solvent will meet all the desired criteria and, thus, compromise is necessary. The main disadvantage of solvent extraction is that solvent extraction systems seldom produce a raffinate that is suitable for direct discharge to surface waters. Therefore, a polishing treatment step is generally required.

Process cost is always a determining factor with solvent extraction. These costs are relatively small with single-stage extraction units (i.e., simple mixer–settler) combined with efficient solvent and solute recovery. In certain cases, the process may yield a profit due to credit received for recovered material. Any extraction requiring more than the equivalent of 10 theoretical stages may require custom-designed equipment, leading to high capital cost.

10. COST

Owing to its limited use in wastewater treatment, there are limited cost data for liquid/liquid extraction. The following costs are in 2004 US Dollars (8). The cost values have been adjusted from the original 1989 for (a, c, and d) (Cost Index 383.14) and from 1976 for (b) (Cost Index 202.71) to 2004 (Cost Index 506.13) using the US Corps of Engineers Utilities Cost index (9):

(a) Wastewater containing 15,800 mg/L phenol—Capital and operating cost is $8.32/1000 gal treated.

(b) One study found operating costs were found to be inversely proportional to the phenol concentration ranging from \$0.05/lb of phenol recovered to \$4.20/lb recovered for phenol concentrations of 1% to 0.01%, respectively.
(c) Polar priority pollutants extracted from waste water—Capital and operating costs range between \$5.54 to \$16.10 per 1000 gal treated.
(d) PCBs extracted from mineral oil using diethylene glycol monomethyl ether—Estimated cost is \$2.11/gal (based on a 500,000 gal/yr plant).

11. DESIGN CRITERIA

Design is specific to the solute being recovered and the waste stream characteristics. The major design parameters are the choice of solvent, distribution coefficient, and solvent flow rate (relative to the feed flow rate).

From an engineering analysis perspective there are two types of liquid/liquid extraction. Type 1 involves two bulk liquids that are totally immiscible in each other. In this type the only significant chemical transport between the two bulk phases is the solute transport. Type 2 liquid/liquid extraction involves two bulk liquids that are partially immiscible, meaning that both phases will contain significant fractions of both liquids in addition to the solute. For illustrating the critical design criteria (equilibrium and engineering factors), this chapter will focus on type 1 liquid/liquid extraction. The engineering analysis for type 2 liquid/liquid extraction is more complicated; however, the general trends developed below for type 1 liquid/liquid extraction also apply to type 2.

Engineering analysis of extractions has two aspects. Part 1 is the determination of the system equilibrium conditions or the thermodynamic driving force for the extraction. Part 2 is the governing equations for the process.

11.1. Part 1—Equilibrium Conditions

When two immiscible phases in contact with each other reach equilibrium, the solute distributes between the two immiscible phases with a different concentration in each phase. For instance, if acetone (the solute) is equilibrated between octanol and water, the acetone's octanol concentration, C_o, and water concentration, C_w, are related by the octanol/water distribution coefficient, $K_{o/w}$, in L of water per L of organic phase:

$$K_{o/w} = C_o/C_w \tag{1}$$

where C_o = acetone's octanol concentration, mol/L, and C_w = water concentration, mol/L.

In a type 1 extraction system, the distribution coefficient is functionally similar to a Henry's law constant in an air stripping operation. For most organic chemicals of environmental concern, the distribution coefficient between an organic phase and water may be assumed to be a constant due to the generally low solubility of organics in water.

Some general trends for organic liquid/water distribution coefficients, $K_{org/w}$, exist depending on the polarity of the organic solute. Apolar and weakly polar compounds partition strongly into an organic phase regardless of the polarity of the organic phase; therefore, $K_{org/w}$ values vary little between different organic liquid/water systems. Monopolar solutes are organic compounds that contain functionality for only one-half of a hydrogen bond, such as the hydrogen-acceptor property of oxygen in acetone or hydrogen-donor property of the hydrogen in trichloromethane (chloroform). Complementary monopolar functionality in the organic extraction phase will enhance the partitioning of the solute into the organic phase. For instance, consider the following acetone $K_{\text{org/w}}$ values, noting that acetone is an H-acceptor monopolar solute (10):

(a) *n*-Hexane/water $K_{\text{hex/w}} = 0.12$ (*n*-hexane is an apolar solvent)
(b) Diethylether/water $K_{\text{d/w}} = 0.62$ (diethylether is an H-acceptor mono-polar solvent)
(c) Chloroform/water $K_{\text{c/w}} = 5.25$ (chloroform is an H-donor mono-polar solvent)
(d) *n*-Octanol/water $K_{\text{o/w}} = 0.58$ (*n*-octanol is a bipolar solvent)

Therefore, monopolar solute $K_{\text{org/w}}$values vary significantly between different organic liquid/water systems in a predicable way. As shown above, the complementary H-donor functionality of chloroform increases the distribution coefficient of acetone (an H-acceptor) by a factor of 10. Therefore, chloroform would be the better solvent for the extraction of acetone from water.

Bipolar solutes contain both the H-donor and H-acceptor functionalities of a hydrogen bond. Bipolar solutes partition very poorly into nonpolar liquids. Therefore, bipolar solute partitioning depends on the polarity of the organic phase, meaning that $K_{\text{org/w}}$'s vary significantly between different organic liquid/water systems.

11.2. Estimating $K_{org/w}$ Values

It is always advisable to measure the distribution coefficient for the specific liquid/liquid extraction before designing a full treatment system; however, for a preliminary trade-off study between different treatment alternatives, this may not be practical. In addition, the selection of the extraction solvent would be facilitated if we could narrow the choices to a subset of organic solvents. There are a number of organic liquid/water distribution coefficients, $K_{\text{org/w}}$, available in the literature; however, by far the system with the most extensive literature data is the octanol/water system. Most organic solutes of environmental concern have published values for their octanol/water distribution coefficient, $K_{\text{o/w}}$. Alternatively, there are methods of estimating a solute's $K_{\text{o/w}}$ if it is unknown (10). Unfortunately, as illustrated above for acetone, octanol is not always the best choice as an extraction liquid. However, the above discussion about the trends of distribution coefficients, based on their organic functionality (apolar, bipolar, aromatic, etc.), points the way toward estimating other distribution coefficients.

Schwarzenbach et al. (10) describe a model for estimating $K_{\text{org/w}}$ distributions for a broad range of organic solutes in four representative solvents; *n*-hexadecane (apolar solvent), chloroform (H-donor mono-polar solvent), diethylether (H-acceptor mono-polar solvent), and *n*-octanol (*n*-octanol is a bipolar solvent). We can use this model to narrow down the choices of extraction solvents to one of four categories of organic solvents. *Note that while chloroform is an H-donor solvent this is not true for all chlorinated solvents; in fact, carbon tetrachloride is an apolar solvent.* The model takes into account the solute size (molecular volume, V_m in cm^3/mol), H-donor strength (α), H-acceptor strength (β), polarizability (π), and van der Waal interaction (W) strength (10):

$$\ln K_{\text{org/w}} = s[V_m^{2/3}W] + p(\pi) + a(\alpha) + b(\beta) + v(V_m) + \text{constant} \tag{2}$$

where s, p, a, b, v, and constant are solvent specific parameters (Table 1), π, α, and β are solute chemical or chemical class parameters (Table 2), V_m = solute's molecular volume best calculated from an atomic group contribution method (see Table 3) instead

Table 1
Solvent Constants for Use in Eq. (2)

Solvent	*s*	*p*	*a*	*b*	*v*	Constant	ln $K_{org/w}$ range	R^2	*n*
n-Hexadecane (apolar)	0.75	–3.61	–8.06	–11.41	0.069	–0.16	–10.0 to 6.11	0.99	302
Trichloromethane (H-donor)	–0.01	0.01	–3.45	–3.38	0.042	0.3	–2.1 to 3.7	1	40
Diethylether (H-acceptor)	–0.11	–0.12	–0.49	–10.54	0.1	–0.1	–0.5 to 5.6	0.97	35
n-Octanol (bipolar)	0.62	–2.53	–0.35	–7.88	0.063	–0.25	–3.2 to 13.0	0.98	260

Source: Schwarzenbach et al. (10) quoting Abraham et al. (11,12). This material is used by permission of John Wiley & Sons, Inc. and reproduced by permission of The Royal Society of Chemistry. *n* is the number of compounds used in this regression, and R^2 is the regression's coefficient of multiple determinations.

Table 2
Solute Constants for Use in Eq. (2)

Solute compound or chemical group	α	β	π	Solute compound or chemical group	α	β	π
Alkanes (C_nH_{2n+2})	0	0	0	Benzonitrile			1.11
Cycloalkanes			0.1	Nitrobenzene			1.11
l-Alkenes (I-C_nH_{2n})	0	0.07	0.08	Aniline	0.26	0.41	
l-Alkines			0.23	Benzaldehyde	0	0.39	1.00
Aliphatic ethers (ROR′)	0	0.45	0.25	Phenol	0.6	0.31	0.89
Aliphatic aldehydes (RCHO)	0	0.45	0.65	Alkylphenol			0.80–0.90
Carboxylic acid esters (RCOOR’)	0	0.45		2-Chlorophenol			0.88
				4-Chlorophenol			1.08
Aliphatic Carboxylic acid esters		0.55–0.60		2-Nitrophenol			1.05
Aliphatic ketones (RCOR′)	0	0.51	0.68	4-Nitrophenol			1.72

Aliphatic amines (R-NH_2)	0.16	0.61	0.35
Aliphatic alcohols (R-OH)	0.37	0.48	
Primary aliphatic alcohols (R-CH_2OH)			0.42
Secondary aliphatic alcohols (RR′CHOH)			0.36
Carboxylic acids (R-COOH)	0.6	0.45	
Aliphatic Carboxylic acids			0.63
Benzene	0	0.14	0.52
Methylbenzene	0	0.14	0.52
Ethylbenzene	0	0.15	
Dimethylbenzene	0	0.16	
1,2-Dimethylbenzene			0.56
1,4-Dimethylbenzene			0.52
Trimethylbenzene	0	0.19	
1,2,3-Trimethylbenzene			0.61
1,3,5-Trimethylbenzene			0.52
Chlorobenzene	0	0.07	0.65
1,2-Dichlorobenzene	0	0.04	0.76
1,3-Dichlorobenzene	0	0.02	
1,4-Dichlorobenzene			0.75
Poly-chlorobenzene (Cl_n, $n > 2$)	0	0	
1,2,3-Trichlorobenzene			0.86
1,3,5-Trichlorobenzene			0.73
1,2,3,4-Tetrachlorobenzene			0.92
1,2,3,5-Tetrachlorobenzene			0.86
Pyridine	0	0.52	
Naphthalene	0	0.2	0.92
Indane	0	0.17	1.04
Acenaphthene	0	0.2	
Fluorene	0	0.2	
Phenanthrene	0	0.26	
Anthracene	0	0.26	
Fluoranthene	0	0.2	
Benzo(*a*)fluorene	0	0.2	
Pyrene	0	0.29	
Benzo(*a*)anthracene	0	0.33	
Chrysene	0	0.33	
Perylene	0	0.4	
Benzo(*a*)pyrene	0	0.44	
Benzo(ghi)perylene	0	0.46	
Dichloromethane	0.1	0.05	
Trichloromethane	0.15	0.02	0.49
Tribromomethane			0.68
1,1,1-Trichloroethane	0	0.09	0.76
1,1,2,2-Tetrachloro-ethane	0.16	0.12	
Trichloroethene	0.08	0.03	
Tetrachloromethane	0	0	0.38
Tetrachloroethene	0	0	0.42
Water	0.82	0.35	

Source: Schwarzenbach et al. (10) quoting Abraham et al. (11,12). This material is used by permission of John Wiley & Sons, Inc. and reproduced by permission of The Royal Society of Chemistry.

Table 3
Molar Volume Group Contribution Method for Use in Eq. (2)

Atom or bond volume	Characteristic atom or bond volume (cm^3/mol)
Any bond type, single, double, triple or aromatic count as one bond	–6.56 Note this is the only negative characteristic volume
Carbon	16.35
Hydrogen	8.71
Oxygen	12.43
Nitrogen	14.39
Phosphorous	24.87
Fluorine	10.48
Chlorine	20.95
Bromine	26.21
Iodine	34.53
Sulfur	22.91
Silicon	26.83
Arsenic	29.42
Tin	39.35
Selenium	27.81
Boron	18.32
Antimony	37.74
Germanium	31.02
Tellurium	36.14

Source: Schwarzenbach et al. (10) and Abraham and McGowan (13). This material is used by permission of John Wiley & Sons, Inc.

Example: Acetone has three carbons, six hydrogens, one oxygen, and nine bonds; therefore, $V(\text{cm}^3/\text{mol}) = 3 \times 16.35 + 6 \times 8.71 + 1 \times 12.43 + 9 \times (-6.56) = 54.7$.

of estimating it from the pure liquid density and molecular weight, cm^3/mol, $W = [n_{Di}^{\,2} - 1]/[n_{Di}^{\,2} + 2]$, and n_{Di} = the solute's refractive index.

Alternatively, the following can be used to estimate the representative apolar solvent (hexadecane) distribution coefficient, $K_{\text{h/w}}$, from the representative bipolar solvent (octanol) distribution coefficients, $K_{\text{o/w}}$:

$$\log[K_{\text{h/w}}] = a \log[K_{\text{o/w}}] + b \tag{3}$$

where a and b (Table 4) depend on the organic class of the solute.

The reader is cautioned about using Eq. (3) for a solute that is not in the class for which the "a" and "b" values were defined. Equation (3) is useful because of the wide availability of $K_{\text{o/w}}$ values in the literature.

The above discussion should help the reader narrow down the choices of an extraction solvent to one of four solvent classes: apolar, H-donor, H-acceptor, or bipolar. However, as mentioned in the introduction to this chapter, sometimes liquid/liquid extraction is done with a solvent mixture such as crude oil. In these cases a first approximation of the distribution coefficient may be made with the following formula:

$$K_{\text{Mix/w}} = C_{\text{Mix}} / C_{\text{w}} = 1/[V_{\text{Mix}}\, C^{\text{sat}}(L)] \tag{4}$$

Table 4
$K_{h/w}$ vs $K_{o/w}$ Slopes and Intercepts for Use in Eq. (3)

Chemical group	*a* (slope)	*b* (intercept)	R^2	*N*
Apolar and weakly polar organics	1.21	–0.43	0.97	89
Aliphatic carboxylic acids	1.21	–2.88	N/A	N/A
Aliphatic alcohols	1.21	–1.74	N/A	N/A

Source: Reference (10). This material is used by permission of John Wiley & Sons, Inc.

However, Eq. (4) should be limited to apolar and monopolar solutes distribution from water to an apolar solvent mixture or a mixture with the same monopolarity as the solute, for instance

(a) Aliphatic and benzene compounds extracted with light petroleum distillates.
(b) PAHs extracted with diesel fuel.
(c) PCBs extracted with hydraulic oil mixtures.

Note that Eq. (4) should not be used to estimate the distribution coefficient of bipolar solutes extracted with apolar solvent mixtures. Also, $C^{sat}(L)$ is the water solubility of the solute in its liquid state at 25°C. If the solute is a solid or gas at 25°C, then the water solubility must be corrected for the free energy of fusion or condensation, refer to ref. 10 for this correction, which follows the same scheme defined later for Eq. (16).

11.3. Environmental Factors Affecting Organic Liquid/Water Distribution Coefficients

The following are some environmental factors that can affect the value of a distribution coefficient obtained in the literature or by one of the above estimation methods:

(a) *Temperature*: Weak dependence on temperature for the majority of organic solutes of environmental concern.
(b) *Salt solutions*: As a first approximation dissolved salt will increase the distribution coefficient (increase the organic phase concentration relative to the water concentration). For details on calculating the scale of the effect, refer to ref. 10.
(c) *pH*: If the solute is an organic acid (i.e., phenol) or an organic base (i.e., aniline), then the pH of the aqueous solution will have a dramatic affect on the distribution coefficient $D_{org/w}$ in L_w/L_o. The following equations are applicable over the ranges indicated; however, be aware that salt counter ions in solution, such as K^+, will complicate the prediction of distribution coefficients of organic acids (or bases) with pH.

$$\text{Acids with pH} < \text{p}Ka + 2,\ D_{org/w} = \alpha \times K_{org/w} \tag{5}$$

$$\text{Bases with pH} > \text{p}Ka - 2,\ D_{org/w} = (1 - \alpha) \times K_{org/w} \tag{6}$$

$$\alpha = \frac{1}{1 + 10^{\text{pH}-\text{p}Ka}} \tag{7}$$

p*Ka* = Negative log (base 10) of the acid dissociation constant of the solute.

11.4. Part 2—Governing Equations and Relationships

Consider a single stage extraction process, Fig. 2A, where a feed liquid (i.e., water) containing a solute (i.e., acetone) contacts an extraction solvent (i.e., chloroform). In this

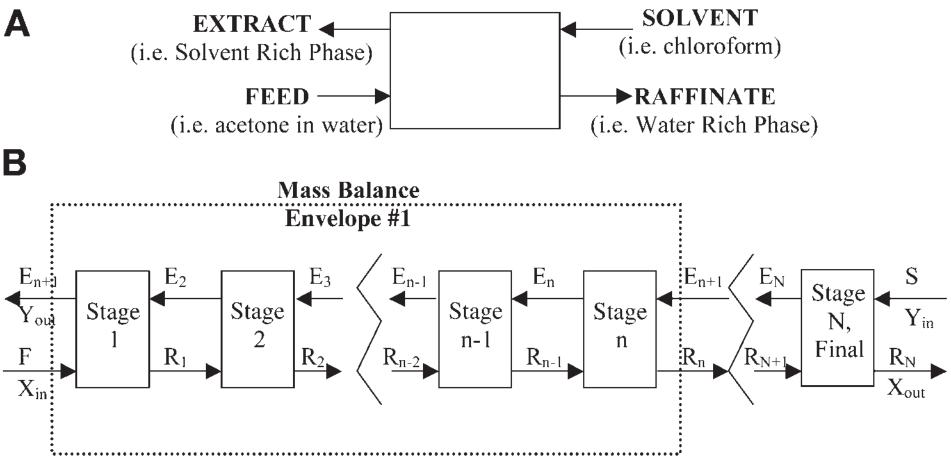

Fig. 2. Extraction engineering terms and analysis diagrams: **(A)** single-stage and extraction fluid names. **(B)** Multiple-stage analysis diagram.

single stage the two liquids (feed and solvent) are well mixed and then are allowed to phase separate. The two liquids that exit the single stage will be a majority water phase containing less acetone then the feed water phase and a majority solvent phase containing some acetone. The majority water phase will also contain some chloroform so its description is usually *water-rich phase*. The water-rich phase, because it contains less acetone then the feed, is "refined" compared to the feed, so it is also called the *raffinate* (meaning "refined phase"). Similarly, the majority solvent phase will also contain some water so its description is *solvent-rich phase*. The solvent-rich phase, because it contains acetone extracted from the water rich phase, is called the *extract*. These names apply to governing relationships for single- and multiple-stage operations: feed (F), solvent (S), raffinate (R), and extract (E).

Now consider a multiple-stage process with countercurrent flow of the raffinate and extract phases, Fig. 2B. Countercurrent is the most efficient multistage configuration. One can write a mass balance around the *n*th stage, as indicated by envelope # 1, using the following units for a continuous flowing process:

F, E_1, R_n, and E_{n+1} in volume/time (for example L/min)
Solute concentrations X and Y in moles/volume (for example mol/L)

One obtains the following two equations:

$$\text{Mass in} = \text{Mass out} \rightarrow \mathrm{F} + \mathrm{E}_{n+1} = \mathrm{R} + \mathrm{E}_1 \tag{8}$$

$$\text{Solute in} = \text{Solute out} \rightarrow \mathrm{X}_{\text{in}}\mathrm{F} + \mathrm{Y}_{n+1}\mathrm{E}_{n+1} = \mathrm{X}_n\mathrm{R}_n + \mathrm{Y}_{\text{out}}\mathrm{E}_1 \tag{9}$$

where the subscript refers to the stage the liquid comes from: X_i is the concentration of the solute in the water-rich phase and Y_i is the concentration of solute in the solvent-rich phase.

Rearranging Eq. (8) results in the operating Eq. (10):

$$Y_{n+1} = X_n(\mathrm{R}_n/\mathrm{E}_{n+1}) + (Y_{\text{out}}\mathrm{E}_1 - X_{\text{in}}F)/E_{n+1} \tag{10}$$

Because envelope # 1 in Fig. 2B could be drawn around any stage from stage 1 through the final stage, N, Eq. (10) relates the concentration in the extract, Y_{i+1}, to the concentration in the raffinate, X_i, at any point along the "train" of stages in a countercurrent process. Equation (10) also applies to a single-stage process. In using Eq. (10), for extraction of organic chemicals of environmental interest, we note that in general the concentrations of the solute are so low in the water that the solute has no effect on the solubility of the extraction solvent in the water or the water in the extracting solvent (i.e., no co-solvent effects). Therefore, we can, in general, assume that after the initial contact of the feed and solvent streams, the ratio of $(\mathrm{R}_n/\mathrm{E}_{n+1})$ remains constant from stage to stage. This assumption of constant $(\mathrm{R}_n/\mathrm{E}_{n+1})$ is the defining assumption of type 1 liquid/liquid extractions and means that Eq. (10) is a straight line with a slope of (R/E) and a y-intercept defined by the feed entering and the final extract leaving Stage 1, $(Y_{\mathrm{out}}\mathrm{E} - X_{\mathrm{in}}\mathrm{F})/\mathrm{E}$:

$$Y_{n+1} = X_n(\mathrm{R}/\mathrm{E}) + (Y_{\mathrm{out}}\mathrm{E} - X_{\mathrm{in}}\mathrm{F})/\mathrm{E} \tag{11}$$

If we assume that each stage results in the exit streams being in equilibrium, we can also write a second equation relating Y_n to X_n, from the previous discussion on equilibrium:

$$Y_n = K_{\mathrm{org/w}}X_n \tag{12}$$

The engineering analysis has now been reduced to defining a system of equations that starts at Stage 1 and uses Eqs. (11) and (12) to solve for the X's and Y's in each sequential stage until the final stage N. Given a ratio of R/E, this system of equations can be solved for N, the number of stages needed to achieve a desired X_{out} in the final raffinate, or given an N, what the final exit conditions of all streams will be. Although there are computational methods for solving this system of equations, there is a closed-form solution for the situation where both Eqs. (11) and (12) are straight lines. This closed-form solution is the Kremser, Eqs. (13) and (14):

$$N = \frac{\log\left[\dfrac{X_{\mathrm{in}} - Y_{\mathrm{in}}/K_{\mathrm{org/w}}}{X_{\mathrm{out}} - Y_{\mathrm{in}}/K_{\mathrm{org/w}}}\left(1 - \dfrac{1}{A}\right) + \dfrac{1}{A}\right]}{\log A} \tag{13}$$

and

$$A = \frac{K_{\mathrm{org/w}}\mathrm{E}}{\mathrm{R}} \tag{14}$$

where A is the extraction factor (unitless), N is the total number of stages, X_{in} is the concentration of the solute in the Feed entering the process, X_{out} is the concentration of solute in the raffinate leaving the process, and Y_{in} is the concentration of the solute in the entering solvent which may not be zero due to the overall system (see Fig. 1).

Figure 3 shows a convenient graphical form of Eq. (13) for quick solutions. For a more-detailed graphical form of Eq. (13), see Treybal (14). In using Fig. 3, note that the ratio of concentrations is inverted from the one in Eq. (13). This was done to ensure that Fig. 3's y-axis is always less than 1. Also if $Y_{\mathrm{in}} = 0$, then Fig. 3's y-axis shows the "fraction of solute not extracted."

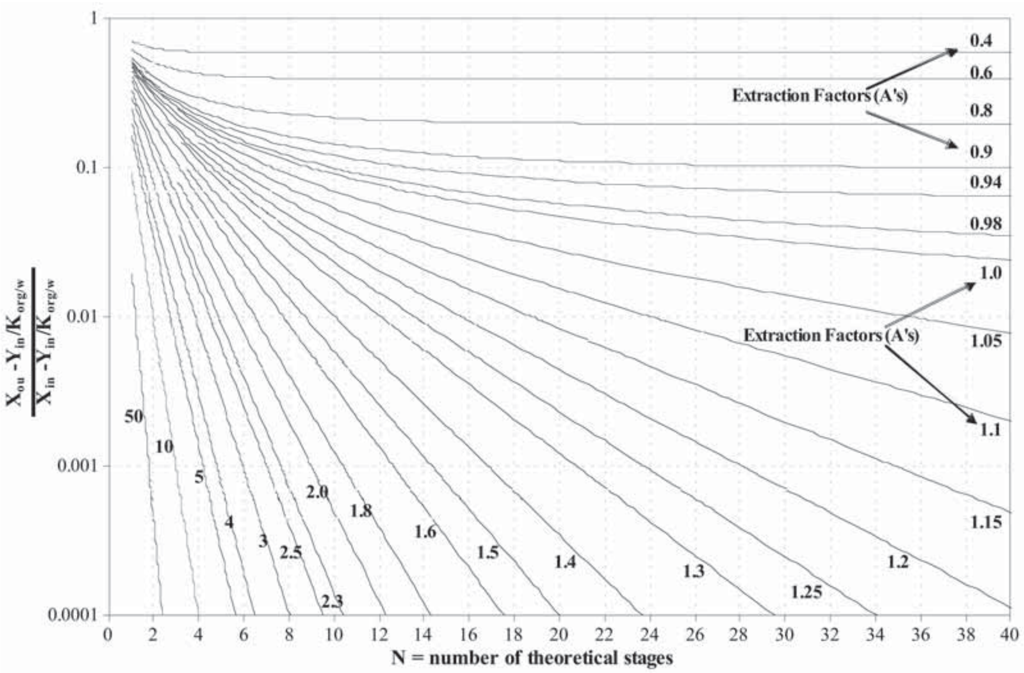

Fig. 3. Graphical representation of the Kremser equation.

Note in Fig. 3 the curve for $A = 1$, which is the critical value of the dimensionless group, the extraction factor. Based on the critical value of 1 for the extraction factor, A, the following can be observed in Fig. 3:

(a) If $A < 1$, the amount extracted from the water is limited to the value of A, even for an infinite number of stages. In other words, the maxium "fraction not extracted" = $1 - A$.

(b) If $A > 1$, any amount can be extracted, given enough stages, and the number of stages needed for the extraction reduces as A increases.

(c) Capital cost (number of stages) decreases as A increases; however, operation cost for a fixed volume of feed needing treatment increases since A increases if E or the volume of solvent used, increases.

The use of volume flow rates in Eqs. (8)–(14) instead of molar flow rates is, in general, arbitrary. However, for environmental treatments, the volumetric flow rates are usually more convenient because the bulk volumes of the solvent-rich phase in environmental treatments generally remain constant between stages. Also allowing the assumption of R_n/E_{n+1} being a constant may or may not be possible with molar flow rates. In addition, it is usually difficult to know the molar content of complex solvents like crude oil. Alternatively, if the solute has concentrations high enough that its extraction results in a significant change in R_n relative to E_{n+1}, converting to solute-free concentrations and flow rates would still allow the use of Eq. (13). For details on using solute-free concentrations and flow rates refer to Treybal (14).

11.5. Type 2 Liquid/Liquid Extraction

Type 2 liquid/liquid extraction involves two bulk liquids that are partially immiscible. Therefore, both phases contain significant fractions of both liquids in addition to the solute. However, since organics of environmental concern (the solute) generally have low solubility in water, some type 2 extractions can be treated as three processes in series. The first process is only stage 1 in the countercurrent extraction train; the second process is stages 2 through *N*–1 and treated as a type 1 liquid/liquid extraction; finally, the third process is stage *N*. Here we assume that the water becomes saturated with the solvent in stage 1 and the solvent is saturated with water in stage *N*. The E/R ratio, while not constant between stages 1 and 2, is constant from stage 2 through stage *N*–1.

However, there are cases where the solute has a high concentration in the raffinate (water) phase. The engineering calculations for these systems are beyond the scope of this chapter and the reader is referred to detailed texts on the subject, such as Treybal (14) or McCabe et al. (15). The reader should note that the general qualitative trends relative to the extraction factor in the Kremser chart still apply to Type II liquid/liquid extraction even if the numerical solutions do not.

12. LEACHING

Leaching is a unit operation for removing one or more soluble constituents from a solid by a liquid solvent. Generally, a leaching process involves three consecutive steps:

1st. The change of phase of the solute as it dissolves in the solvent.
2nd. Its diffusion through solvent in the pores of the solid to the outside of the particles.
3rd. The transfer of the solute from the solution in contact with the particles to the main bulk of the solution.

The second and third steps are usually the rate-controlling steps. To enhance the solubility and minimize the mass-transfer limitations, the design of a leaching unit will have to take into consideration the effects of particle size, solvent, temperature, and agitation.

12.1. Solubility and Mass-Transfer Factors

12.1.1. Particle Size

The smaller the size, the larger is the interfacial area between the solid and liquid and, therefore, the higher is the rate of transfer of material; moreover, the shorter is the distance the solute must diffuse with the solid. Nevertheless, fine particles may impede the subsequent particle–liquid separation and liquid circulation. To achieve a uniform dissolution and facilitate the separation, it is generally desirable to choose particles of a narrow size range.

12.1.2. Solubility

The ultimate leaching efficiency in the absence of mass-transfer limitations is governed by the solubility of the solute in the solvent; the extent to which solid can dissolve in liquids vary enormously. The solubility can be either experimentally determined or, alternatively, it can be estimated based on thermodynamics principles. If the pure solute is a solid at the extraction temperature, the following relates the fugacity of this pure solid solute to its fugacity in the liquid solution:

$$x_2 = \frac{f_2^S}{\gamma_2 \, f_2^L} \tag{15}$$

where x_2 = the mole fraction of the solute in the solvent, γ_2 = the activity coefficient of the solute in the solution, $f_2{}^s$ = the fugacity of the pure solute at solution temperature, bars, and $f_2{}^L$ = the fugacity of the subcooled solute in liquid state and solution temperature, bars.

The subscript 2 denotes the component # 2 in the solution, or the solute. The subcooled pure liquid solute is chosen as the hypothetical standard state for convenience; this has fair accuracy provided that the solution temperature is not far removed from the triple point of the solute. The fugacity ratio in Eq. (16) can be related to the change of Gibbs energy of the solute from solid to subcooled liquid state. By designing a three-segment route from its solid state to subcooled liquid state through its triple point, Prausnitz et al. (16) derived an expression for the estimation for this fugacity ratio:

$$\ln \frac{f_2^L}{f_2^S} = \frac{\Delta h^f}{R\,T_t}\left(\frac{T_t}{T}-1\right) - \frac{\Delta c_p}{R}\left(\frac{T_t}{T}-1\right) + \frac{\Delta c_p}{R}\ln\frac{T_t}{T} \tag{16}$$

where T_t = the triple point temperature of the solute, Δh^f = enthalpy of fusion of the solute at its triple point temperature, energy/mol, c_p= the heat capacity, energy/mol·temp, R = the universal gas constant, and $\Delta c_p = c_{p,\text{ liquid}} - c_{p,\text{ solid}}$.

Equations (15) and (16) suggest that for ideal solutions, i.e., for the solutions involving molecules of similar sizes and intermolecular forces, $\gamma_2 \approx 1$ and the solubility can be estimated based on enthalpy of fusion, heat capacities of solute in solid and liquid states, and triple point temperature. Moreover, Eqs. (15) and (16) imply that solubility increases with temperature.

The activity coefficient has to be estimated for nonideal solutions. There is no general method for predicting activity coefficients of solid solutes in liquid solvents. For nonpolar solutes and solvents, however, a reasonable estimate can frequently be made with the regular solution theory, or the Scatchard–Hildebrand relation,

$$\ln\gamma_2 = \frac{v_2^L(\delta_1-\delta_2)^2\,\Phi_1^2}{R\,T} \tag{17}$$

where v_2^L= the molar volume of the subcooled liquid, volume/mol, δ_1 = solubility parameter of the solvent, energy/volume, δ_2 = solubility parameter of the subcooled solute, energy/volume, and Φ_1 = volume fraction of the solvent, or,

$$\Phi_1 = \frac{x_1\,v_1^L}{x_1\,v_1^L + x_2\,v_2^L} \tag{18}$$

In using Eqs. (17) and (18), the molar liquid volume of the solvent, v_1^L, can be estimated by resorting to generalized density correlation chart (17). The solubility parameter of the solvent can be determined based on its definition, or,

$$\delta_1 = \left(\frac{\Delta u_1}{v_1^L}\right)^{1/2} \tag{19}$$

where Δu_1= the internal energy of vaporization of the solvent.

For the pure solute, however, its molar volume and solubility parameter at subcooled liquid temperature will have to be estimated by using a three-segment route identical to that used in the derivation of Eq. (16). The resultant expression for molar volume can be expressed as follows (16):

$$v^L = v^S + \left(v_t^L - v_t^S\right) + \left(v_t^S\alpha^S - v_t^L\alpha^L\right)\left(T_t - T\right) \tag{20}$$

where α^s and α^L are the volumetric coefficient of expansion of the solute in solid and liquid state, respectively, $(\text{temp})^{-1}$.

Alternatively, the molar volume of liquids may be estimated by generalized correlation methods (17) or group contribution methods (see Table 3). The subscript 2 is omitted in Eq. (20). The solubility parameter can be estimated based on its definition, or,

$$\delta_2 = \left(\frac{\Delta u_2}{v_2^L} \right)^{1/2} \tag{21}$$

Nevertheless, the heat of vaporization derived from the three-segment route can be expressed as follows (16):

$$\Delta u_2 = \Delta h^{sb} - \Delta h^f + \Delta c_p (T_t - T) - P^s (v^G - v^L) \tag{22}$$

where Δh^{sb} = enthalpy of sublimation of the solute at the extraction temperature T, energy/mol, Δh^f = enthalpy of fusion of the solid at its triple point temperature, P^s = saturation pressure of the subcooled liquid at T, and v^G = molar volume of the saturated vapor in equilibrium with the solid at T.

For the prediction of solubility of polar solutes in polar solvents, the regular solution theory, Eq. (17), has been modified to take into account the additional interactions between the solvent and the solute. Some of these modified methods are discussed by Prausnitz et al. (16).

12.1.3. *Temperature*

As discussed in the last section, Eqs. (15) and (16) suggest that the solubility of solid solutes increases with increasing temperature. Furthermore, the diffusion coefficient increases with increasing temperature, and this is expected to enhance the dissolution rate. In some cases, however, secondary considerations, such as reactions of the solute, can place a limit on the operation temperature.

12.1.4. *Agitation*

Agitation usually enhances diffusion, reduces mass transfer limitation, and, therefore, increase dissolution rate. Vigorous agitation of solid is applied only to leaching of fine particles.

12.2. *Equipment and Applications*

Three types of leaching unit operations have been developed (15,18):

(a) Stationary percolation.
(b) Moving-bed.
(c) Agitators.

Stationary percolation is conducted in a tank or a series of countercurrent-flow tanks with perforated bottoms to support the solid particles and permit drainage of the solution. To allow filling and discharge of one tank at a time without disturbing the continuous operation of other tanks, the piping is designed so that the solvent can be introduced to any tank and the solution can be withdrawn from any other tank simultaneously.

Several types of moving beds have been adopted for leaching. The Bollman extractor involves a chain of perforated baskets that moves downward at one side of the bucket elevator and upward at other side. The solid is fed into the top basket on the downward side, and is discharged from the top basket on the upward side. The solvent is sprayed onto the solid that is about to be discharged, and passes downward through the baskets in a countercurrent flow. The solvent is then allowed to flow down through the baskets moving downward in co-current flow.

The Hildebrandt extractor consists of a U-shaped screw conveyer with a separated helix in each of the downward, horizontal, and upward sections. Solids are fed to one leg and fresh solvent is fed to the other to give countercurrent flow. In a Dorr classifier, solid is introduced near the bottom of a sloping tank and is gradually moved up by means of a rake. The solvent enters at the top and flows in the opposite direction of the solid and passes under a baffle before finally being discharged over a weir. A number of these units can be connected in series to give countercurrent flow.

To enhance the extraction efficiency, impermeable particles have to be ground before leaching. The flow resistance between the solvent and the fine particles, however, is much higher than those in the stationary percolation and moving-bed extractors. Alternatively, agitators have been used to disperse and leach fine particles. Dispersion of particles can be achieved either by a mechanical stirrer or by flow mixing. The leached residue is then separated from the solution by settling or by filtration. Stirred tanks are the simplest agitators.

The following is a representative list of leaching applications:

(a) Extraction of contaminants from soil.
(b) Extraction of oil from seeds.
(c) Extraction of potassium sulfate from alums.
(d) Extraction of wax from waxed papers.
(e) Extraction of salts from pigments.
(f) Coffee from coffee bean grounds.

The design of a multistaged extraction process follows the same procedure as the liquid–liquid extraction process that was discussed previously in this chapter. If one can assume that 100% of the solute is dissolved in the solvent, then it is possible to use the Kremser relationship [Eq. (13) and Fig. 3] by defining the volume of the raffinate, R, to be the liquid trapped and entrained in the solids. Under this definition, the extract, E, is the volume of the liquid decanted in each countercurrent stage. The distribution coefficient, K, is equal to 1, since $Y = X$ in each stage. The Kremser relationship applies to stages 2 through N; however, stage 1, because it has no entrained liquid entering it, must be treated as a separate unit.

13. EXTRACTION AND DESTRUCTION OF HAZARDOUS MATERIALS BY SUPERCRITICAL FLUIDS

Under supercritical conditions, a gas, such as carbon dioxide, possesses liquid-like density and solubility, and gas-like diffusivity and viscosity, along with zero surface tension. Thus, supercritical fluids work extremely well as a processing media for a wide variety of chemical, biological, and polymer extractions. This solvent power of supercritical fluid has been known since 1879. Nevertheless, its application was not considered until recently when the sharp increases in energy cost, environmental regulations, and performance demands on materials have caused industry to consider alternative means of waste treatment. As a consequence, the fundamentals of supercritical fluid extraction (SFE) have been investigated extensively in the last three decades, and many technologies have been commercialized (19–23).

In addition to its high dissolution efficiency, another powerful aspect to SFE is its ability to precisely control which component(s) of a complex matrix are extracted and which ones are left behind. This is accomplished through precise control of several key operating parameters such as temperature, pressure, flow rates, and processing time. Yields are much greater with SFE than extractions performed by traditional techniques, and product purity is usually high. Decomposition of materials almost never occurs due to the relatively mild processing temperatures.

13.1. Principles

Quantitative analysis of solubility of a solute around the critical point of a solvent requires fundamental understanding of the pressure-temperature-composition (P-T-x) phase diagram of the system. During SFE, the most important regions in the P-T-x diagram are those of two-phase liquid–vapor (LV), solid–vapor (SV), or liquid–liquid (L-L) equilibria; three-phase liquid–liquid–vapor (LLV), solid–liquid–vapor (SLV), or solid–solid–vapor (SSV) equilibria, and sometimes four-phase liquid–liquid–solid–vapor (LLSV) or liquid–solid–solid–vapor (LSSV) equilibria. The literature is full of publications that deal with two modeling efforts using either equation-of-state or experimental work that cover wide ranges of temperature and pressure. Prausnitz et al. (16), McHugh and Krukonis (20), Williams (24), and Streett (25) discuss the most frequently encountered types of phase diagrams in details. For the same reason, recent design of bench-scale SFE apparatus often includes direct visualization of the materials under extraction conditions.

Solid–vapor (SV) equilibria are often adopted for the estimation of solubility under SFE conditions. This case is relatively simple because the solubility of gas in solid can almost always be ignored, and the solid solute can be considered pure. Under SV equilibrium, the fugacity of the pure solid, or component 2, is equal to the fugacity of the solute in the solution, i.e.,

$$f_2^S = \hat{f}_2^V \equiv \hat{\phi}_2 y_2 P \tag{23}$$

where $f_2{}^S$ = fugacity of pure solid, or the solute, $\hat{f}_2{}^V$ = fugacity of the solute in the solution, $\hat{\phi}_2$ = fugacity coefficient of the solute in the solution, y_2 = molar fraction of the solute in the solution, or the solubility, and P = system pressure.

The fugacity of pure condensed solid is given by

$$f_2^S = P_2^{\mathrm{Sat}} \phi_2^{\mathrm{Sat}} \exp\left(\int_{P_2^{\mathrm{Sat}}}^{P} \frac{v_2^S}{RT} dP \right) \tag{24}$$

where P_2^S = saturation pressure of the solute at system temperature, T, ϕ_2^{Sat} = fugacity coefficient of the solute at the saturation pressure, and v_2^S = molar volume of the solid solute.

Combining Eqs. (23) and (24) yields the expression for solubility

$$y_2 = \frac{P_2^{\mathrm{Sat}}}{P} E_h \tag{25}$$

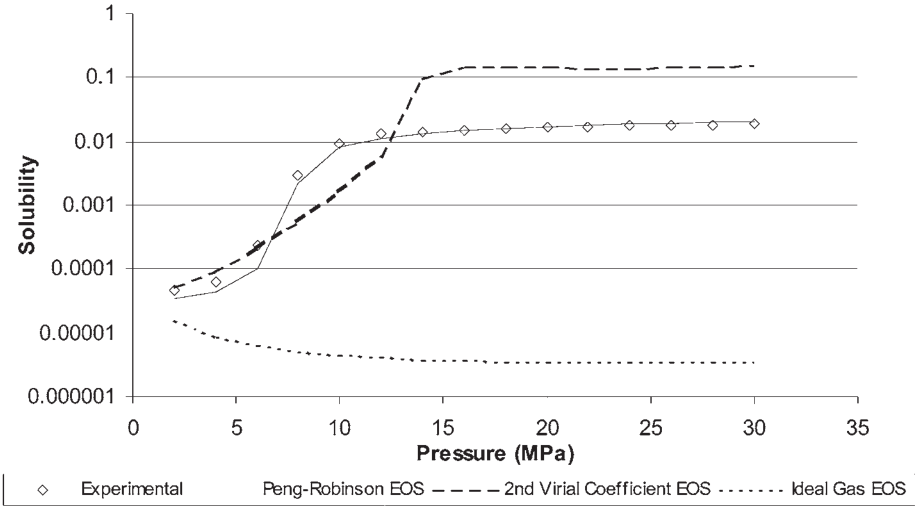

Fig. 4. Predicted solubilities of naphthalene in supercritical carbon dioxide at 308.15 K.

where the enhancement factor, E_h, is defined as

$$E_h \equiv \frac{\phi_2^{\text{Sat}}}{\hat{\phi}_2} \exp\left(\int_{P_2^{\text{Sat}}}^{P} \frac{v_2^S}{RT} dP \right) \tag{26}$$

The quantities on the right-hand sides of Eqs. (24) and (25) are either available in the literature or can be estimated using elementary methods in thermodynamics. Among these quantities, $\hat{\phi}_2$ is an index of departure from the ideal gas state, and it has the most significant influences on solubility. Cubic equation of states (EOS) is often used for the prediction of solubility values (16). By using the Peng–Robinson EOS and Eqs. (25) and (26), Smith and Chen (26) demonstrated that the solubility of naphthalene in supercritical carbon dioxide could be accurately predicted as shown in Fig. 4. When the critical conditions of the solutes are not available or if they undergo chemical transformation before reaching their critical conditions, these properties can be estimated by group contribution methods (27).

For a LV system under equilibrium, the fugacity of solid on the left-hand side of Eq. (23) will be replaced by the fugacity of the solute in the liquid phase, $\hat{f}_2^L$. This quantity, in turn, can be estimated through, $\gamma_2 x_2 f_2^0$, where γ_2 = activity coefficient of the solute, x_2 = molar fraction of the solute in the liquid solution, and f_2^0 = fugacity of pure solute at a standard, liquid state.

Vapor–liquid phase equilibrium calculations have to be conducted for the estimation of solubility in the vapor phase (16,17). Alternatively, a cubic EOS can be applied for the estimation of properties of the liquid phase. The equality of fugacity in the two phases can be written as

$$\hat{\phi}_2^V y_2 = \hat{\phi}_2^L x_2 \tag{27}$$

where $\hat{\phi}_2^L$ = the fugacity coefficient of the solute in the vapor phase.

The two fugacity coefficients in Eq. (27) can be estimated based on partial molar residual volumes through a cubic EOS and a mixing rule (16,17). For instance, when the Peng–Robinson EOS is used, the fugacity coefficients of both liquid and liquid phase can be expressed as (16,17):

$$\ln\hat{\phi}_2 = \frac{b_2}{b}\left(\frac{PV}{RT}-1\right) - \ln\frac{P(V-b)}{RT} - \frac{a}{2\sqrt{2}bRT}\left(\frac{2\sum_{j=1}^{2} y_j a_{j2}}{a} - \frac{b_2}{b}\right)\ln\left(\frac{V+\left(1+\sqrt{2}\right)b}{V+\left(1-\sqrt{2}\right)b}\right) \tag{28}$$

where mixture parameters a and b follow a specific mixing rule.

If the van der Waals mixing rule is adopted,

$$a = \sum_i \sum_j y_i y_j a_{ij} \tag{29}$$

$$b = \sum_i y_i b_i \tag{30}$$

where the binary parameter, a_{ij}, energy·volume/mol, is the geometric mean of the individual parameter of the pure species adjusted by an experimentally determined binary interaction parameter, k_{ij}, then

$$a_{ij} = \left(a_i a_j\right)^{0.5}\left(1-k_{ij}\right) \tag{31}$$

In designing an equilibrium-staged extraction unit, the partition coefficient, $K = y/x$, is estimated by Eq. (27). We assume that there are two sets of parameters and variables in Eq. (28), including a, b, V, and y_j, one set for each phase. Dickson et al. (28) have presented a detailed calculation of this type.

If the system contains more phases, such terms as LLV, SLV equilibria, fugacity of the solute in each phase will have to be included in the calculation. The principle remains the same as that discussed above, but the calculations will become more involved.

Carbon dioxide, water, ethane, ethylene, propane, ammonia, xenon, nitrous oxide, and fluoroform have been considered useful solvents for SFE. Carbon dioxide has so far been the most widely used as a supercritical solvent because of its convenient critical temperature, 304°K, low cost, chemical stability, nonflammability, and nontoxicity. Its polar character as a solvent is intermediate between a truly nonpolar solvent such as hexane and a weakly polar solvent. Moreover, CO_2 also has a large molecular quadrupole. Therefore, it has some limited affinity with polar solutes. To improve its affinity, additional species are often introduced into the solvent as modifiers. For instance, methanol increases CO_2's polarity, aliphatic hydrocarbons decrease it, toluene imparts aromaticity, R-2-butanol adds chirality, and tributyl phosphate enhances the solvation of metal complexes.

13.2. *Applications*

Supercritical fluid extraction has been widely used in petroleum, pharmaceutical, food, polymer, and environmental industries (20,21). Supercritical fluids have also been adopted as a reacting medium, such as that in the destruction of hazardous wastes. Examples of these technologies include:

(a) Petroleum

1st. deasphalting, or separating lubricating oil from naphthenic, by near critical propane
2nd. residuum oil supercritical extraction, or ROSE, by butane and pentane

(b) Pharmaceutical
  1st. extracting vitamin A from fish oils by propane
  2nd. extracting chemotherapeutic agents by supercritical CO_2
  3rd. extracting natural antioxidants by supercritical CO_2

(c) Food
  1st. concentrating the polyunsaturated triglycerides in vegetable oils by propane
  2nd. decaffeinating coffee by supercritical solvents such as CO_2
  3rd. extracting and fractionating spices and herbals by supercritical CO_2

(d) Polymer
  1st. extracting cyclic and low-molecular-weight oligomers from polyoxyalkylene by supercritical propylene
  2nd. fractionating of polypropylene, polybutene-1, and Nylon-6 by supercritical CO_2

(e) Environmental
  1st. regenerating of sorbents from waste water treatment by supercritical CO_2
  2nd. destructing contaminants in municipal and industrial liquid wastes and sludge by supercritical water oxidation
  3rd. extracting natural pesticides by supercritical CO_2

14. EXAMPLE PROBLEMS

14.1. Example 1—Preliminary Design of the Minimum Solvent Flow Rate and Number of Extraction Stages

Do a preliminary design of liquid/liquid extraction of wastewater containing 1 mol/L of acetone. Use chloroform for the solvent. Determine the following for 99.9% removal of the acetone from the 100 L/min flow rate of wastewater; assuming the feed solvent acetone concentration is zero, $Y_{in} = 0$:

(a) Minimum flow rate of chloroform, E_{min}
(b) Number of theoretical extractions stages if the solvent flow rate is $1.2 \times E_{min}$

Solution:

Because the mole fraction of acetone in the waste water is less than 0.1 (in fact it is 0.018) and the chloroform water solubility is very low (0.071 mol/L), we can assume this is a type 1 liquid/liquid extraction for the purposes of a preliminary design.

(a) Calculation of E_{min}

E_{min} is an engineering design quantity and is the flow rate of solvent needed for the extraction given an infinite number of equilibrium stages. E_{min}, therefore, defines the lower limit on the required flow rate of the solvent to achieve the extraction. As the solvent flow rate is increased from E_{min}, the number of required stages decreases; however, the operation cost increase; $1.2 \times \mathrm{E}_{min}$ is a "rule-of-thumb" for a preliminary design for an optimal solvent flow rate. So under these conditions we can use the definition of the extraction factor to obtain E_{min}:

$$A_{min} = \frac{K_{c/w} E_{min}}{\mathrm{R}} \tag{32}$$

where A_{min} = fraction recovered = 0.999 and $K_{c/w}$ = 5.25, and R = raffinate flow rate, assumed equal to the wastewater feed rate = 100 L/min.
Solving Eq. (32) yields:

$$E_{min} = 19.03 \text{ L/min}$$

(b) Calculation the number of ideal extractions stages

Use $E = 1.2 \times E_{\text{min}} = 1.2 \times 19.03$ L/min = 22.8 L/min
Calculate a new extraction factor from:

$$A = \frac{(5.25)(22.8)}{100} = 1.2$$

In Fig. 3, the intersection of $A = 1.2$ with the y-axis grid of 0.001 gives the number of theoretical stages, 28. This is a very large number of theoretical stages. Inspecting Fig. 3, we see that we can reduce the number of stages to 9 if we use an extraction factor of 2, which relates to a solvent flow rate of 38.06 L/min.
Therefore, in conclusion a reasonable preliminary design for the extractor would be 10 stages using a flow rate of 39 L/min to allow for margin of errors in the assumptions.

14.2. Example 2—Extraction of Phenol with Caustic Water Recovery

Consider the extraction of phenol from wastewater using toluene followed by the recovery of the toluene by using a caustic water solution. For this problem use the following data:

Wastewater feed rate is 100 L/min
Phenol concentration in the feed waste water = 0.75 mol/L
Toluene flow rate = 150 L/min
The waste water extractor has 8 theoretical stages
Phenol distribution between toluene and water, $K_{\text{toluene/w}} = 1.32$
pKa of phenol = 9.95
Caustic water flow rate in the toluene recovery unit = 10 L/min
The toluene recovery unit has six theoretical stages

Determine the following
(a) The extraction factor of the wastewater extractor if the feed wastewater has a pH of 9.1.
(b) The fraction of phenol extracted in the wastewater extractor, assuming $Y_{\text{in}} = 0$.
(c) If the pH of the wastewater was adjusted to 7.9, how much could the toluene flow rate be decreased to in order to achieve the same percentage of phenol extraction?
(d) The required pH of the caustic wash to recover 99.9% of the acetone from the toluene. Assume the wastewater's pH was 7.9.
(e) After start-up, the caustic wash has an overall stage efficiency of 67% compared to the theoretical stages. Determine the faction extracted from the waste water under these conditions.

Solution:

(a) The extraction factor
The first step is the calculation of the effective distribution coefficient, $D_{\text{org/w}}$, for the waste water pH, using Eq. (7) followed by Eq. (5);

$$\alpha = \frac{1}{1 + 10^{(9.1 - 9.95)}}$$

$$\alpha = 0.876$$

$$\mathrm{D}_{\text{org/w}} = 0.876 \times 1.32$$

$$\mathrm{D}_{\text{org/w}} = 1.1566$$

Now the extraction factor is

$$A = \frac{(1.1566)(150)}{100} = 1.7$$

Table 5
Representative Solvent/Water Distributions for Butanoic Acid

	Eq. (2)		Eq. (3)	
Solvent	$K_{org/w}$	$\log(K_{org/w})$	$K_{org/w}$	$\log(K_{org/w})$
n-Hexadecane (apolar)	0.0175	–1.76	0.0119	–1.92
Trichloromethane (H-donor)	0.825	–0.083		
Diethylether (H-acceptor)	5.95	0.77		
n-Octanol (bipolar)	5.79	0.76	6.17	0.79*

*Literature value from ref. (10)

Table 6
Control Technology Summary for Solvent Extraction (29)

		Effluent concentration		Removal efficiency (%)	
Pollutant	Data points	Range	Median	Range	Median
Classical pollutants, mg/L					
COO	5	54–18,000	1100	31–72	50
Chlorine, total	2	35–170	100	87–94	88
Toxic pollutants, µg/L					
Xylene	2	>1000–<1000	<1000	>97–>98	98
Phenol	8	2119–4.6E6	900,000	3–96	64
Cresol	5	803–3.3E5	40,000	74–98	91
Benzene	6	7000–35,000	8100	75–97	96
Ethylbenzene	1		4000		97
Toluene	2	1600–2300	2400	94–96	95
Styrene	1		4000		>93
Acetone	3	12,000–22,000	6000	40–57	52
MEK	4	3500–55,000	36,000	50–95	63
1,2-Dichloroethane	1		<20,000		>99
1,2-Dichloropropane	1		97,000		85
1,1,2,2-Tetrachloroethane	1		9200		92
1,1,2-Trichloroethane	1		16,000		90

Source: US EPA (29).
Blanks indicate data not available.

(b) The extracted factor
Inspecting Fig. 3, the y-axis for $A = 1.7$ and $N = 8$ is 0.006.
Therefore, the fraction extracted for $Y_{in} = 0$ is
(1-y-axis) = (1 – 0.006) = 0.994.

(c) Amount of toluene saved by adjusting the pH to 7.9
Recalculatd the effective distribution coefficient, $D_{org/w}$:

$$\alpha = \frac{1}{1+10^{(7.9-9.95)}}$$

$$\alpha = 0.991$$

$$D_{org/w} = 0.991 \times 1.32$$

$$D_{org/w} = 1.308$$

Table 7
Solvent Extraction Performance in Petroleum Refining Industry (Lube Oil Refining Subcategory) Using Extractor (Spray Column Contactor and Stripping Column) and Solvent (Isobutylene)

Design or operating parameters	
Unit configuration	Spray column contactor and stripping column
Column specifications	0.0254 m diameter × 0.914 m glass pipe
Type of solvent	Isobutylene
Solvent flow rate	0.014 m^3/h
Wastewater flow rate	0.003 m^3/h

	Removal data		
	Concentration		
Pollutant/parameter	Influent	Effluent	Percent removal
Toxic pollutants (µg/L)			
Phenol	23,000,000	4,600,000	80
Benzene	170,000	7000	96
Acetone	37,000	16,000	57
MEK	230,000	12,000	95
o-Cresol	2,000,000	50,000	98

Source: US EPA (29).
Blanks indicate data not available.

Now to obtain same extraction factor (1.7) as before, we invert Eq. (14) and solve for E.

$$\mathrm{E} = \frac{A\mathrm{R}}{K_{\mathrm{org/w}}} = \frac{(1.7)(100)}{1.308} = 130\ \mathrm{L/min}$$

So adjusting the pH would save 20 L/min of toluene flow. Note the rule-of-thumb here is that $D_{\mathrm{org/w}} = K_{\mathrm{org/w}}$ for organic acids at $\mathrm{pH} < \mathrm{p}Ka - 2$ and for organic bases at $\mathrm{pH} > \mathrm{p}Ka + 2$.

(d) Required pH of caustic wash
Note that the recovery column is still a liquid/liquid extractor; however, the toluene's role is now the raffinate and the caustic water is the solvent. In addition, the distribution coefficient needs to be defined as $C_{\mathrm{w}}/C_{\mathrm{org}}$ or the inverse of the definition for the wastewater extractor. The first step is to determine the required extractor factor to achieve 0.999 recovery for six theoretical stages. Find the intersection for y-axis = 1–0.999 = 0.001 and x-axis = 6 stages. The A for this intersection is 3. Now solve Eq. (14) for the required $K_{\mathrm{w/org}}$:

$$K_{\mathrm{w/org}} = \frac{AR}{E} = \frac{(3)(130)}{10} = 39$$

So if we need $K_{\mathrm{w/org}} = 39$, then $D_{\mathrm{org/w}}$ from Eq. (8) will be equal to 1/39 or 0.02564. Solving Equation (5) for a gives $\alpha = 0.02564/1.32 = 0.0194$.
Now solve Equation (7) for pH given $\alpha = 0.0194$, pH = 11.65.

(e) Fraction extracted
Finally, if the solvent recovery unit is operating at 67% efficiency, then it operates as though it has only four theoretical stages. This means that the fraction of phenol recovery from the toluene reduces to 0.1 (verify this for yourself using Fig. 3).

Table 8
Solvent Extraction Performance in Petroleum Refining Industry (Lube Oil Refining Subcategory) Using Extractor (Rotating Disk Contactor and Stripping Column) and Solvents (Isobutylene & *n*-Butyl Acetate)

Design or operating parameters	
Unit configuration	Rotating disk contactor and stripping column
Column specifications	0.0762 m diameter × 1.22 m glass pipe
Type of solvent	48.7 wt. % *n*-butyl acetate, 51.3 wt. % isobutylene
Solvent flow rate	0.004 m^3/h
Wastewater flow rate	0.015 m^3/h

	Removal data		
	Concentration		
Pollutant/parameter	Influent	Effluent	Percent removal
Toxic pollutants (μg/L)			
Phenol	17,000,000	1,900,000	89
Benzene	37,000	9200	75
Acetone	25,000	12,000	52
MEK	110,000	55,000	50
o-Cresol	2,700,000	120,000	96

Source: US EPA (29).
Blanks indicate data not available.

This means that the toluene leaving the caustic wash still contains a significant concentration of phenol and this phenol recycles back to the wastewater extractor. Therefore, the task is to calculate the reduction in phenol extracted from the wastewater due to the phenol content of the recycled toluene compared to feeding fresh toluene. Assume the waste water pH is adjusted to 7.9 (i.e., the solvent flow rate is 130 L/min).

The solution to this problem comes from realizing that the number of stages and extraction factor of the wastewater extractor are unaffected by phenol in the solvent feed. Therefore the *y*-axis in Fig. 3 remains the same for any value of Y_{in}. With this realization we can develop a system of equations that can be solved for X_{out} given $X_{in} = 0.75$ mol/L. The first equation is the definition of the y-axis for the wastewater extractor using $X_{in} = 0.75$ and $D_{org/w} = 1.308$:

$$\frac{X_{out} - Y_{in}/1.308}{0.75 - Y_{in}/1.308} = 0.006 \tag{EP-1}$$

The second equation relates Y_{in} and Y_{out} via the fraction recovered in the caustic waste

$$Y_{in} = 0.1Y_{out} \tag{EP-2}$$

The third equation is a mass balance around the waste water extractor and relates Y_{in}, Y_{out}, and X_{out}:

$$(X_{in} - X_{out})\mathrm{R} = (Y_{out} - Y_{in})\mathrm{E} \tag{EP-3}$$

Noting that in Eq. (EP-3); $X_{in} = 0.75$ mol/L, R = 100 L/min, and E = 130 L/min, the system of equations, (EP-1)–(EP-3), is a system of three equations with three unknowns.

Table 9
Solvent Extraction Performance in Organic Chemicals Industry (Ethylene Oxychlorination Subcategory) Using Extractor (Multi-stage Extractor and Stripper) and Solvent (paraffin)

Design or operating parameters	
Unit configuration	Multistage
Column specifications	Extractor: 0.10 m diameter × 3.0 m; stripper: 0.05 m diameter × 2.25 m
Type of solvent	C_{10}–C_{12} paraffin
Solvent flow rate	0.205 L/min
Wastewater flow rate	0.76–3.76 L/min

	Removal Data			
	Concentration			
Pollutant/parameter	Influent	Effluent	Percent removal	H_2O to solvent ratio
Toxic pollutants (μg/L)				
1,2,-Dichloroethane	920,000	350,000	62	18.3:1
	190,000	20,000	89	13.7:1
	210,000(a)	36,000(a)	83	9.1:1
	460,000(b)	51,000(b)	89	5.5:1
	1,100,000(c)	27,000(c)	98	3.7:1
1,1,2,2-Tetrachloroethane	22,000	6000	73	18.3:1
	200,000	2000	99	13.7:1
	85,000(c)	11,000(c)	87	9.1:1
	51,000(d)	1000(d)	98	5.5:1
	91,000(a)	1000	99	3.7:1
1,1,2-Trichloroethane	110,000	16,000	85	18.3:1
	360,000	30,000	92	13.7:1
	150,000(a)	22,000(a)	85	9.1:1
	110,000(e)	5400(e)	95	5.5:1
	110,000(a)	8700(a)	92	3.7:1
Classical pollutants, mg/L:				
Total Chlorine	1600	510	68	18.3:1
	910	81	91	13.7:1
	550	85(a)	85	9.1:1
	1800	110(a)	94	5.5:1
	1800	84(c)	95	3.7:1

Source: US EPA (29).
(a) Average of three one-day composites.
(b) Average of four one-day composites.
(c) Average of two one-day composites.
(d) Average of six one-day composites.
(e) Average of five one-day composites.

The solution of the equations yields the following:

$$X_{out} = 0.0457 \text{ mol/L}$$

$$Y_{out} = 0.542 \text{ mol/L}$$

$$Y_{in} = 0.0542 \text{ mol/L}$$

Table 10
Solvent Extraction Performance in Organic Chemicals Industry (Styrene Production Subcategory) Using Extractor (Rotating Disk Contactor and Stripping Column) and Solvent (Isobutylene)

Design or operating parameters	
Unit configuration	Rotating disk contactor and stripping column
Column specifications	0.0762 m diameter by 1.22 m glass pipe
Type of solvent	Isobutylene
Solvent flow rate	0.451 m^3/h
Wastewater flow rate	2.49 m^3/h

	Removal data		
	Concentration		
Pollutant/parameter	Influent	Effluent	Percent removal
Toxic pollutants (µg/L)			
Benzene	290,000	10,000	97
Ethylbenzene	120,000	4000	97
Styrene	15,000	<1000	>93

Source: US EPA (29).

Table 11
Solvent Extraction Performance in Organic Chemicals Industry (Ethylene Quench Subcategory) Using Extractor (Rotating Disk Contactor and Stripping Column) and Solvent (Isobutylene)

Design or operating parameters	
Unit configuration	Rotating disk contactor and stripping column
Column specifications	0.076 m diameter by 1.22 m glass pipe
Type of solvent	Isobutylene
Solvent flow rate	0.652 m^3/h
Wastewater flow rate	3.84 m^3/h

	Removal data		
	Concentration		
Pollutant/parameter	Influent	Effluent	Percent removal
Classical pollutants (mg/L)			
COD	1900	1200	37
Toxic pollutants (µg/L)			
Phenol	67,000	63,000	6
Benzene	71,000	2900	96
Toluene	40,000	2300	94
Xylene	40,000	<1000	>98

Source: US EPA (29).
Blanks indicate data not available.

The reader should confirm that this Y_{in} used in Eq. (EP-1) results in the given X_{out} value. Finally the fraction extracted with $Y_{in} = 0.0542$ mol/L is:

Fraction extracted = 1 – 0.0457/0.75 = 0.939 (compare to 0.994 for $Y_{in} = 0$).

Table 12
Solvent Extraction Performance in Organic Chemicals Industry (Cresylic acid Recovery Subcategory) Using Extractor (Spray Column Contactor and Stripping Column) and Solvent (Isobutylene)

Design or operating parameters	
Unit configuration	Spray column contactor and stripping column
Column specifications	0.025 m diameter by 0.91 m glass pipe
Type of solvent	Isobutylene
Solvent flow rate	18.5 m^3/h
Wastewater flow rate	6.14 m^3/h

	Removal data		
	Concentration		
Pollutant/parameter	Influent	Effluent	Percent removal
Classical pollutants (mg/L)			
COD	4000	1100	72
Toxic pollutants (µg/L)			
Phenol	580,000	160,000	72
o-Cresol	310,000	31,000	90
m, *p*-Cresol	290,000	25,000	91
Xylene	230,000	<10,000	96

Source: US EPA (29).

14.3. *Example 3—Selecting an Extraction Solvent*

Choose a solvent to treat a waste water stream saturated with butanoic acid, $C_4H_8O_2$, at a concentration of 0.64 mol/L. The following are some useful data for butanoic acid:

pKa = 4.85
Melting temperature = –5.7 °C
Boiling Point = 163.7 °C
C^{sat} = 0.64 mol/L [Because at ambient temperatures butanoic acid is a liquid, this is also the $C^{sat}(L)$ value]
Refractive index = 1.398
$\log(K_{o/w}) = 0.79$

Solution:

You are aware that methyl isobutyl ketone is used to extract salicylic acids from wastewaters (see Applications section). Salicylic acid is an aromatic carboxylic acid; however, butanoic acid is an aliphatic acid. So the question becomes if a ketone (an H-acceptor) would still be a good choice for the extraction of an aliphatic acid.

First, calculate the distribution coefficients for the four representative solvents: octanol, hexadecane, diethylether, and chloroform.

Hexadecane/water distribution coefficient using Eq. (3)

$$\log[K_{h/w}] = 1.21\log[K_{o/w}] + (-2.88)$$

$$\log[K_{h/w}] = -1.92$$

There is no single parameter model for calculating the diethylether and chloroform distribution coefficients, so you need to use the multiple parameter model given in Eq. (2) and Tables 1–3.

Table 13
Solvent Extraction Performance in Organic Chemicals Industry (Ethylene Oxychlorination Subcategory) Using Extractor (Multistage Extractor and Stripper) and Solvent (Paraffin)

Design or operating parameters	
Unit configuration	Multistage
Column specifications	Extractor: 0.10 m diameter × 3.0 m; Stripper: 0.05 m diameter × 2.25 m
Type of solvent	C_{10}–C_{12} paraffin
Solvent flow rate	0.27 L/min
Wastewater flow rate	1.23–5.32 L/min

	Removal data			
	Concentration			
Pollutant/parameter	Influent	Effluent	Percent removal	H_2O to solvent ratio
Classical pollutants (mg/L)				
TOC	58	37	36	5:1
	73	48	34	6.5:1
	59	38	36	8:1
	76	39	49	10:1
	54	75	NM	16.5:1
	120	86	30[a]	20:1
Total chlorine	150	3.2	98	5:1
	180	3.0	98	6.5:1
	160	1.8	99	8:1
	300	6.6	98	10:1
	270	16	94	16.5:1
	690	180	74	20:1

Source: US EPA (29).
[a] Average of two 1-d composites.
NM, not meaningful.

Given in Table 5 are all the calculated distribution coefficients. In these calculations butanoic acid has a calculated group contribution molar volume of 74.66 cm^3/mol (see Table 3). Table 5 indicates that apolar and H-donor type solvents would be poor extraction solvents for butanoic acid. Both the H-acceptor and bi-polar solvents have similar values. Since methyl isobutyl ketone is an H-acceptor solvent and has a proven application extracting another organic acid it seams reasonable to initially explore its use as the solvent for the extraction of butanoic acid from wastewater. It is interesting to note that the model gives a reasonable estimate of the $K_{o/w}$ distribution compared to the literature value, also noted in Table 5.

14.4. *Example 4—Performance of Solvent Extraction*

Search the US EPA data and the literature, and discuss the performance of the solvent extraction process for the following environmental tasks:

(a) Average efficiency of solvent extraction for removing both classical and toxic pollutants.
(b) Performance data of solvent extraction for treatment of the petroleum refining industry wastewaters.
(c) Performance data of solvent extraction for treatment of the organic chemicals manufacturing industry wastewaters.

Solution:

(a) Extraction reduces phenol concentrations from levels of several percent down to levels of a few parts per million. Removal efficiencies of 90–98 % are possible in most applications, and with special equipment (e.g., centrifugal and rotating disk contactors, for instance) removal efficiencies of about 99% have been achieved (29). Removal of classical pollutants (COD, chlorine) and toxic pollutants (xylene, phenol, cresol, benzene, toluene, styrene, acetone, MEK, etc.) was reported by the US EPA (29), as shown in Table 6. Removal of metals and non-metal inorganics by solvent extraction has also been reported in the literature (30).

(b) Based on the US EPA data (29), the performance of solvent extraction in the petroleum refining industry are summarized in Tables 7 and 8.

(c) Again, based on the US EPA data (29), the performance of solvent extraction in the organic chemicals industry are summarized in Tables 9 to 13.

NOMENCLATURE

A	Extraction factor, dimensionless
a	Constant or parameter in property correlations
a	Parameter in the van der Waals equation of state, energy·volume/mol^2
a_{ij}	Interaction parameter between two species following van der Waals equation of state, energy·volume/mol^2
b	Parameter in the van der Waals equation of state, volume/mol
b	Constant or parameter in property correlations
C^{sat}	Saturated water solubility of the solute in is standard pure state (gas, liquid, or solid), mol/L
$C^{\mathrm{sat}}(L)$	Saturated water solubility of the solute in its LIQUID state at 25°C, mol/L
C_{o}	Solute concentration in octanol, mol/L
C_{Mix}	Solute concentration in a mixture of solvents, mol/L
C_{w}	Solute concentration in water, mol/L
c_p	Heat capacity, energy/mol·temperature
$D_{\mathrm{org/w}}$	Effective distribution coefficient of a solute between an organic solvent and water, L_w/L_{org}
E_h	Enhancement factor
E_{i}	Extraction solvent flow rate from stage "*i*," volume/time
E_{min}	Minimum extraction solvent flow rate, volume/time
F	Feed (i.e., contaminated wastewater) to the extractor, volume/time
$\hat{f}_2^V$	Fugacity of the solute in the solution, pressure
f_2^S	Fugacity of the pure solute at solution temperature, pressure
f_2^L	Fugacity of the subcooled solute in liquid state and solution temperature, pressure
$K_{\mathrm{c/w}}$	Distribution coefficient of a solute between chloroform and water, L_w/L_{org}
$K_{\mathrm{d/w}}$	Distribution coefficient of a solute between diethylether and water, L_w/L_{org}
$K_{\mathrm{h/w}}$	Distribution coefficient of a solute between hexadecane and water, L_w/L_{org}
$K_{\mathrm{hex/w}}$	Distribution coefficient of a solute between *n*-hexane and water, L_w/L_{org}
$K_{\mathrm{o/w}}$	Distribution coefficient of a solute between *n*-octanol and water, L_w/L_{org}
$K_{\mathrm{org/w}}$	Distribution coefficient of a solute between an organic solvent and water, L_w/L_{org}

$K_{\text{Mix/w}}$	Distribution coefficient of a solute between a mixture of organic solvents and water, L_w/L_{org}
$K_{\text{toluene/w}}$	Distribution coefficient of a solute between an toluene and water, L_w/L_{org}
$K_{\text{w/org}}$	Distribution coefficient of a solute between water and an organic solvent, L_w/L_{org}
k_j	Binary interaction parameter in the combining rule
N	The total number of stages is an extractor or the designation of the final extractor stage
n_{Di}	Solute's refractive index
P	System pressure
P^s	Saturation pressure of the subcooled liquid
p	Solvent specific parameters for property correlations
$\text{p}Ka$	Negative log (base 10) of the acid dissociation constant of the solute
R	Universal gas constant
R_i	Raffinate flow rate from stage "*i*," volume/time
S	Solvent feed rate entering stage *N*, volume/time
s	Solvent specific parameters for property correlations
T_t	Triple point temperature of the solute
V	Volume
V_m	Molecular volume of the solute from Table 3, volume/mol
V_{Mix}	Molecular volume of a mixture of solvents, volume/mol
V^G	Molar volume of the saturated vapor in equilibrium with the solid
v_1^L	Molar liquid volume of the solvent, volume/mol
v_2^L	Molar volume of the subcooled liquid, volume/mol
v_2^S	Molar volume of the solid solute, volume/mol
W	van der Waal interaction strength of the solute or its chemical class
X_i	Concentration of the solute in the raffinate exiting stage "*i*," moles/volume
$\underline{X}_{\text{in}}$	Concentration of the solute in the Feed entering the process, moles/volume
X_{out}	Concentration of solute in the raffinate leaving the process, moles/volume
x_2	Mole fraction of the solute in the solvent
Y_i	Concentration of solute in the extract exiting stage "*i*," moles/volume
Y_{in}	Concentration of the solute in the entering solvent, moles/volume
y_2	Molar fraction of the solute in the solution, or the solubility

Greek Containing Symbols

α	H-donor strength of the solute or its chemical class
α^L	Volumetric coefficient of expansion of the solute in liquid state
α^s	volumetric coefficient of expansion of the solute in solid state
β	H-acceptor strength of the solute or its chemical class
Δc_p	$c_{p,\text{ liquid}} - c_{p,\text{ solid}}$, energy/mol·temperature
Δh^f	Enthalpy of fusion of the solute at its triple point temperature, energy/mol
Δh^{sb}	Enthalpy of sublimation of the solute at the extraction temperature, energy/mol
Δu_1	Internal energy of vaporization of the solvent, energy/mol
δ_1	Solubility parameter of the solvent, energy/mol$^{1/2}$

δ_2	Solubility parameter of the subcooled solute, energy/mol$^{1/2}$
Φ_1	Volume fraction of the solvent
$\hat{\phi}_2$	Fugacity coefficient of the solute in the solution
$\hat{\phi}_2^L$	Fugacity coefficient of the solute in the vapor phase
ϕ_2^{Sa}	Fugacity coefficient of the solute at the saturation pressure
γ_2	Activity coefficient of the solute in the solution
π	Polarizability of the solute or its chemical class

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Appendix
Conversion Factors for Environmental Engineers

Lawrence K. Wang

CONTENTS

ABSTRACT

With the current trend toward metrication, the question of using a consistent system of units has been a problem. Wherever possible, the authors of this Handbook of Environmental Engineering series have used the British system (fps) along with the metric equivalent (mks, cgs, or SIU) or vice versa. For the convenience of the readers around the world, this book provides a 55-page detailed *Conversion Factors for Environmental Engineers*. In addition, the basic and supplementary units, the derived units and quantities, important physical constants, the properties of water, and the Periodic Table of the Elements, are also presented in this document.

Key Words: Conversion factors, British units, metric units, physical constants, water properties, periodic table of the elements, environmental engineers, Lenox Institute of Water Technology.

I. CONSTANTS AND CONVERSION FACTORS

Multiply	by	to obtain
abamperes	10	amperes
abamperes	2.99796×10^{10}	statamperes
abampere-turns	12.566	gilberts
abcoulombs	10	coulombs (abs)
abcoulombs	2.99796×10^{10}	statcoulombs
abcoulombs/kg	30577	statcoulombs/dyne
abfarads	1×10^{9}	farads (abs)
abfarads	8.98776×10^{20}	statfarads
abhenries	1×10^{-9}	henries (abs)
abhenries	1.11263×10^{-21}	stathenries
abohms	1×10^{-9}	ohms (abs)
abohms	1.11263×10^{-21}	statohms
abvolts	3.33560×10^{-11}	statvolts
abvolts	1×10^{-8}	volts (abs)
abvolts/centimeters	2.540005×10^{-8}	volts (abs)/inch
acres	0.4046	ha
acres	43560	square feet
acres	4047	square meters
acres	1.562×10^{-3}	square miles
acres	4840	square yards
acre-feet	43560	cubic feet
acre-feet	1233.5	cubic meters
acre-feet	325850	gallons (U.S.)
amperes (abs)	0.1	abamperes
amperes (abs)	1.036×10^{-5}	faradays/second
amperes (abs)	2.9980×10^{9}	statamperes

Multiply	by	to obtain
ampere-hours (abs)	3600	coulombs (abs)
ampere-hours	0.03731	faradays
amperes/sq cm	6.452	amps/sq in
amperes/sq cm	10^4	amps/sq meter
amperes/sq in	0.1550	amps/sq cm
amperes/sq in	1,550.0	amps/sq meter
amperes/sq meter	10^{-4}	amps/sq cm
amperes/sq meter	6.452×10^{-4}	amps/sq in
ampere-turns	1.257	gilberts
ampere-turns/cm	2.540	amp-turns/in
ampere-turns/cm	100.0	amp-turns/meter
ampere-turns/cm	1.257	gilberts/cm
ampere-turns/in	0.3937	amp-turns/cm
ampere-turns/in	39.37	amp-turns/meter
ampere-turns/in	0.4950	gilberts/cm
ampere-turns/meter	0.01	amp-turns/cm
ampere-turns/meter	0.0254	amp-turns/in
ampere-turns/meter	0.01257	gilberts/cm
angstrom units	1×10^{-8}	centimeters
angstrom units	3.937×10^{-9}	inches
angstrom unit	1×10^{-10}	meter
angstrom unit	1×10^{-4}	micron or (Mu)
ares	0.02471	acre (US)
ares	1076	square feet
ares	100	square meters
ares	119.60	sq. yards
assay tons	29.17	grams

Multiply	by	to obtain
astronomical unit	1.495×10^{8}	kilometers
atmospheres (atm)	.007348	tons/sq. inch
atmospheres	76.0	cms of mercury
atmospheres	1.01325×10^{6}	dynes/square centimeter
atmospheres	33.90	ft of water (at 4°C)
atmospheres	29.92	in. of mercury (at 0°C)
atmospheres	1.033228	kgs/sq cm
atmospheres	10,332	kgs/sq meter
atmospheres	760.0	millimeters of mercury
atmospheres	14.696	pounds/square inch
atmospheres	1.058	tons/sq. foot
avograms	1.66036×10^{-24}	grams
bags, cement	94	pounds of cement
barleycorns (British)	1/3	inches
barleycorns (British)	8.467×10^{-3}	meters
barrels (British, dry)	5.780	cubic feet
barrels (British, dry)	0.1637	cubic meters
barrels (British, dry)	36	gallons (British)
barrels, cement	170.6	kilograms
barrels, cement	376	pounds of cement
barrels, cranberry	3.371	cubic feet
barrels, cranberry	0.09547	cubic meters
barrels, oil	5.615	cubic feet
barrels, oil	0.1590	cubic meters
barrels, oil	42	gallons (U.S.)
barrels, (U.S., dry)	4.083	cubic feet
barrels (U.S., dry)	7056	cubic inches
barrels (U.S., dry)	0.11562	cubic meters
barrels (U.S., dry)	105.0	quarts (dry)

Multiply	by	to obtain
barrels (U.S., liquid)	4.211	cubic feet
barrels (U.S., liquid)	0.1192	cubic meters
barrels (U.S., liquid)	31.5	gallons (U.S.)
bars	0.98692	atmospheres
bars	10^6	dynes/sq cm
bars	1.0197×10^4	kgs/sq meter
bars	1000	millibar
bars	750.06	mm of Hg (0^oC)
bars	2,089	pounds/sq ft
bars	14.504	pounds/sq in
barye	1.000	dynes/sq cm
board feet	1/12	cubic feet
board feet	144 sq.in. x 1 in.	cubic inches
boiler horsepower	33475	Btu (mean)/hour
boiler horsepower	34.5	pounds of water evaporated from and at 212^oF (per hour)
bolts (U.S., cloth)	120	linear feet
bolts (U.S., cloth)	36.576	meters
bougie decimales	1	candles (int)
Btu (mean)	251.98	calories, gram (g. cal)
Btu (mean)	0.55556	centigrade heat units (chu)
Btu (mean)	1.0548×10^{10}	ergs
Btu (mean)	777.98	foot-pounds
Btu (mean)	3.931×10^{-4}	horsepower-hrs (hp-hr)
Btu (mean)	1055	joules (abs)
Btu (mean)	0.25198	kilograms, cal (kg. cal.)
Btu (mean)	107.565	kilogram-meters
Btu (mean)	2.928×10^{-4}	kilowatt-hr (Kwh)
Btu (mean)	10.409	liter-atm
Btu (mean)	6.876×10^{-5}	pounds of carbon to CO_2
Btu (mean)	0.29305	watt-hours

Multiply	by	to obtain
Btu (mean)/cu ft	37.30	joule/liter
Btu/hour	0.2162	foot-pound/sec
Btu/hour	0.0700	gram-cal./sec
Btu/hour	3.929×10^{-4}	horsepower-hrs (hp-hr)
Btu/hour	0.2930711	watt (w)
Btu/hour (feet)$^{\circ}$F	1.730735	joule/sec (m)$^{\circ}$k
Btu/hour (feet^{2})	3.15459	joule/m^{2}-sec.
Btu (mean)/hour(feet^{2})$^{\circ}$F	1.3562×10^{-4}	gram-calorie/second (cm^{2})$^{\circ}$C
Btu (mean)/hour(feet^{2})$^{\circ}$F	3.94×10^{-4}	horsepower/(ft^{2})$^{\circ}$F
Btu (mean)/hour(feet^{2})$^{\circ}$F	5.678264	joule/sec.(m^{2})$^{\circ}$k
Btu (mean)/hour(feet^{2})$^{\circ}$F	4.882	kilogram-calorie/hr(m^{2})$^{\circ}$C
Btu (mean)/hour(feet^{2})$^{\circ}$F	5.682×10^{-4}	watts/(cm^{2})$^{\circ}$C
Btu (mean)/hour(feet^{2})$^{\circ}$F	2.035×10^{-3}	watts/(in.^{2})$^{\circ}$C
Btu(mean)/(hour)(feet^{2}) ($^{\circ}$F/inch)	3.4448×10^{-4}	calories, gram(15^{0}C)/sec (cm^{2})($^{\circ}$C/cm)
Btu(mean)/(hour)(feet^{2})($^{\circ}$F/in.)	1	chu/(hr)(ft^{2})($^{\circ}$C/in.)
Btu(mean)/(hour)(feet^{2}) ($^{\circ}$F/inch)	1.442×10^{-3}	joules (abs)/(sec)(cm^{2}) ($^{\circ}$C/cm)
Btu(mean)/(hour)(feet^{2}) ($^{\circ}$F/inch)	1.442×10^{-3}	watts/(cm^{2})($^{\circ}$C/cm)
Btu/min	12.96	ft lb/sec
Btu/min	0.02356	hp
Btu/min	0.01757	kw
Btu/min	17.57	watts
Btu/min/ft^{2}	0.1221	watts/sq. inch
Btu/pound	0.5556	calories-gram(mean)/gram
Btu/pound	0.555	kg-cal/kg
Btu/pound/$^{\circ}$F	1	calories, gram/gram/$^{\circ}$C
Btu/pound/$^{\circ}$F	4186.8	joule/kg/$^{\circ}$k
Btu/second	1054.350	watt(w)
buckets (British, dry)	1.818×10^{4}	cubic cm
buckets (British, dry)	4	gallons (British)
bushels (British)	1.03205	bushels (U.S.)

Multiply	by	to obtain
bushels (British)	1.2843	cubic feet
bushels (British)	0.03637	cubic meters
bushels (U.S.)	1.2444	cubic feet
bushels (U.S.)	2150.4	cubic inch
bushels (U.S.)	0.035239	cubic meters
bushels (U.S.)	35.24	liters (1)
bushels (U.S.)	4	pecks (U.S.)
bushels (U.S.)	64	pints (dry)
bushels (U.S.)	32	quarts (dry)
butts (British)	20.2285	cubic feet
butts (British)	126	gallons (British)
cable lengths	720	feet
cable lengths	219.46	meters
calories (thermochemical)	0.999346	calories (Int.Steam Tables)
calories, gram (g. cal or simply cal.)	3.9685×10^{-3}	Btu (mean)
calories, gram (mean)	0.001459	cubic feet atmospheres
calories, gram (mean)	4.186×10^{7}	ergs
calories, gram (mean)	3.0874	foot-pounds
calories, gram (mean)	4.186	joules (abs)
calories, gram (mean)	0.001	kg. cal (calories, kilogram)
calories, gram (mean)	0.42685	kilograms-meters
calories, gram (mean)	0.0011628	watt-hours
calories, gram (mean)/gram	1.8	Btu (mean)/pound
cal/gram-^{o}C	4186.8	joule/kg-^{o}k
candle power (spherical)	12.566	lumens
candles (int)	0.104	carcel units
candles (int)	1.11	hefner units
candles (int)	1	lumens(int)/steradian
candles(int)/square centimeter	2919	foot-lamberts
candles(int)/square centimeter	3.1416	lamberts

Multiply	by	to obtain
candles(int)/square foot	3.1416	foot-lamberts
candles (int)/square foot	3.382×10^{-3}	lamberts
candles(int)/square inch	452.4	foot-lamberts
candles (int)/square inch	0.4870	lamberts
candles(int)/square inch	0.155	stilb
carats(metric)	3.0865	grains
carats(metric)	0.2	grams
centals	100	pounds
centares(centiares)	1.0	sq. meters
centigrade heat units (chu)	1.8	Btu
centigrade heat units (chu)	453.6	calories, gram (15°C)
centigrade heat units(chu)	1897.8	joules (abs)
centigrams	0.01	grams
centiliters	0.01	liters
centimeters	0.0328083	feet (U.S.)
centimeters	0.3937	inches (U.S.)
centimeters	0.01	meters
centimeters	6.214×10^{-6}	miles
centimeters	10	millimeters
centimeters	393.7	mils
centimeters	0.01094	yards
cm of mercury	0.01316	atm
cm of mercury	0.4461	ft of water
cm of mercury	136.0	kgs./square meter
cm of mercury	1333.22	newton/meter^2 (N/m^2)
cm of mercury	27.85	psf
cm of mercury	0.1934	psi
cm of water (4°C)	98.0638	newton/meter^2 (N/m^2)
centimeters-dynes	1.020×10^{-3}	centimeter-grams
centimeter-dynes	1.020×10^{-8}	meter-kilograms

Multiply	by	to obtain
centimeter-dynes	7.376×10^{-8}	pound-feet
centimeter-grams	980.7	centimeter-dynes
centimeter-grams	10^{-5}	meter-kilograms
centimeter-grams	7.233×10^{-5}	pound-feet
centimeters/second	1.969	fpm
centimeters/second	0.0328	fps
centimeters/second	0.036	kilometers/hour
centimeters/second	0.1943	knots
centimeters/second	0.6	m/min
centimeters/second	0.02237	miles/hour
centimeters/second	3.728×10^{-4}	miles/minute
cms/sec./sec.	0.03281	feet/sec/sec
cms./sec./sec.	0.036	kms./hour/sec.
cms/sec./sec.	0.02237	miles/hour/sec.
centipoises	3.60	kilograms/meter hour
centipoises	10^{-3}	kilograms/meter second
centipoises	0.001	newton-sec/m^2
centipoises	2.089×10^{-5}	pound force second/square foot
centipoises	2.42	pounds/foot hour
centipoises	6.72×10^{-4}	pounds/foot second
centistoke	1.0×10^{-6}	meter^2/sec
chains (engineers' or Ramden's)	100	feet
chains (engineers' or Ramden's)	30.48	meters
chains (surveyors' or Gunter's)	66	feet
chains (surveyors' or Gunter's)	20.12	meters
chaldrons (British)	32	bushels (British)
chaldrons (U.S.)	36	bushels (U.S.)
cheval-vapours	0.9863	horsepower
cheval-vapours	735.5	watts (abs)
cheval-vapours heures	2.648×10^{6}	joules (abs)

Multiply	by	to obtain
chu/(hr)(ft^2)(°C/in.)	1	Btu/(hr)(ft^2)(°F/in.)
circular inches	0.7854	square inches
circular millimeters	7.854×10^{-7}	square meters
circular mils	5.067×10^{-6}	square centimeters
circular mils	7.854×10^{-7}	square inches
circular mils	0.7854	square mils.
circumferences	360	degrees
circumferences	400	grades
circumferences	6.283	radians
cloves	8	pounds
coombs (British)	4	bushels (British)
cords	8	cord feet
cords	8' x 4' x 4'	cubic feet
cords	128	cubic feet
cords	3.625	cubic meters
cord-feet	4' x 4' x 1'	cubic feet
coulombs (abs)	0.1	abcoulombs
coulombs (abs)	6.281×10^{18}	electronic charges
coulombs (abs)	2.998×10^{9}	statcoulombs
coulombs (abs)	1.036×10^{-5}	faradays
coulombs/sq cm	64.52	coulombs/sq in
coulombs/sq cm	10^{4}	coulombs/sq meter
coulombs/sq in	0.1550	coulombs/sq cm
coulombs/sq in	1,550	coulombs/sq meter
coulombs/sq meter	10^{-4}	coulombs/sq cm
coulombs/sq meter	6.452×10^{-4}	coulombs/sq in
cubic centimeters	3.531445×10^{-5}	cubic feet (U.S.)
cubic centimeters	6.102×10^{-2}	cubic inches
cubic centimeters	10^{-6}	cubic meters
cubic centimeters	1.308×10^{-6}	cubic yards
cubic centimeters	2.6417×10^{-4}	gallons (U.S.)

Multiply	by	to obtain
cubic centimeters	0.001	liters
cubic centimeters	0.033814	ounces (U.S.,fluid)
cubic centimeters	2.113×10^{-3}	pints (liq.)
cubic centimeters	1.057×10^{-3}	quarts (liq.)
cubic feet (British)	0.9999916	cubic feet(U.S.)
cubic feet (U.S.)	0.8036	bushels(dry)
cubic feet (U.S.)	28317.016	cubic centimeters
cubic feet (U.S.)	1728	cubic inches
cubic feet (U.S.)	0.02832	cubic meters
cubic feet (U.S.)	0.0370	cubic yard
cubic feet (U.S.)	7.48052	gallons (U.S.)
cubic feet (U.S.)	28.31625	liters
cubic feet (U.S.)	59.84	pints (liq.)
cubic feet (U.S.)	29.92	quarts (liq.)
cubic feet of common brick	120	pounds
cubic feet of water (60°F)	62.37	pounds
cubic foot-atmospheres	2.7203	Btu (mean)
cubic foot-atmospheres	680.74	calories, gram (mean)
cubic foot-atmospheres	2116	foot-pounds
cubic foot-atmospheres	2869	joules (abs)
cubic foot-atmospheres	292.6	kilogram-meters
cubic foot-atmospheres	7.968×10^{-4}	kilowatt-hours
cubic feet/hr	0.02832	m^3/hr
cubic feet/minute	472.0	cubic cm/sec
cubic feet/minute	1.6992	cu m/hr
cubic feet/minute	0.0283	cu m/min
cubic feet/minute	0.1247	gallons/sec
cubic feet/minute	0.472	liter/sec
cubic feet/minute	62.4	lbs. of water/min
cubic feet/min/1000 cu ft	0.01667	liter/sec/cu m
cubic feet/second	1.9834	acre-feet/day

Multiply	by	to obtain
cubic feet/second	1.7	cu m/min
cubic feet/second	0.02832	m^3/sec
cubic feet/second	448.83	gallons/minute
cubic feet/second	1699	liter/min
cubic feet/second	28.32	liters/sec
cubic feet/second (cfs)	0.64632	million gallons/day (mgd)
cfs/acre	0.07	m^3/sec-ha
cfs/acre	4.2	cu m/min/ha
cfs/sq mile	0.657	cu m/min/sq km
cubic inches (U.S.)	16.387162	cubic centimeters
cubic inches (U.S.)	5.787×10^{-4}	cubic feet
cubic inches (U.S.)	1.0000084	cubic inches (British)
cubic inches (U.S.)	1.639×10^{-5}	cubic meters
cubic inches (U.S.)	2.143×10^{-5}	cubic yards
cubic inches (U.S.)	4.329×10^{-3}	gal (U.S.)
cubic inches (U.S.)	1.639×10^{-2}	liters
cubic inches (U.S.)	16.39	ml
cubic inches (U.S.)	0.55411	ounces (U.S.,fluid)
cubic inches (U.S.)	0.03463	pints (liq.)
cubic inches (U.S.)	0.01732	quarts (liq.)
cubic meters	8.1074×10^{-4}	acre-feet
cubic meters	8.387	barrels (U.S.,liquid)
cubic meters	28.38	bushels (dry)
cubic meters	10^6	cubic centimeters
cubic meters	35.314	cubic feet (U.S.)
cubic meters	61023	cubic inches (U.S.)
cubic meters	1.308	cubic yards (U.S.)
cubic meters	264.17	gallons (U.S.)
cubic meters	999.973	liters
cubic meters	2113	pints (liq.)

Multiply	by	to obtain
cubic meters (m^3)	1057	quarts (liq.)
cubic meters/day	0.183	gallons/min
cubic meters/ha	106.9	gallons/acre
cubic meters/hour	0.2272	gallons/minute
cubic meters/meter-day	80.53	gpd/ft
cubic meters/minute	35.314	cubic ft/minute
cubic meters/second	35.314	cubic ft/sec.
cubic meters/second	22.82	mgd
cubic meters/sec-ha	14.29	cu ft/sec-acre
cubic meters/meters^2-day	24.54	gpd/ft^2
cubic yards (British)	0.9999916	cubic yards (U.S.)
cubic yards (British)	0.76455	cubic meters
cubic yards (U.S.)	7.646×10^5	cubic centimeters
cubic yards (U.S.)	27	cubic feet (U.S.)
cubic yards (U.S.)	46,656	cubic inches
cubic yards (U.S.)	0.76456	cubic meters
cubic yards (U.S.)	202.0	gal (U.S.)
cubic yards (U.S.)	764.6	liters
cubic yards (U.S.)	1616	pints (liq.)
cubic yards (U.S.)	807.9	quarts (liq.)
cubic yards of sand	2700	pounds
cubic yards/minute	0.45	cubic feet/second
cubic yards/minute	3.367	gallons/second
cubic yards/minute	12.74	liters/second
cubits	45.720	centimeters
cubits	1.5	feet
dalton	1.65×10^{-24}	gram
days	1440	minutes
days	86,400	seconds
days(sidereal)	86164	seconds(mean solar)

Multiply	by	to obtain
debye units (dipole moment)	10^{18}	electrostatic units
decigrams	0.1	grams
deciliters	0.1	liters
decimeters	0.1	meters
degrees(angle)	60	minutes
degrees(angle)	0.01111	quadrants
degrees(angle)	0.01745	radians
degrees(angle)	3600	seconds
degrees/second	0.01745	radians/seconds
degrees/second	0.1667	revolutions/min
degrees/second	0.002778	revoltuions/sec
degree Celsius	$^{o}F=(^{o}Cx9/5)+32$	fahrenheit
degree Celsius	$^{o}K={}^{o}C+273.15$	kelvin
degree Fahrenheit	$^{o}C=(^{o}F-32)x5/9$	celsius
degree Fahrenheit	$^{o}K=(^{o}F+459.67)/1.8$	kelvin
degree Rankine	$^{o}K={}^{o}R/1.8$	kelvin
dekagrams	10	grams
dekaliters	10	liters
dekameters	10	meters
drachms(British,fluid)	3.5516 x 10^{-6}	cubic meters
drachms(British,fluid)	0.125	ounces(British,fluid)
drams(apothecaries' or troy)	0.1371429	ounces(avoirdupois)
drams (apothecaries' or troy)	0.125	ounces(troy)
drams(U.S.,fluid or apoth.)	3.6967	cubic cm
drams(avoirdupois)	1.771845	grams
drams(avoirdupois)	27.3437	grains
drams(avoirdupois)	0.0625	ounces
drams(avoirdupois)	0.00390625	pounds(avoirdupois)
drams(troy)	2.1943	drams(avoirdupois)

Multiply	by	to obtain
drams(troy)	60	grains
drams(troy)	3.8879351	grams
drams(troy)	0.125	ounces(troy)
drams(U.S.,fluid)	3.6967×10^{-6}	cubic meters
drams(U.S.,fluid)	0.125	ounces (fluid)
dynes	0.00101972	grams
dynes	10^{-7}	joules/cm
dynes	10^{-5}	joules/meter(newtons)
dynes	1.020×10^{-6}	kilograms
dynes	1×10^{-5}	newton(N)
dynes	7.233×10^{-5}	poundals
dynes	2.24809×10^{-6}	pounds
dyne-centimeters(torque)	7.3756×10^{-8}	pound-feet
dynes/centimeter	1	ergs/square centimeter
dynes/centimeter	0.01	ergs/square millimeter
dynes/square centimeter	9.8692×10^{-7}	atmospheres
dynes/square centimeter	10^{-6}	bars
dynes/square centimeter	2.953×10^{-5}	inch of mercury at 0°C
dynes/square centimeter	4.015×10^{-4}	inch of water at 4°C
dynes/square centimeter	0.01020	kilograms/square meter
dynes/square centimeter	0.1	newtons/square meter
dynes/square centimeter	1.450×10^{-5}	pounds/square inch
electromagnetic fps units of magnetic permeability	0.0010764	electromagnetic cgs units of magnetic permeability
electromagnetic fps units of magnetic permeability	1.03382×10^{-18}	electrostatic cgs units of magnetic permeability
electromagnetic cgs units, of magnetic permeability	1.1128×10^{-21}	electrostatic cgs units of magnetic permeability
electromagnetic cgs units of mass resistance	9.9948×10^{-6}	ohms (int)-meter-gram
electronic charges	1.5921×10^{-19}	coulombs (abs)
electron-volts	1.6020×10^{-12}	ergs
electron-volts	1.0737×10^{-9}	mass units

Multiply	by	to obtain
electron-volts	0.07386	rydberg units of energy
electronstatic cgs units of Hall effect	2.6962×10^{31}	electromagnetic cgs units of Hall effect
electrostatic fps units of charge	1.1952×10^{-6}	coulombs (abs)
electrostatic fps units of magnetic permeability	929.03	electrostatic cgs units of magnetic permeability
ells	114.30	centimeters
ells	45	inches
ems, pica(printing)	0.42333	centimeters
ems, pica(printing)	1/6	inches
ergs	9.4805×10^{-11}	Btu (mean)
ergs	2.3889×10^{-8}	calories, gram (mean)
ergs	1	dyne-centimeters
ergs	7.3756×10^{-8}	foot-pounds
ergs	0.2389×10^{-7}	gram-calories
ergs	1.020×10^{-3}	gram-centimeters
ergs	3.7250×10^{-14}	horsepower-hrs
ergs	10^{-7}	joules (abs)
ergs	2.390×10^{-11}	kilogram-calories (kg. cal.)
ergs	1.01972×10^{-8}	kilogram-meters
ergs	0.2778×10^{-13}	kilowatt-hrs
ergs	0.2778×10^{-10}	watt-hours
ergs/second	5.692×10^{-9}	Btu/min
ergs/second	4.426×10^{-6}	foot-pounds/min
ergs/second	7.376×10^{-8}	foot-pounds/sec
ergs/second	1.341×10^{-10}	horsepower
ergs/second	1.434×10^{-9}	kg.-calories/min
ergs/second	10^{-10}	kilowatts
farad (international of 1948)	0.9995	farad (F)
faradays	26.80	ampere-hours
faradays	96500	coulombs (abs)
faradays/second	96500	amperes (abs)

Multiply	by	to obtain
farads (abs)	10^{-9}	abfarads
farads (abs)	10^{6}	microfarads
farads (abs)	8.9877×10^{11}	statfarads
fathoms	6	feet
fathom	1.829	meter
feet (U.S.)	1.0000028	feet (British)
feet (U.S.)	30.4801	centimeters
feet (U.S.)	12	inches
feet (U.S.)	3.048×10^{-4}	kilometers
feet (U.S.)	0.30480	meters
feet (U.S.)	1.645×10^{-4}	miles (naut.)
feet (U.S.)	1.893939×10^{-4}	miles (statute)
feet (U.S.)	304.8	millimeters
feet (U.S.)	1.2×10^{4}	mils
feet (U.S.)	1/3	yards
feet of air (1 atmosphere, 60°F)	5.30×10^{-4}	pounds/square inch
feet of water	0.02950	atm
feet of water	0.8826	in. of mercury
feet of water at 39.2°F	0.030479	kilograms/square centimeter
feet of water at 39.2 °F	2988.98	newton/meter^2 (N/m^2)
feet of water at 39.2°F	304.79	kilograms/square meter
feet of water	62.43	pounds/square feet (psf)
feet of water at 39.2°F	0.43352	pounds/square inch (psi)
feet/hour	0.08467	mm/sec
feet/min	0.5080	cms/sec
feet/min	0.01667	feet/sec
feet/min	0.01829	kms/hr
feet/min	0.3048	meters/min
feet/min	0.01136	miles/hr
feet/sec	30.48	cms/sec
feet/sec	1.097	kms/hr

Multiply	by	to obtain
feet/sec	0.5921	knots
feet/sec	18.29	meters/min
feet/sec	0.6818	miles/hr
feet/sec	0.01136	miles/min
feet/sec/sec	30.48	cms/sec/sec
feet/sec/sec	1.097	kms/hr/sec
feet/sec/sec	0.3048	meters/sec/sec
feet/sec/sec	0.6818	miles/hr/sec
feet/100 feet	1.0	per cent grade
firkins (British)	9	gallons (British)
firkins (U.S.)	9	gallons (U.S.)
foot-candle (ft-c)	10.764	lumen/sq m
foot-poundals	3.9951×10^{-5}	Btu (mean)
foot-poundals	0.0421420	joules (abs)
foot-pounds	0.0012854	Btu (mean)
foot-pounds	0.32389	calories, gram (mean)
foot-pounds	1.13558×10^{7}	ergs
foot-pounds	32.174	foot-poundals
foot-pounds	5.050×10^{-7}	hp-hr
foot-pounds	1.35582	joules (abs)
foot-pounds	3.241×10^{-4}	kilogram-calories
foot-pounds	0.138255	kilogram-meters
foot-pounds	3.766×10^{-7}	kwh
foot-pounds	0.013381	liter-atmospheres
foot-pounds	3.7662×10^{-4}	watt-hours (abs)
foot-pounds/minute	1.286×10^{-3}	Btu/minute
foot-pounds/minute	0.01667	foot-pounds/sec
foot-pounds/minute	3.030×10^{-5}	hp
foot-pounds/minute	3.241×10^{-4}	kg.-calories/min
foot-pounds/minute	2.260×10^{-5}	kw

Multiply	by	to obtain
foot-pounds/second	4.6275	Btu (mean)/hour
foot-pounds/second	0.07717	Btu/minute
foot-pounds/second	0.0018182	horsepower
foot-pounds/second	0.01945	kg.-calories/min
foot-pounds/second	0.001356	kilowatts
foot-pounds/second	1.35582	watts (abs)
furlongs	660.0	feet
furlongs	201.17	meters
furlongs	0.125	miles (U.S.)
furlongs	40.0	rods
gallons (Br.)	3.8125×10^{-2}	barrels (U.S.)
gallons (Br.)	4516.086	cubic centimeters
gallons (Br.)	0.16053	cu ft
gallons (Br.)	277.4	cu. inches
gallons (Br.)	1230	drams (U.S. fluid)
gallons (Br.)	4.54596	liters
gallons (Br.)	7.9620×10^{4}	minims (Br.)
gallons (Br.)	7.3783×10^{4}	minims (U.S.)
gallons (Br.)	4545.96	ml
gallons (Br.)	1.20094	gallons (U.S.)
gallons (Br.)	160	ounces (Br., fl.)
gallons (Br.)	153.72	ounces (U.S., fl.)
gallons (Br.)	10	pounds (avoirdupois) of water at 62°F
gallons (U.S.)	3.068×10^{-4}	acre-ft
gallons (U.S.)	0.031746	barrels (U.S.)
gallons (U.S.)	3785.434	cubic centimeters
gallons (U.S.)	0.13368	cubic feet (U.S.)
gallons (U.S.)	231	cubic inches
gallons (U.S.)	3.785×10^{-3}	cubic meters

Multiply	by	to obtain
gallons (U.S.)	4.951×10^{-3}	cubic yards
gallons (U.S.)	1024	drams (U.S., fluid)
gallons (U.S.)	0.83268	gallons (Br.)
gallons (U.S.)	0.83267	imperial gal
gallons (U.S.)	3.78533	liters
gallons (U.S.)	6.3950×10^{4}	minims (Br.)
gallons (U.S.)	6.1440×10^{4}	minims (U.S.)
gallons (U.S.)	3785	ml
gallons (U.S.)	133.23	ounces (Br., fluid)
gallons (U.S.)	128	ounces (U.S., fluid)
gallons	8	pints (Liq.)
gallons	4	quarts (Liq.)
gal water (U.S.)	8.345	lb of water
gallons/acre	0.00935	cu.m/ha
gallons/day	4.381×10^{-5}	liters/sec
gpd/acre	0.00935	cu m/day/ha
gpd/acre	9.353	liter/day/ha
gallons/capita/day	3.785	liters/capita/day
gpd/cu yd	5.0	l/day/cu m
gpd/ft	0.01242	cu m/day/m
gpd/sq ft	0.0408	cu m/day/sq m
gpd/sq ft	1.698×10^{-5}	cubic meters/hour/sq. meter
gpd/sq ft	0.283	cu. meter/minute/ha
gpm	8.0208	cfh
gpm	2.228×10^{-3}	cfs
gpm	4.4021	cubic meters/hr
gpm	0.00144	mgd
gpm	0.0631	liters/sec
gpm/sq ft	2.445	cu. meters/hour/sq. meter
gpm/sq ft	40.7	l/min/sq m
gpm/sq ft	0.679	liter/sec/sq. meter

Multiply	by	to obtain
gallons/sq ft	40.743	liters/sq. meter
gausses (abs)	3.3358×10^{-4}	electrostatic cgs units of magnetic flux density
gausses (abs)	0.99966	gausses (int)
gausses (abs)	1	lines/square centimeter
gausses (abs)	6.452	lines/sq. in
gausses (abs)	1	maxwells (abs)/square centimeters
gausses (abs)	6.4516	maxwells (abs)/square inch
gausses (abs)	10^{-8}	webers/sq cm
gausses (abs)	6.452×10^{-8}	webers/sq in
gausses (abs)	10^{-4}	webers/sq meter
gilberts (abs)	0.07958	abampere turns
gilberts (abs)	0.7958	ampere turns
gilberts (abs)	2.998×10^{10}	electrostatic cgs units of magneto motive force
gilberts/cm	0.7958	amp-turns/cm
gilberts/cm	2.021	amp-turns/in
gilberts/cm	79.58	amp-turns/meter
gills (Br.)	142.07	cubic cm
gills (Br.)	5	ounces (British, fluid)
gills (U.S.)	32	drams (fluid)
gills	0.1183	liters
gills	0.25	pints (liq.)
grade	.01571	radian
grains	0.036571	drams (avoirdupois)
grains	0.01667	drams (troy)
grains (troy)	1.216	grains (avdp)
grains (troy)	0.06480	grams
grains (troy)	6.480×10^{-5}	kilograms
grains (troy)	64.799	milligrams
grains (troy)	2.286×10^{-3}	ounces (avdp)
grains (troy)	2.0833×10^{-3}	ounces (troy)
grains (troy)	0.04167	pennyweights (troy)

Multiply	by	to obtain
grains	1/7000	pounds (avoirdupois)
grains	1.736×10^{-4}	pounds (troy)
grains	6.377×10^{-8}	tons (long)
grains	7.142×10^{-8}	tons (short)
grains/imp gal	14.254	mg/l
grains/imp.gal	14.254	parts/million
grains/US gal	17.118	mg/l
grains/US gal	17.118	parts/million
grains/US gal	142.86	lb/mil gal
grams	0.5611	drams (avdp)
grams	0.25721	drams (troy)
grams	980.7	dynes
grams	15.43	grains
grams	9.807×10^{-5}	joules/cm
grams	9.807×10^{-3}	joules/meter (newtons)
grams	10^{-3}	kilograms
grams	10^{3}	milligrams
grams	0.0353	ounces (avdp)
grams	0.03215	ounces (troy)
grams	0.07093	poundals
grams	2.205×10^{-3}	pounds
grams	2.679×10^{-3}	pounds (troy)
grams	9.842×10^{-7}	tons (long)
grams	1.102×10^{-6}	tons (short)
grams-calories	4.1868×10^{7}	ergs
gram-calories	3.0880	foot-pounds
gram-calories	1.5597×10^{-6}	horsepower-hrs
gram-calories	1.1630×10^{-6}	kilowatt-hrs
gram-calories	1.1630×10^{-3}	watt-hrs
gram-calories	3.968×10^{-3}	British Thermal Units (Btu)

Multiply	by	to obtain
gram-calories/sec	14.286	Btu/hr
gram-centimeters	9.2967×10^{-8}	Btu (mean)
gram-centimeters	2.3427×10^{-5}	calories, gram (mean)
gram-centimeters	980.7	ergs
gram-centimeters	7.2330×10^{-5}	foot-pounds
gram-centimeters	9.8067×10^{-5}	joules (abs)
gram-centimeters	2.344×10^{-8}	kilogram-calories
gram-centimeters	10^{-5}	kilogram-meters
gram-centimeters	2.7241×10^{-8}	watt-hours
grams-centimeters^2 (moment of inertia)	2.37305×10^{-6}	pounds-feet^2
grams-centimeters^2 (moment of inertia)	3.4172×10^{-4}	pounds-inch^2
gram-centimeters/second	1.3151×10^{-7}	hp
gram-centimeters/second	9.8067×10^{-8}	kilowatts
gram-centimeters/second	0.065552	lumens
gram-centimeters/second	9.80665×10^{-5}	watt (abs)
grams/cm	5.600×10^{-3}	pounds/inch
grams/cu cm	62.428	pounds/cubic foot
grams/cu cm	0.03613	pounds/cubic inch
grams/cu cm	8.3454	pounds/gallon (U.S.)
grams/cu cm	3.405×10^{-7}	pounds/mil-foot
grams/cu ft	35.314	grams/cu meter
grams/cu ft	10^{6}	micrograms/cu ft
grams/cu ft	35.314×10^{6}	micrograms/cu meter
grams/cu ft	35.3145×10^{3}	milligrams/cu meter
grams/cu ft	2.2046	pounds/1000 cu ft
grams/cu m	0.43700	grains/cubic foot
grams/cu m	0.02832	grams/cu ft
grams/cu m	28.317×10^{3}	micrograms/cu ft
grams/cu m	0.06243	pounds/cu ft
grams/liter	58.417	grains/gallon (U.S.)

Multiply	by	to obtain
grams/liter	9.99973×10^{-4}	grams/cubic centimeter
grams/liter	1000	mg/l
grams/liter	1000	parts per million (ppm)
grams/liter	0.06243	pounds/cubic foot
grams/liter	8.345	lb/1,000 gal
grams/sq centimeter	2.0481	pounds/sq ft
grams/sq centimeter	0.0142234	pounds/square inch
grams/sq ft	10.764	grams/sq meter
grams/sq ft	10.764×10^{3}	kilograms/sq km
grams/sq ft	1.0764	milligrams/sq cm
grams/sq ft	10.764×10^{3}	milligrams/sq meter
grams/sq ft	96.154	pounds/acre
grams/sq ft	2.204	pounds/1000 sq ft
grams/sq ft	30.73	tons/sq mile
grams/sq meter	0.0929	grams/sq ft
grams/sq meter	1000	kilograms/sq km
grams/sq meter	0.1	milligrams/square cm
grams/sq meter	1000	milligrams/sq meter
grams/sq meter	8.921	pounds/acre
grams/sq meter	0.2048	pounds/1000 sq ft
grams/sq meter	2.855	tons/sq mile
g (gravity)	9.80665	meters/sec^{2}
g (gravity)	32.174	ft/sec^{2}
hand	10.16	cm
hands	4	inches
hectare (ha)	2.471	acre
hectares	1.076×10^{5}	sq feet
hectograms	100	grams
hectoliters	100	liters
hectometers	100	meters
hectowatts	100	watts

Multiply	by	to obtain
hemispheres	0.5	spheres
hemispheres	4	spherical right angles
hemispheres	6.2832	steradians
henries (abs)	10^9	abhenries
henries	1,000.0	millihenries
henries (abs)	1.1126×10^{-12}	stathenries
hogsheads (British)	63	gallons (British)
hogsheads (British)	10.114	cubic ft
hogsheads (U.S.)	8.422	cubic feet
hogsheads (U.S.)	0.2385	cubic meters
hogsheads (U.S.)	63	gallons (U.S.)
horsepower	2545.08	Btu(mean)/hour
horsepower	42.44	Btu/min
horsepower	7.457×10^9	erg/sec
horsepower	33,000	ft lb/min
horsepower	550	foot-pounds/second
horsepower	7.6042×10^6	g cm/sec
horsepower, electrical	1.0004	horsepower
horsepower	10.70	kg.-calories/min
horsepower	0.74570	kilowatts (g = 980.665)
horsepower	498129	lumens
horsepower, continental	736	watts (abs)
horsepower, electrical	746	watts (abs)
horsepower (boiler)	9.803	kw
horsepower (boiler)	33.479	Btu/hr
horsepower-hours	2545	Btu (mean)
horsepower-hours	2.6845×10^{13}	ergs
horsepower-hours	6.3705×10^7	ft poundals
horsepower-hours	1.98×10^6	foot-pounds
horsepower-hours	641,190	gram-calories
horsepower-hours	2.684×10^6	joules

Multiply	by	to obtain
horsepower-hours	641.7	kilogram-calories
horsepower-hours	2.737×10^5	kilogram-meters
horsepower-hours	0.7457	kilowatt-hours (abs)
horsepower-hours	26494	liter atmospheres (normal)
horsepower-hours	745.7	watt-hours
hours	4.167×10^{-2}	days
hours	60	minutes
hours	3600	seconds
hours	5.952×10^{-3}	weeks
hundredweights (long)	112	pounds
hundredweights (long)	0.05	tons (long)
hundredweights (short)	1600	ounces (avoirdupois)
hundredweights (short)	100	pounds
hundredweights (short)	0.0453592	tons (metric)
hundredweights (short)	0.0446429	tons(long)
inches (British)	2.540	centimeters
inches (U.S.)	2.54000508	centimeters
inches (British)	0.9999972	inches (U.S.)
inches	2.540×10^{-2}	meters
inches	1.578×10^{-5}	miles
inches	25.40	millimeters
inches	10^3	mils
inches	2.778×10^{-2}	yards
inches^2	6.4516×10^{-4}	meter^2
inches^3	1.6387×10^{-5}	meter^3
in. of mercury	0.0334	atm
in. of mercury	1.133	ft of water
in. of mercury (0°C)	13.609	inches of water (60°F)
in. of mercury	0.0345	kgs./square cm.
in. of mercury at 32°F	345.31	kilograms/square meter
in. of mercury	33.35	millibars
in. of mercury	25.40	millimeters of mercury

Multiply	by	to obtain
in. of mercury (60^{o}F)	3376.85	newton/meter^2
in. of mercury	70.73	pounds/square ft
in. of mercury at 32^{o}F	0.4912	pounds/square inch
in. of water	0.002458	atmospheres
in. of water	0.0736	in. of mercury
in. of water (at 4^{o}C)	2.540×10^{-3}	kgs/sq cm
in. of water	25.40	kgs./square meter
in. of water (60^{o}F)	1.8663	millimeters of mercury (0^{o}C)
in. of water (60^{o}F)	248.84	newton/meter^2
in. of water	0.5781	ounces/square in
in. of water	5.204	pounds/square ft
in. of water	0.0361	psi
inches/hour	2.54	cm/hr
international ampere	.9998	ampere(absolute)
international volt	1.0003	volts (absolute)
international volt	1.593×10^{-19}	joules (absolute)
international volt	9.654×10^{4}	joules
joules	9.480×10^{-4}	Btu
joules (abs)	10^{7}	ergs
joules	23.730	foot poundals
joules (abs)	0.73756	foot-pounds
joules	3.7251×10^{-7}	horsepower hours
joules	2.389×10^{-4}	kg-calories
joules (abs)	0.101972	kilogram-meters
joules	9.8689×10^{-3}	liter atmospheres (normal)
joules	2.778×10^{-4}	watt-hrs
joule-sec	1.5258×10^{33}	quanta
joules/cm	1.020×10^{4}	grams
joules/cm	10^{7}	dynes
joules/cm	100.0	joules/meter(newtons)
joules/cm	723.3	poundals

Multiply	by	to obtain
joules/cm	22.48	pounds
joules/liter	0.02681	Btu/cu. ft
joules/m^2-sec	0.3167	Btu/ft^2-hr
joules/sec	3.41304	Btu/hr
joules/sec	0.056884	Btu/min
joules/sec	1×10^7	erg/sec
joules/sec	44.254	ft lb/min
joules/sec	0.73756	ft lb/sec
joules/sec	1.0197×10^4	g cm/sec
joules/sec	1.341×10^{-3}	HP
joules/sec	0.01433	kg cal/min
joules/sec	0.001	kilowatts
joules/sec	668	lumens
joules/sec	1	watts
kilograms	564.38	drams (avdp)
kilograms	257.21	drams (troy)
kilograms	980,665	dynes
kilograms	15432	grains
kilograms	1,000	grams
kilograms	0.09807	joules/cm
kilograms	9.807	joules/meter (newtons)
kilograms	1×10^6	milligrams
kilograms	35.274	ounces (avdp)
kilograms	32.151	ounces (troy)
kilograms	70.93	poundals
kilograms	2.20462	pounds (avdp)
kilograms	2.6792	pounds (troy)
kilograms	9.84207×10^{-4}	tons (long)
kilograms	0.001	tons (metric)
kilograms	0.0011023	tons (short)
kilogram-calories	3.968	British Thermal Units

Multiply	by	to obtain
kilogram-calories	3086	foot-pounds
kilogram-calories	1.558×10^{-3}	horsepower-hours
kilogram-calories	4,186	joules
kilogram-calories	426.6	kilogram-meters
kilogram-calories	4.186	kilojoules
kilogram-calories	1.162×10^{-3}	kilowatt-hours
kg-cal/min	238.11	Btu/hr
kg-cal/min	3.9685	Btu/min
kg-cal/min	6.9770×10^{8}	erg/sec
kg-cal/min	3087.4	ft-lb/min
kg-cal/min	51.457	ft-lb/sec
kg-cal/min	7.1146×10^{5}	g cm/sec
kg-cal/min	0.0936	hp
kg-cal/min	69.769	joules/sec
kg-cal/min	0.0698	kw
kg-cal/min	46636	lumens
kg-cal/min	69.767	watts
kgs-cms.squared	2.373×10^{-3}	pounds-feet squared
kgs-cms. squared	0.3417	pounds-inches squared
kilogram-force (kgf)	9.80665	newton
kilogram-meters	0.0092967	Btu (mean)
kilogram-meters	2.3427	calories, gram (mean)
kilogram-meters	9.80665×10^{7}	ergs
kilogram-meters	232.71	ft poundals
kilogram-meters	7.2330	foot-pounds
kilogram-meters	3.6529×10^{-6}	horsepower-hours
kilogram-meters	9.80665	joules (abs)
kilogram-meters	2.344×10^{-3}	kilogram-calories
kilogram-meters	2.52407×10^{-6}	kilowatt-hours (abs)
kilogram-meters	2.7241×10^{-6}	kilowatt-hours
kilogram-meters	0.096781	liter atmospheres (normal)

Multiply	by	to obtain
kilogram-meters	6.392×10^{-7}	pounds carbon to CO_2
kilogram-meters	9.579×10^{-6}	pounds water evap. at 212°F
kilograms/cubic meter	10^{-3}	grams/cubic cm
kilograms/cubic meter	0.06243	pounds/cubic foot
kilograms/cubic meter	3.613×10^{-5}	pounds/cubic inch
kilograms/cubic meter	3.405×10^{-10}	pounds/mil. foot
kilograms/m^3-day	0.0624	lb/cu ft-day
kilograms/cu meter-day	62.43	pounds/1000 cu ft-day
kilograms/ha	0.8921	pounds/acre
kilograms/meter	0.6720	pounds/foot
kilograms/sq cm	980,665	dynes
kilograms/sq cm	0.96784	atmosphere
kilograms/sq cm	32.81	feet of water
kilograms/sq cm	28.96	inches of mercury
kilograms/sq cm	735.56	mms. of mercury
kilograms/sq cm	2,048	pounds/sq ft
kilograms/sq cm	14.22	pounds/square inch
kilograms/sq km	92.9×10^{-6}	grams/sq ft
kilograms/sq km	0.001	grams/sq meter
kilograms/sq km	0.0001	milligrams/sq cm
kilograms/sq km	1.0	milligrams/sq meter
kilograms/sq km	8.921×10^{-3}	pounds/acre
kilograms/sq km	204.8×10^{-6}	pounds/1000 sq ft
kilograms/sq km	2.855×10^{-3}	tons/sq mile
kilograms/sq meter	9.6784×10^{-5}	atmospheres
kilograms/sq meter	98.07×10^{-6}	bars
kilograms/sq meter	98.0665	dynes/sq centimeters
kilograms/sq meter	3.281×10^{-3}	feet of water at 39.2°F
kilograms/sq meter	0.1	grams/sq centimeters
kilograms/sq meter	2.896×10^{-3}	inches of mercury at 32°F
kilograms/sq meter	0.07356	mm of mercury at 0°C
kilograms/sq meter	0.2048	pounds/square foot

Multiply	by	to obtain
kilograms/sq meter	0.00142234	pounds/square inch
kilograms/sq mm.	10^6	kgs./square meter
kilojoule	0.947	Btu
kilojoules/kilogram	0.4295	Btu/pound
kilolines	1,000.0	maxwells
kiloliters	10^3	liters
kilometers	10^5	centimeters
kilometers	3281	ft
kilometers	3.937×10^4	inches
kilometers	10^3	meters
kilometers	0.53961	miles (nautical)
kilometers	0.6214	miles (statute)
kilometers	10^6	millimeters
kilometers	1093.6	yards
kilometers/hr	27.78	cm/sec
kilometers/hr	54.68	feet/minute
kilometers/hr	0.9113	ft/sec
kilometers/hr	0.5396	knot
kilometers/hr	16.67	meters/minute
kilometers/hr	0.2778	meters/sec
kilometers/hr	0.6214	miles/hour
kilometers/hour/sec	27.78	cms/sec/sec
kilometers/hour/sec	0.9113	ft/sec/sec
kilometers/hour/sec	0.2778	meters/sec/sec
kilometers/hour/sec	0.6214	miles/hr/sec
kilometers/min	60	kilometers/hour
kilonewtons/sq m	0.145	psi
kilowatts	56.88	Btu/min
kilowatts	4.425×10^4	foot-pounds/min
kilowatts	737.6	ft-lb/sec
kilowatts	1.341	horsepower

Multiply	by	to obtain
kilowatts	14.34	kg-cal/min
kilowatts	10^3	watts
kilowatt-hrs	3413	Btu (mean)
kilowatt-hrs	3.600×10^{13}	ergs
kilowatt-hrs	2.6552×10^6	foot-pounds
kilowatt-hrs	859,850	gram-calories
kilowatt-hrs	1.341	horsepower hours
kilowatt-hrs	3.6×10^6	joules
kilowatt-hrs	860.5	kg-calories
kilowatt-hrs	3.6709×10^5	kilogram-meters
kilowatt-hrs	3.53	pounds of water evaporated from and at 212°F
kilowatt-hrs	22.75	pounds of water raised from 62° to 212°F
knots	6,080	feet/hr
knots	1.689	feet/sec
knots	1.8532	kilometers/hr
knots	0.5144	meters/sec
knots	1.0	miles (nautical)/hour
knots	1.151	miles (statute)/hour
knots	2,027	yards/hr
lambert	2.054	candle/in^2
lambert	929	footlambert
lambert	0.3183	stilb
langley	1	15° gram-calorie/cm^2
langley	3.6855	Btu/ft^2
langley	0.011624	Int. kw-hr/m^2
langley	4.1855	joule (abs)/cm^2
leagues (nautical)	3	miles (nautical)
leagues (statute)	3	miles (statute)
light years	63274	astronomical units
light years	9.4599×10^{12}	kilometers
light years	5.8781×10^{12}	miles

Multiply	by	to obtain
lignes (Paris lines)	1/12	ponces (Paris inches)
lines/sq cm	1.0	gausses
lines/sq in	0.1550	gausses
lines/sq in	1.550×10^{-9}	webers/sq cm
lines sq in	10^{-8}	webers/sq in
lines/sq in	1.550×10^{-5}	webers/sq meter
links (engineer's)	12.0	inches
links (Gunter's)	0.01	chains (Gunter's)
links (Gunter's)	0.66	feet
links (Ramden's)	0.01	chains (Ramden's)
links (Ramden's)	1	feet
links (surveyor's)	7.92	inches
liters	8.387×10^{-3}	barrels (U.S.)
liters	0.02838	bushels (U.S. dry)
liters	1000.028	cubic centimeters
liters	0.035316	cubic feet
liters	61.025	cu in
liters	10^{-3}	cubic meters
liters	1.308×10^{-3}	cubic yards
liters	270.5179	drams (U.S. fl)
liters	0.21998	gallons (Br.)
liters	0.26417762	gallons (U.S.)
liters	16894	minims (Br.)
liters	16231	minims (U.S.)
liters	35.196	ounces (Br. fl)
liters	33.8147	ounces (U.S. fl)
liters	2.113	pints (liq.)
liters	1.0566828	quarts (U.S. liq.)
liter-atmospheres (normal)	0.096064	Btu (mean)
liter-atmospheres (normal)	24.206	calories, gram (mean)
liter-atmospheres (normal)	1.0133×10^{9}	ergs

Multiply	by	to obtain
liter-atmospheres (normal)	74.735	foot-pounds
liter-atmospheres (normal)	3.7745×10^{-5}	horsepower hours
liter-atmospheres (normal)	101.33	joules (abs)
liter-atmospheres (normal)	10.33	kilogram-meters
liter-atmospheres (normal)	2.4206×10^{-2}	kilogram calories
liter-atmospheres (normal)	2.815×10^{-5}	kilowatt-hours
liter/cu m -sec	60.0	cfm/1000 cu ft
liters/minute	5.885×10^{-4}	cubic feet/sec
liters/minute	4.403×10^{-3}	gallons/sec
liter/person-day	0.264	gpcd
liters/sec	2.119	cu ft /min
liters/sec	3.5316×10^{-2}	cu ft /sec
liters/sec	15.85	gallons/minute
liters/sec	0.02282	mgd
$\log_{10}N$	2.303	$\log_e N$ or ln N
$\log_e N$ or ln N	0.4343	$\log_{10}N$
lumens	0.07958	candle-power (spherical)
lumens	0.00147	watts of maximum visibility radiation
lumens/sq. centimeters	1	lamberts
lumens/sq cm/steradian	3.1416	lamberts
lumens/sq ft	1	foot-candles
lumens/sq ft	10.764	lumens/sq meter
lumens/sq ft/steradian	3.3816	millilamberts
lumens/sq meter	0.09290	foot-candles or lumens/sq
lumens/sq meter	10^{-4}	phots
lux	0.09290	foot-candles
lux	1	lumens/sq meter
lux	10^{-4}	phots
maxwells	0.001	kilolines
maxwells	10^{-8}	webers

Multiply	by	to obtain
megajoule	0.3725	horsepower-hour
megalines	10^6	maxwells
megohms	10^{12}	microhms
megohms	10^6	ohms
meters	10^{10}	angstrom units
meters	100	centimeters
meters	0.5467	fathoms
meters	3.280833	feet (U.S.)
meters	39.37	inches
meters	10^{-3}	kilometers
meters	5.396×10^{-4}	miles (naut.)
meters	6.2137×10^{-4}	miles (statute)
meters	10^3	millimeters
meters	10^9	millimicrons
meters	1.09361	yards (U.S.)
meters	1.179	varas
meter-candles	1	lumens/sq meter
meter-kilograms	9.807×10^7	centimeter-dynes
meter-kilograms	10^5	centimeter-grams
meter-kilograms	7.233	pound-feet
meters/minute	1.667	centimeters/sec
meters/minute	3.281	feet/minute
meters/minute	0.05468	feet/second
meters/minute	0.06	kilograms/hour
meters/minute	0.03238	knots
meters/minute	0.03728	miles/hour
meters/second	196.8	feet/minute
meters/second	3.281	feet/second
meters/second	3.6	kilometers/hour
meters/second	0.06	kilometers/min
meters/second	1.944	knots

Multiply	by	to obtain
meters/second	2.23693	miles/hour
meters/second	0.03728	miles/minute
meters/sec/sec	100.0	cms/sec/sec
meters/sec/sec	3.281	feet/sec/sec
meters/sec/sec	3.6	kms./hour/sec
meters/sec/sec	2.237	miles/hour/sec
microfarad	10^{-6}	farads
micrograms	10^{-6}	grams
micrograms/cu ft	10^{-6}	grams/cu ft
micrograms/cu ft	35.314×10^{-6}	grams/cu m
micrograms/cu ft	35.314	microgram/cu m
micrograms/cu ft	35.314×10^{-3}	milligrams/cu m
micrograms/cu ft	2.2046×10^{-6}	pounds/1000 cu ft
micrograms/cu m	28.317×10^{-9}	grams/cu ft
micrograms/cu m	10^{-6}	grams/ cu m
micrograms/cu m	0.02832	micrograms/cu ft
micrograms/cu m	0.001	milligrams/cu m
micrograms/cu m	62.43×10^{-9}	pounds/1000 cu ft
micrograms/cu m	$\frac{0.02404}{\text{molecular weight of gas}}$	ppm by volume (20°C)
micrograms/cu m	834.7×10^{-6}	ppm by weight
micrograms/liter	1000.0	micrograms/cu m
micrograms/liter	1.0	milligrams/cu m
micrograms/liter	62.43×10^{-9}	pounds/cu ft
micrograms/liter	$\frac{24.04}{\text{molecular weight of gas}}$	ppm by volume (20°C)
micrograms/liter	0.8347	ppm by weight
microhms	10^{-12}	megohms
microhms	10^{-6}	ohms
microliters	10^{-6}	liters
microns	10^{4}	angstrom units
microns	1×10^{-4}	centimeters
microns	3.9370×10^{-5}	inches

Multiply	by	to obtain
microns	10^{-6}	meters
miles (naut.)	6,080.27	feet
miles (maut.)	1.853	kilometers
miles (naut.)	1.853	meters
miles (naut.)	1.1516	miles (statute)
miles (naut.)	2,027	yards
miles (statute)	1.609×10^5	centimeters
miles (statute)	5,280	feet
miles (statute)	6.336×10^4	inches
miles (statute)	1.609	kilometers
miles (statute)	1,609	meters
miles (statute)	0.8684	miles (naut.)
miles (statute)	320	rods
miles (statute)	1,760	yards
miles/hour	44.7041	centimeter/second
miles/hour	88	feet/min
miles/hour	1.4667	feet/sec
miles/hour	1.6093	kilometers/hour
miles/hour	0.02682	kms/min
miles/hour	0.86839	knots
miles/hour	26.82	meters/min
miles/hour	0.447	meters/sec
miles/hour	0.1667	miles/min
miles/hour/sec	44.70	cms/sec/sec
miles/hour/sec	1.4667	ft/sec/sec
miles/hour/sec	1.6093	kms/hour/sec
miles/hour/sec	0.4470	m /sec/sec
miles/min	2682	centimeters/sec
miles/min	88	ft/sec
miles/min	1.609	km/min
miles/min	0.8684	knots/min

Multiply	by	to obtain
miles/min	60	miles/hour
miles-feet	9.425×10^{-6}	cu inches
millibars	0.00987	atmospheres
millibars	0.30	inches of mercury
millibars	0.75	millimeters of mercury
milliers	10^{3}	kilograms
millimicrons	1×10^{-9}	meters
milligrams	0.01543236	grains
milligrams	10^{-3}	grams
milligrams	10^{-6}	kilograms
milligrams	3.5274×10^{-5}	ounces (avdp)
milligrams	2.2046×10^{-6}	pounds (avdp)
milligrams/assay ton	1	ounces (troy)/ton(short)
milligrams/cu m	283.2×10^{-6}	grams/cu ft
milligrams/cu m	0.001	grams/cu m
milligrams/cu m	1000.0	micrograms/cu m
milligrams/cu m	28.32	micrograms/cu ft
milligrams/cu m	1.0	micrograms/liter
milligrams/cu m	62.43×10^{-6}	pounds/1000 cu ft
milligrams/cu m	$\frac{24.04}{\text{molecular weight of gas}}$	ppm by volume (20°C)
milligrams/cu m	0.8347	ppm by weight
milligrams/joule	5.918	pounds/horsepower-hour
milligrams/liter	0.05841	grains/gallon
milligrams/liter	0.07016	grains/imp gal
milligrams/liter	0.0584	grains/US gal
milligrams/liter	1.0	parts/million
milligrams/liter	8.345	lb/mil gal
milligrams/sq cm	0.929	grams/sq ft
milligrams/sq cm	10.0	grams/sq meter
milligrams/sq cm	10^{4}	kilograms/sq km
milligrams/sq cm	10^{4}	milligrams/sq meter

Multiply	by	to obtain
milligrams/sq cm	2.048	pounds/1000 sq ft
milligrams/sq cm	89.21	pounds/acre
milligrams/sq cm	28.55	tons/sq mile
milligrams/sq meter	92.9×10^{-6}	grams/sq ft
milligrams/sq meter	0.001	grams/sq meter
milligrams/sq meter	1.0	kilograms/sq km
milligrams/sq meter	0.0001	milligrams/sq cm
milligrams/sq meter	8.921×10^{-3}	pounds/acre
milligrams/sq meter	204.8×10^{-6}	pounds/1000 sq ft
milligrams/sq meter	2.855×10^{-3}	tons/sq mile
millihenries	0.001	henries
milliters	1	cubic centimeters
milliliters	3.531×10^{-5}	cu ft
milliliters	6.102×10^{-2}	cu in
milliliters	10^{-6}	cu m
milliliters	2.642×10^{-4}	gal (U.S.)
milliliters	10^{-3}	liters
milliliters	0.03381	ounces (U.S. fl)
millimeters	0.1	centimeters
millimeters	3.281×10^{-3}	feet
millimeters	0.03937	inches
millimeters	10^{-6}	kilometers
millimeters	0.001	meters
millimeters	6.214×10^{-7}	miles
millimeters	39.37	mils
millimeters	1.094×10^{-3}	yards
millimeters of mercury	1.316×10^{-3}	atmospheres
millimeters of mercury	0.0394	inches of mercury
millimeters of mercury (0°C)	0.5358	inches of water (60°F)
millimeters of mercury	1.3595×10^{-3}	kgs/sq cm

Multiply	by	to obtain
millimeter of mercury ($0^{o}C$)	133.3224	newton/meter^2
millimeters of mercury	0.01934	pounds/sq in
millimeters/sec	11.81	feet/hour
million gallons	306.89	acre-ft
million gallons	3,785.0	cubic meters
million gallons	3.785	mega liters (1×10^6)
million gallons/day (mgd)	1.547	cu ft/sec
mgd	3,785	cu m/day
mgd	0.0438	cubic meters/sec
mgd	43.808	liters/sec
mgd/acre	9,360	cu m/day/ha
mgd/acre	0.039	cu meters/hour/sq meter
mils	0.002540	centimeters
mils	8.333×10^{-5}	feet
mils	0.001	inches
mils	2.540×10^{-8}	kilometers
mils	25.40	microns
mils	2.778×10^{-5}	yards
miner's in.	1.5	cu ft/min
miner's inches (Ariz.,Calif. Mont., and Ore.)	0.025	cubic feet/second
miner's in. (Colorado)	0.02604	cubic feet/second
miner's inches (Ida., Kan., Neb., Nev., N.Mex., N.Dak., S.Dak. and Utah)	0.020	cubic feet/second
minims (British)	0.05919	cubic centimeter
minims (U.S.)	0.06161	cubic centimeters
minutes (angles)	0.01667	degrees
minutes (angles)	1.852×10^{-4}	quadrants
minutes (angles)	2.909×10^{-4}	radians
minutes (angle)	60	seconds (angle)
months (mean calendar)	30.4202	days

Multiply	by	to obtain
months (mean calendar)	730.1	hours
months (mean calendar)	43805	minutes
months (mean calendar)	2.6283×10^6	seconds
myriagrams	10	kilograms
myriameters	10	kilometers
myriawatts	10	kilowatts
nepers	8.686	decibels
newtons	10^5	dynes
newtons	0.10197	kilograms
newtons	0.22481	pounds
newtons/sq meter	1.00	pascals (Pa)
noggins (British)	1/32	gallons (British)
No./cu.cm.	28.316×10^3	No./cu.ft.
No./cu.cm.	10^6	No./cu. meter
No./cu.cm.	1000.0	No./liter
No./cu.ft.	35.314×10^{-6}	No./cu.cm.
No./cu.ft.	35.314	No./cu. meter
No./cu.ft.	35.314×10^{-3}	No./liter
No./cu. meter	10^{-6}	No./cu.cm.
No./cu. meter	28.317×10^{-3}	No./cu.ft.
No./cu. meter	0.001	No./liter
No./liter	0.001	No./cu.cm.
No./liter	28.316	No./cu.ft.
No./liter	1000.0	No./cu. meter
oersteds (abs)	1	electromagnetic cgs units of magnetizing force
oersteds (abs)	2.9978×10^{10}	electrostatic cgs units of magnetizing force
ohms	10^9	abohms
ohms	1.1126×10^{-12}	statohms
ohms	10^{-6}	megohms
ohms	10^6	microhms

Multiply	by	to obtain
OHM (International)	1.0005	OHM (absolute)
ounces (avdp)	16	drams (avoirdupois)
ounces (avdp)	7.2917	drams (troy)
ounces (avdp)	437.5	grains
ounces (avdp)	28.349527	grams
ounces (avdp)	0.028350	kilograms
ounces (avdp)	2.8350×10^{4}	milligrams
ounces (avdp)	0.9114583	ounces (troy)
ounces (avdp)	0.0625	pounds (avoirdupois)
ounces (avdp)	0.075955	pounds (troy)
ounces (avdp)	2.790×10^{-5}	tons (long)
ounces (avdp)	2.835×10^{-5}	tons (metric)
ounces (avdp)	3.125×10^{-5}	tons (short)
ounces (Br. fl)	2.3828×10^{-4}	barrels (U.S.)
ounces (Br. fl)	1.0033×10^{-3}	cu ft
ounces (Br. fl)	1.73457	cu in
ounces (Br. fl)	7.6860	drams (U.S. fl)
ounces (Br. fl)	6.250×10^{-3}	gallons (Br.)
ounces (Br. fl)	0.07506	gallons (U.S.)
ounces (Br. fl)	2.84121×10^{-2}	liters
ounces (Br. fl)	480	minims (Br.)
ounces (Br. fl)	461.160	minims (U.S.)
ounces (Br. fl)	28.4121	ml
ounces (Br. fl)	0.9607	ounces (U.S. fl)
ounces (troy)	17.554	drams (avdp)
ounces (troy)	8	drams (troy)
ounces (troy)	480	grains (troy)
ounces (troy)	31.103481	grams
ounces (troy)	0.03110	kilograms
ounces (troy)	1.09714	ounces (avoirdupois)
ounces (troy)	20	pennyweights (troy)
ounces (troy)	0.068571	pounds (avdp)

Multiply	by	to obtain
ounces (troy)	0.08333	pounds (troy)
ounces (troy)	3.061×10^{-5}	tons (long)
ounces (troy)	3.429×10^{-5}	tons (short)
ounces (U.S. fl)	2.48×10^{-4}	barrels (U.S.)
ounces (U.S. fl)	29.5737	cubic centimeters
ounces (U.S. fl)	1.0443×10^{-3}	cu ft
ounces (U.S. fl)	1.80469	cubic inches
ounces (U.S. fl)	8	drams (fluid)
ounces (U.S. fl)	6.5053×10^{-3}	gallons (Br.)
ounces (U.S. fl)	7.8125×10^{-3}	gallons (U.S.)
ounces (U.S. fl)	29.5729	milliliters
ounces (U.S. fl)	499.61	minims (Br.)
ounces (U.S. fl)	480	minims (U.S.)
ounces (U.S. fl)	1.0409	ounces (Br. fl)
ounces/sq inch	4309	dynes/sq. cm
ounces/sq. inch	0.0625	pounds/sq inch
paces	30	inches
palms (British)	3	inches
parsecs	3.260	light years
parsecs	3.084×10^{13}	kilometers
parsecs	3.084×10^{16}	meters
parsec	19×10^{12}	miles
parts/billion (ppb)	10^{-3}	mg/1
parts/million (ppm)	0.07016	grains/imp. gal.
parts/million	0.058417	grains/gallon (U.S.)
parts/million	1.0	mg/liter
parts/million	8.345	lbs/million gal
ppm by volume (20°C)	$\frac{\text{molecular weight of gas}}{24.04}$	micrograms/liter
ppm by volume (20°C)	$\frac{\text{molecular weight of gas}}{0.02404}$	micrograms/cu meter
ppm by volume (20°C)	$\frac{\text{molecular weight of gas}}{24.04}$	milligrams/cu meter
ppm by volume (20°C)	$\frac{\text{molecular weight of gas}}{28.8}$	ppm by weight

Multiply	by	to obtain
ppm by volume ($20^\circ C$)	$\frac{\text{molecular weight of gas}}{385.1 \times 10^{6}}$	pounds/cu ft
ppm by weight	1.198×10^{-3}	micrograms/cu meter
ppm by weight	1.198	micrograms/liter
ppm by weight	1.198	milligrams/cu meter
ppm by weight	$\frac{28.8}{\text{molecular weight of gas}}$	ppm by volume ($20^\circ C$)
ppm by weight	7.48×10^{-6}	pounds/cu ft
pecks (British)	0.25	bushels (British)
pecks (British)	554.6	cubic inches
pecks (British)	9.091901	liters
pecks (U.S.)	0.25	bushels (U.S.)
pecks (U.S.)	537.605	cubic inches
pecks (U.S.)	8.809582	liters
pecks (U.S.)	8	quarts (dry)
pennyweights	24	grains
pennyweights	1.555174	grams
pennyweights	0.05	ounces (troy)
pennyweights (troy)	4.1667×10^{-3}	pounds (troy)
perches (masonry)	24.75	cubic feet
phots	929.0	foot-candles
phots	1	lumen incident/sq cm
phots	10^{4}	lux
picas (printers')	1/6	inches
pieds (French feet)	0.3249	meters
pints (dry)	33.6003	cubic inches
pints (liq.)	473.179	cubic centimeters
pints (liq.)	0.01671	cu feet
pints (liq.)	4.732×10^{-4}	cu meters
pints (liq.)	6.189×10^{-4}	cu yards
pints (liq.)	0.125	gallons
pints (liq.)	0.4732	liters
pints (liq.)	16	ounces (U.S. fluid)

Multiply	by	to obtain
pints (liq.)	0.5	quarts (liq.)
planck's constant	6.6256×10^{-27}	erg-seconds
poise	1.00	gram/cm sec
poise	0.1	newton-second/meter^2
population equivalent (PE)	0.17	pounds BOD
pottles (British)	0.5	gallons (British)
pouces (Paris inches)	0.02707	meters
pouces (Paris inches)	0.08333	pieds (Paris feet)
poundals	13,826	dynes
poundals	14.0981	grams
poundals	1.383×10^{-3}	joules/cm
poundals	0.1383	joules/meter (newton)
poundals	0.01410	kilograms
poundals	0.031081	pounds
pounds (avdp)	256	drams (avdp)
pounds (avdp)	116.67	drams (troy)
pounds (avdp)	444,823	dynes
pounds (avdp)	7000	grains
pounds (avdp)	453.5924	grams
pounds (avdp)	0.04448	joules/cm
pounds (avdp)	4.448	joules/meter (newtons)
pounds (avdp)	0.454	kilograms
pounds (avdp)	4.5359×10^{5}	milligrams
pounds (avdp)	16	ounces (avdp)
pounds (avdp)	14.5833	ounces (troy)
pounds (avdp)	32.17	poundals
pounds (avdp)	1.2152778	pounds (troy)
pounds (avdp)	4.464×10^{-4}	tons (long)
pounds (avdp)	0.0005	tons (short)
pounds (troy)	210.65	drams (avdp)
pounds (troy)	96	drams (troy)

Multiply	by	to obtain
pounds (troy)	5,760	grains
pounds (troy)	373.2418	grams
pounds (troy)	0.37324	kilograms
pounds (troy)	3.7324×10^5	milligrams
pounds (troy)	13.1657	ounces (avdp)
pounds (troy)	12.0	ounces (troy)
pounds (troy)	240.0	pennyweights (troy)
pounds (troy)	0.8229	pounds (avdp)
pounds (troy)	3.6735×10^{-4}	tons (long)
pounds (troy)	3.7324×10^{-4}	tons (metric)
pounds (troy)	4.1143×10^{-4}	tons (short)
pounds (avdp)-force	4.448	newtons
pounds-force-sec/ft^2	47.88026	newton-sec/meter^2
pounds (avdp)-mass	0.4536	kilograms
pounds-mass/ft^3	16.0185	kilogram/meter^3
pounds-mass/ft-sec	1.4882	mewton-sec/meter^2
pounds of BOD	5.882	population equivalent (PE)
pounds of carbon to CO_2	14544	Btu (mean)
pounds of water	0.0160	cu ft
pounds of water	27.68	cu in
pounds of water	0.1198	gal
pounds of water evaporated at 212°F	970.3	Btu
pounds of water per min	2.699×10^{-4}	cubic feet/sec
pound-feet	13,825	centimeter-grams
pound-feet (torque)	1.3558×10^7	dyne-centimeters
pound-feet	0.1383	meter-kilograms
pounds-feet squared	421.3	kgs.-cms. squared
pounds-feet squared	144	pounds-ins. squared
pounds-inches squared	2,926	kgs.-cms. squared
pounds-inches squared	6.945×10^{-3}	pounds-feet squared
pounds/acre	0.0104	grams/sq ft

Multiply	by	to obtain
pounds/acre	0.1121	grams/sq meter
pounds/acre	1.121	kg/ha
pounds/acre	112.1	kilograms/sq km
pounds/acre	0.01121	milligrams/sq cm
pounds/acre	112.1	milligrams/sq meter
pounds/acre	0.023	pounds/1000 sq ft
pounds/acre	0.32	tons/sq mile
pounds/acre/day	0.112	g/day/sq m
pounds/cu ft	0.0160	g/ml
pounds/cu ft	16.02	kg/cu m
pounds/cu ft	16.018×10^9	micrograms/cu meter
pounds/cu ft	16.018×10^6	micrograms/liter
pounds/cu ft	16.018×10^6	milligrams/cu meter
pounds/cu ft	$\frac{385.1 \times 10^6}{\text{molecular weight of gas}}$	ppm by volume (20°C)
pounds/cu ft	133.7×10^3	ppm by weight
pounds/cu ft	5.787×10^{-4}	lb/cu in
pounds/cu ft	5.456×10^{-9}	pounds/mil-foot
pounds/1000 cu ft	0.35314	grams/cu ft
pounds/1000 cu ft	16.018	grams/cu m
pounds/1000 cu ft	353.14×10^3	micrograms/cu ft
pounds/1000 cu ft	16.018×10^6	microgram/cu m
pounds/1000 cu ft	16.018×10^3	milligrams/cu m
pounds/cubic inch	27.68	grams/cubic cm
pounds/cubic inch	2.768×10^4	kgs/cubic meter
pounds/cubic inch	1728	pounds/cubic foot
pounds/cubic inch	9.425×10^{-6}	pounds/mil foot
pounds/day/acre-ft	3.68	g/day/cu m
pounds/day/cu ft	16	kg/day/cu m
pounds/day/cu yd	0.6	kg/day/cu m
pounds/day/sq ft	4,880	g/day/sq m
pounds/ft	1.488	kg/m

Multiply	by	to obtain
pounds/gal	454 g/3.785 l=119.947	g/liter
pounds/1000-gal	120	g/1000-liters
pounds/horsepower-hour	0.169	mg/joule
pounds/in	178.6	g/cm
pounds/mil-foot	2.306×10^6	gms/cu cm
pounds/mil gal	0.12	g/cu m
pounds/sq ft	4.725×10^{-4}	atmospheres
pounds/sq ft	0.01602	ft of water
pounds/sq ft	0.01414	inches of mercury
pounds/sq ft	4.8824×10^{-4}	kgs/sq cm
pounds/sq ft	4.88241	kilograms/square meter
pounds/sq ft	47.9	newtons/sq m
pounds/sq ft	6.944×10^{-3}	pounds/sq inch
pounds/1000 sq ft	0.4536	grams/sq ft
pounds/1000 sq ft	4.882	grams/sq meter
pounds/1000 sq ft	4882.4	kilograms/sq km
pounds/1000 sq ft	0.4882	milligrams/sq cm
pounds/1000 sq ft	4882.4	milligrams/sq meter
pounds/1000 sq ft	43.56	pounds/acre
pounds/1000 sq ft	13.94	tons/sq mile
pounds/sq in	0.068046	atmospheres
pounds/sq in	2.307	ft of water
pounds/sq in	70.307	grams/square centimeter
pounds/sq in	2.036	in of mercury
pounds/sq in	0.0703	kgs/square cm
pounds/sq in	703.07	kilograms/square meter
pounds/sq in	51.715	millimeters of mercury
pounds/sq in	6894.76	newton/meter^2
pounds/sq in	51.715	millimeters of mercury at 0°C
pounds/sq in	144	pounds/sq foot

Multiply	by	to obtain
pounds/sq in (abs)	1	pound/sq in (gage) + 14.696
proof (U.S.)	0.5	percent alcohol by volume
puncheons (British)	70	gallons (British)
quadrants (angle)	90	degrees
quadrants (angle)	5400	minutes
quadrants (angle)	3.24×10^5	seconds
quadrants (angle)	1.571	radians
quarts (dry)	67.20	cubic inches
quarts (liq.)	946.4	cu cms
quarts (liq.)	0.033420	cubic feet
quarts (liq.)	57.75	cubic inches
quarts (liq.)	9.464×10^{-4}	cubic meters
quarts (liq.)	1.238×10^{-3}	cu yards
quarts (liq.)	0.25	gallons
quarts (liq.)	0.9463	liters
quarts (liq.)	32	ounces (U.S., fl)
quarts (liq.)	0.832674	quarts (British)
quintals (long)	112	pounds
quintals (metric)	100	kilograms
quintals (short)	100	pounds
quires	24	sheets
radians	57.29578	degrees
radians	3438	minutes
radians	0.637	quadrants
radians	2.063×10^5	seconds
radians/second	57.30	degrees/second
radians/second	9.549	revolutions/min
radians/second	0.1592	revolutions/sec
radians/sec/sec	573.0	revs/min/min
radians/sec/sec	9.549	revs/min/sec
radians/sec/sec	0.1592	revs/sec/sec

Multiply	by	to obtain
reams	500	sheets
register tons (British)	100	cubic feet
revolutions	360	degrees
revolutions	4	quadrants
revolutions	6.283	radians
revolutions/minute	6	degrees/second
revolutions/minute	0.10472	radians/second
revolutions/minute	0.01667	revolutions/sec
revolutions/minute^2	0.0017453	radians/sec/sec
revs/min/min	0.01667	revs/min/sec
revs/min/min	2.778×10^{-4}	revs/sec/sec
revolutions/second	360	degrees/second
revolutions/second	6.283	radians/second
revolutions/second	60	revs/minute
revs/sec/sec	6.283	rads/sec/sec
revs/sec/sec	3600	revs/min/min
revs/sec/sec	60	revs/min/sec
reyns	6.8948×10^{6}	centipoises
rod	.25	chain (gunters)
rods	16.5	feet
rods	5.0292	meters
rods	3.125×10^{-3}	miles
rods (surveyors' means)	5.5	yards
roods (British)	0.25	acres
scruples	1/3	drams (troy)
scruples	20	grains
sections	1	square miles
seconds (mean solar)	1.1574×10^{-5}	days
seconds (angle)	2.778×10^{-4}	degrees
seconds (mean solar)	2.7778×10^{-4}	hours
seconds (angle)	0.01667	minutes

Multiply	by	to obtain
seconds (angle)	3.087×10^{-6}	quadrants
seconds (angle)	4.848×10^{-6}	radians
slugs	14.59	kilogram
slugs	32.174	pounds
space, entire (solid angle)	12.566	steradians
spans	9	inches
spheres (solid angle)	12.57	steradians
spherical right angles	0.25	hemispheres
spherical right angles	0.125	spheres
spherical right angles	1.571	steradians
square centimeters	1.973×10^{5}	circular mils
square centimeters	1.07639×10^{-3}	square feet (U.S.)
square centimeters	0.15499969	square inches (U.S.)
square centimeters	10^{-4}	square meters
square centimeters	3.861×10^{-11}	square miles
square centimeters	100	square millimeters
square centimeters	1.196×10^{-4}	sq yards
square centimeters-square centimeter(moment of area)	0.024025	square inch-square inch
square chains (gunter's)	0.1	acres
square chains (gunter's)	404.7	square meters
square chains (Ramden's)	0.22956	acres
square chains (Ramden's)	10000	square feet
square feet	2.29×10^{-5}	acres
square feet	1.833×10^{8}	circular mils
square feet	144	sq in
square feet	0.092903	square meters
square feet	929.0341	square centimeters
square feet	3.587×10^{-8}	square miles
square feet	1/9	square yards
square feet/cu ft	3.29	sq m/cu m

Multiply	by	to obtain
square foot-square foot (moment of area)	20736	square inch-square inch
square inches	1.273×10^{6}	circular mils
square inches	6.4516258	square centimeters
square inches	6.944×10^{-3}	square feet
square inches	645.2	square millimeters
square inches	10^{6}	square mils
square inches	7.71605×10^{-4}	square yards
square inches-inches sqd.	41.62	sq cms.-cms sqd.
square inches-inches sqd.	4.823×10^{-5}	sq feet-feet sqd.
square kilometers	247.1	acres
square kilometers	10^{10}	sq cms
square kilometers	10.76×10^{6}	sq ft
square kilometers	1.550×10^{9}	sq inches
square kilometers	10^{6}	square meters
square kilometers	0.3861006	square miles (U.S.)
square kilometers	1.196×10^{6}	sq yd
square links (Gunter's)	10^{-5}	acres (U.S.)
square links (Gunter's)	0.04047	square meters
square meters	2.471×10^{-4}	acres (U.S.)
square meters	10^{4}	sq cms
square meters	10.76387	square feet (U.S.)
square meters	1550	square inches
square meters	3.8610×10^{-7}	square miles (statute)
square meters	10^{6}	sq millimeters
square meters	1.196	square yards (U.S.)
square miles	640	acres
square miles	2.78784×10^{7}	square feet
square miles	2.590	sq km
square miles	2.5900×10^{6}	square meters
square miles	3.098×10^{6}	square yards

Multiply	by	to obtain
square millimeters	1.973×10^{3}	circular mils
square millimeters	0.01	square centimeters
square millimeters	1.076×10^{-5}	sq feet
square millimeters	1.550×10^{-3}	square inches
square mils	1.273	circular mils
square mils	6.452×10^{-6}	square centimeters
square mils	10^{-6}	square inches
square rods	272.3	square feet
square yard	2.1×10^{-4}	acres
square yards	8,361	sq cms
square yards	9	square feet
square yards	1296	square inches
square yards	0.8361	square meters
square yards	3.228×10^{-7}	square miles
square yards	8.361×10^{5}	sq millimeters
statamperes	3.33560×10^{-10}	amperes (abs)
statcoulombs	3.33560×10^{-10}	coulombs (abs)
statcoulombs/kilogram	1.0197×10^{-6}	statcoulombs/dyne
statfarads	1.11263×10^{-12}	farads (abs)
stathenries	8.98776×10^{11}	henries (abs)
statohms	8.98776×10^{11}	ohms (abs)
statvolts	299.796	volts(abs)
statvolts/inch	118.05	volts (abs)/centimeter
statwebers	2.99796×10^{10}	electromagnetic cgs units of magnetic flux
statwebers	1	electrostatic cgs units of magnetic flux
stilb	2919	footlambert
stilb	1	int. candle cm^{-2}
stilb	3.142	lambert
stoke (kinematic viscosity)	10^{-4}	$meter^{2}/second$
stones (British)	6.350	kilograms
stones (British)	14	pounds

Multiply	by	to obtain
temp. (degs. C.)+273	1	abs. temp. (degs. C.)
temps (degs. C.)+17.8	1.8	temp. (degs. Fahr.)
temps. (degs. F.)+460	1	abs. temp. (degs. F.)
temps. (degs. F.)-32	5/9	temp. (degs. cent.)
toises (French)	6	paris feet (pieds)
tons (long)	5.734×10^5	drams (avdp)
tons (long)	2.613×10^5	drams (troy)
tons (long)	1.568×10^7	grains
tons (long)	1.016×10^6	grams
tons (long)	1016	kilograms
tons (long)	3.584×10^4	ounces (avdp)
tons (long)	3.267×10^4	ounces (troy)
tons (long)	2240	pounds (avdp)
tons (long)	2722.2	pounds (troy)
tons (long)	1.12	tons (short)
tons (metric)	1000	kilograms
tons (metric)	2204.6	pounds
tons (metric)	1.1025	tons (short)
tons (short)	5.120×10^5	drams (avdp)
tons (short)	2.334×10^5	drams (troy)
tons (short)	1.4×10^7	grains
tons (short)	9.072×10^5	grams
tons (short)	907.2	kilograms
tons (short)	32,000	ounces (avdp)
tons (short)	29,166.66	ounces (troy)
tons (short)	2000	pounds (avdp)
tons (short)	2,430.56	pounds (troy)
tons (short)	0.89287	tons (long)
tons (short)	0.9078	tons (metric)
tons (short)/sq ft	9765	kgs./sq meter
tons (short)/sq ft	13.89	pounds/sq inch

Multiply	by	to obtain
tons (short)/sq in	1.406×10^6	kgs/sq meter
tons (short)/sq in	2000	pounds/sq inch
tons/sq mile	3.125	pounds/acre
tons/sq mile	0.07174	pounds/1000 sq ft
tons/sq mile	0.3503	grams/sq meter
tons/sq mile	350.3	kilograms/sq km
tons/sq mile	350.3	milligrams/sq meter
tons/sq mile	0.03503	milligrams/sq cm
tons/sq mile	0.03254	grams/sq ft
tons of water/24 hours	83.333	pounds of water/hr
tons of water/24 hours	0.16643	gallons/min
tons of water/24 hours	1.3349	cu ft/hr
torr (mm Hg, 0°C)	133.322	newton/meter^2
townships (U.S.)	23040	acres
townships (U.S.)	36	square miles
tuns	252	gallons
volts (abs)	10^8	abvolts
volts (abs)	3.336×10^{-3}	statvolts
volts (international of 1948)	1.00033	volts (abs)
volt/inch	.39370	volt/cm.
watts (abs)	3.41304	Btu (mean)/hour
watts (abs)	0.0569	Btu (mean)/min
watts (abs)	0.01433	calories, kilogram (mean)/ minute
watts (abs)	10^7	ergs/second
watts (abs)	44.26	foot-pounds/minute
watts (abs)	0.7376	foot-pounds/second
watts (abs)	0.0013405	horsepower (electrical)
watts (abs)	1.360×10^{-3}	horsepower (metric)
watts (abs)	1	joules/sec
watts (abs)	0.10197	kilogram-meters/second

Multiply	by	to obtain
watts (abs)	10^{-3}	kilowatts
watt-hours	3.415	British Thermal Units
watt-hours	3.60×10^{10}	ergs
watt-hours	2655	foot-pounds
watt-hours	859.85	gram-calories
watt-hours	1.34×10^{-3}	horsepower-hours
watt-hours	3.6×10^{3}	joule
watt-hours	0.8605	kilogram-calories
watt-hours	367.1	kilogram-meters
watt-hours	10^{-3}	kilowatt-hours
watt (internationl)	1.0002	watt (absolute)
watt/(cm^2)(^oC/cm)	693.6	Btu/(hr)(ft^2)(^oF/in)
wave length of the red line of cadmium	6.43847×10^{-7}	meters
webers	10^{3}	electromagnetic cgs units
webers	3.336×10^{-3}	electrostatic cgs units
webers	10^{5}	kilolines
webers	10^{8}	lines
webers	10^{8}	maxwells
webers	3.336×10^{-3}	statwebers
webers/sq in	1.550×10^{7}	gausses
webers/sq in	10^{8}	lines/sq in
webers/sq in	0.1550	webers/sq cm
webers/sq in	1,550	webers/sq meter
webers/sq meter	10^{4}	gausses
webers/sq meter	6.452×10^{4}	lines/sq in
webers/sq meter	10^{-4}	webers/sq cm
webers/sq meter	6.452×10^{-4}	webers/sq in
weeks	168	hours
weeks	10,080	minutes
weeks	604,800	seconds

Multiply	by	to obtain
yards	91.44	centimeters
yards	3	feet
yards	36	inches
yards	9.144×10^{-4}	kilometers
yards	0.91440	meters
yards	4.934×10^{-4}	miles (naut.)
yards	5.682×10^{-4}	miles (stat.)
yards	914.4	millimeters
years (sidereal)	365.2564	days (mean solar)
years (sidereal)	366.2564	days (sidereal)
years (tropical, mean solar)	365.2422	days (mean solar)
years (common)	8760	hours
years (tropical, mean solar)	8765.8128	hours (mean solar)
years (leap)	366	days
years (leap)	8784	hours
years (tropical, mean solar)	3.155693×10^{7}	seconds (mean solar)
years (tropical, mean solar)	1.00273780	years (sidereal)

II. BASIC AND SUPPLEMENTARY UNITS

A meter(m) is 1 650 763.73 wavelengths in vacuo of the radiation corresponding to the transition between the energy levels $2p_{10}$ and $5d_5$ of the krypton 86 atom.

A kilogram (kg) is the mass of the international prototype in the custody of the Bureau International des Poids et Mesures at Sevres in France.

A second (sec) is the interval occupied by 9 192 631 770 cycles of the radiation corresponding to the transition of the caesium-133 atom when unperturbed by exterior fields.

An ampere is the constant current which if maintained in two parallel recti-linear conductors of infinite length of negligible circular cross-section and placed at a distance of one meter apart in vacuo would produce between these conductors a force equal to 2×10^{-7} newton per meter length.

A kelvin (^{o}K) is the degree interval of the thermodynamic scale on which the temperature of the triple point of water is 273.16 degrees.

A candle is such that the luminance of a full radiator at the temperature of solidification of platinum is 60 units of luminous intensity per square centimeter.

A mole (mol) is the amount of substance which contains as many elementary units as there are atoms in 0.012 kg of carbon - 12. The elementary unit must be specified and may be an atom, an ion, an electron, a photon, etc. or a given group of such entities.

A radian is the angle subtended at the cent of a circle by an arc of the circle equal in length to the radius of the circle.

A steradian is the solid angle which, having its vertex at the center of a sphere, cuts off an area of the surface of the sphere equal to that of a square with sides of length equal to the radius of the sphere.

III. DERIVED UNITS AND QUANTITIES

The liter was defined in 1901 as the volume of 1 kilogram of pure water at normal atmospheric pressure and maximum density equal therefore to 1.000 028 dm^3. This 1901 definition applied for the purpose of the 1963 Weights and Measures Acts.

By a resolution of the twelfth Conference General des Poids et Mesures (CGPM) in 1964 the word "liter" is now recognised as a special name for the dm^3, but is not used to express high precision measurements. It will be used widely in engineering and the retail business, where the discrepancy of 28 parts in 1 million is of negligible significance.

A newton (N) is that force which, when applied to a body of mass of one kilogram gives it an acceleration of one meter per second per second.

Stress is defined as the resultant internal force per unit area resisting change in the shape or size of a body acted on by external forces, and is therefore measured in newtons per square meter. (N/m^2)

A bar is a pressure equivalent to 100 000 newtons acting on an area of one square meter.

A joule (J) is the work done when the point of application of a force of one newton is displaced through a distance of one meter in the direction of the force.

A watt is equal to one joule per second.

Dynamic Viscosity is the property of a fluid whereby it tends to resist relative motion within itself. It is the shear stress, i.e. the tangential force on unit area, between two infinite horizontal planes at unit distance apart, one of which is fixed while the other moves with unit velocity. In other words, it is the shear stress divided by the velocity gradient, i.e. $(N/m^2) \div (m/sec/m) = N\ sec/m^2$

Kinematic Viscosity is the dynamic viscosity of a fluid divided by its density, i.e. $(N\ sec/m^2)/(kg/m^3) = m^2/sec$

Density of Heat Flow Rate (or Heat Flux) is the heat flow rate (W) per unit area, i.e. W/m^2.

Coefficient of Heat Transfer is the heat flow rate (W) per unit area per unit temperature difference, i.e. $W/m^2 {}^oC$.

Thermal Conductivity is the quantity of heat which will be conducted in unit time through unit area of a slab of material of unit thickness with a unit difference of temperature between the faces; in other words, the heat flow rate (W) per unit area per unit temperature gradient, i.e. $W/[m^2({}^oC/m)] = W/m{}^oC$.

The Heat Capacity of a substance is the quantity of heat gained or lost by the substance per unit temperature change, i.e. $J/{}^oC$.

Specific Heat Capacity is the heat capacity per unit mass of the substance, i.e., $J/kg{}^oC$.

Internal Energy is the kinetic energy possessed by the molecules of a substance due to temperature and is measured in joules (J).

Specific Internal Energy (u) is the internal energy per unit mass of the substance, i.e. J/kg. When a small amount of heat is added at constant volume the increase in specific internal energy is given by: $du = c_v\ dT$, where c_v is the specific heat capacity at constant volume, and dT is the increase in absolute temperature.

Specific Enthalpy (h) is defined by the equation: $h = u + pv$ where p is the pressure and v is the specific volume. Specific enthalpy is measured in J/kg. When a small amount of heat is added to a substance at constant pressure, the increase in specific enthalpy is given by:-$dh = cp\ dT$, where cp is the specific heat capacity at constant pressure.

The Specific Latent Heat of a substance is the heat gained per unit mass without an accompanying rise in temperature during a change of state at constant pressure. It is measured in J/kg.

The Entropy (S) of a substance is such that when a small amount of heat is added, the increase in entropy is equal to the quantity of heat added (dQ) divided by the absolute temperature (T) at which the heat is absorbed; i.e. $dS = dQ/T$, measured in $J/^oK$.

The Specific Entropy (s) of a substance is the entropy per unit mass, i.e. J/kg^oK.

A volt is the difference of electric potential between two points of a conductor carrying a constant current of one ampere when the power dissipated is one watt.

A weber (Wb) is the magnetic flux through a conductor with a resistance of one ohm when reversal of the direction of the magnetic flux causes the transfer of one coulomb in the conductor loop.

The magnetic flux density is the normal magnetic flux per unit area and is measured in teslas.

A lumen, the unit of luminous flux, is the flux emitted within unit solid angle of one steradian by a point source having a uniform intensity of one candle.

A lux is an illumination of one lumen per square meter.

Luminance is the luminous intensity per unit area of a source of light or of an illumination. It is measured in candles per square meter.

IV. PHYSICAL CONSTANTS

Standard Temperature and Pressure (S.T.P.) $\left\{\begin{array}{l} = 273.15\ ^{o}\mathrm{K} \text{ and } 1.013 \times 10^{5}\ \mathrm{N/m^{2}} \\ = 0\ ^{o}\mathrm{C} \text{ and } 1.013 \text{ bar} \\ = 0\ ^{o}\mathrm{C} \text{ and } 760 \text{ mm Hg} \end{array}\right.$

Molecular Volume of ideal gas at S.T.P. = 22.41 liters/mol

Gas Constant (R) = 8.314 J/mol ^{o}K

$\mathrm{RT}_{(273.15\ ^{o}\mathrm{K})}$ = 2.271×10^{3} J/mol

Avogadro Constant = 6.023×10^{23}/mol

Boltzmann Constant = 1.3805×10^{-23} J/K

Faraday Constant = 9.6487×10^{4} ^{o}C/mol (=A s/mol)

Planck Constant = 6.626×10^{-34} J sec

Stefan-Boltzman Constant = 5.6697×10^{-8} $\mathrm{W/m^{2}\ K^{4}}$

Ice Point of Water = 273.15 ^{o}K (0^{o}C)

Triple Point of Water = 273.16 ^{o}K (0.01 ^{o}C)

Speed of light = 2.998×10^{8} m/sec

Acceleration of Gravity $\left\{\begin{array}{ll} \text{(Standard)} & = 9.80665\ \mathrm{m/s^{2}} \\ \text{(Greenwich)} & = 9.81188\ \mathrm{m/s^{2}} \end{array}\right.$ $\left[\begin{array}{l}\text{Take g as} \\ 9.81\ \mathrm{m/s^{2}}\end{array}\right]$

Universal Constant of Gravitation = 6.670×10^{-11} Newton $\mathrm{m^{2}/kg^{2}}$

Mass of hydrogen atom = 1.6734×10^{-27} kg

V. PROPERTIES OF WATER*

Temperature (°F)	Specific Weight, γ (lb/ft^3)	Mass Density, ρ (lb-sec^2/ft^4)	Dynamic Viscosity, $\mu \times 10^5$ (lb-sec/ft^2)	Kinematic Viscosity, $\nu \times 10^5$ (ft^2/sec)	Surface Energy,* $\sigma \times 10^3$ (lb/ft)	Vapor Pressure, p_v (lb/in.^{2})	Bulk Modulus, $E \times 10^{-3}$ (lb/in.^{2})
32	62.42	1.940	3.746	1.931	5.18	0.09	290
40	62.43	1.938	3.229	1.664	5.14	0.12	295
50	62.41	1.936	2.735	1.410	5.09	0.18	300
60	62.37	1.934	2.359	1.217	5.04	0.26	312
70	62.30	1.931	2.050	1.059	5.00	0.36	320
80	62.22	1.927	1.799	0.930	4.92	0.51	323
90	62.11	1.923	1.595	0.826	4.86	0.70	326
100	62.00	1.918	1.424	0.739	4.80	0.95	329
110	61.86	1.913	1.284	0.667	4.73	1.24	331
120	61.71	1.908	1.168	0.609	4.65	1.69	333
130	61.55	1.902	1.069	0.558	4.60	2.22	332
140	61.38	1.896	0.981	0.514	4.54	2.89	330
150	61.20	1.890	0.905	0.476	4.47	3.72	328
160	61.00	1.896	0.838	0.442	4.41	4.74	326
170	60.80	1.890	0.780	0.413	4.33	5.99	322
180	60.58	1.883	0.726	0.385	4.26	7.51	318
190	60.36	1.876	0.678	0.362	4.19	9.34	313
200	60.12	1.868	0.637	0.341	4.12	11.52	308
212	59.83	1.860	0.593	0.319	4.04	14.7	300

VI. PERIODIC TABLE OF THE ELEMENTS

Complements of

Lenox Institute of Water Technology

Groups ⇨ Periods & sub-shells ⇩	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIII	10	11 IB	12 IIB	13 IIIA	14 VIA	15 VA	16 VIA	17 VIIA	18 O
1 1s	1 H 1.00794 Hydrogen																1 H 1.00794 Hydrogen	2 He 4.00260 Helium
2 2s2p	3 Li 6.941 Lithium	4 Be 9.01218 Beryllium											5 B 10.811 Boron	6 C 12.011 Carbon	7 N 14.0067 Nitrogen	8 O 15.9994 Oxygen	9 F 18.9984 Fluorine	10 Ne 20.179 Neon
3 3s3p	11 Na 22.9897 Sodium	12 Mg 24.305 Magnesium											13 Al 26.9815 Aluminum	14 Si 28.0855 Silicon	15 P 30.9738 Phosphorus	16 S 32.066 Sulfur	17 Cl 35.4527 Chlorine	18 Ar 39.948 Argon
4 4s3d4p	19 K 39.098 Potassium	20 Ca 40.078 Calcium	21 Sc 44.9559 Scandium	22 Ti 47.88 Titanium	23 V 50.9415 Vanadium	24 Cr 51.996 Chromium	25 Mn 54.938 Manganese	26 Fe 55.847 Iron	27 Co 58.933 Cobalt	28 Ni 58.69 Nickel	29 Cu 63.546 Copper	30 Zn 65.39 Zinc	31 Ga 69.723 Gallium	32 Ge 72.561 Germanium	33 As 74.9216 Arsenic	34 Se 78.96 Selenium	35 Br 79.904 Bromine	36 Kr 83.80 Krypton
5 5s4d5p	37 Rb 85.468 Rubidium	38 Sr 87.62 Strontium	39 Y 88.9059 Yttrium	40 Zr 91.224 Zirconium	41 Nb 92.9064 Niobium	42 Mo 95.94 Molybdenum	43 Tc (98) Technetium	44 Ru 101.07 Ruthenium	45 Rh 102.906 Rhodium	46 Pd 106.42 Palladium	47 Ag 107.868 Silver	48 Cd 112.411 Cadmium	49 In 114.82 Indium	50 Sn 118.710 Tin	51 Sb 121.75 Antimony	52 Te 127.60 Tellurium	53 I 126.90 Iodine	54 Xe 131.29 Xenon
6 6s4f5d6p	55 Cs 132.905 Cesium	56 Ba 137.327 Barium	57 La 138.906 Lanthanum	72 Hf 178.49 Hafnium	73 Ta 180.948 Tantalum	74 W 183.85 Tungsten	75 Re 186.207 Rhenium	76 Os 190.2 Osmium	77 Ir 192.22 Iridium	78 Pt 195.08 Platinum	79 Au 196.97 Gold	80 Hg 200.59 Mercury	81 Tl 204.383 Thallium	82 Pb 207.2 Lead	83 Bi 208.98 Bismuth	84 Po (209) Polonium	85 At (210) Astatine	86 Rn (222) Radon
7 7s5f6d	87 Fr (223) Francium	88 Ra (226) Radium	89 Ac (227) Actinium	104 Rf (261) Rutherfordium	105 Ha (262) Hahnium	106 Sg (263) Seaborgium	107 Ns (262) Nielsbohrium	108 Hs (265) Hassium	109 Mt (266) Metnenium	110		112						

	19	20	21	22	23	24	25	26	27	28	29	30	31	32
6 4f	58 Ce 140.115 Cerium	59 Pr 140.91 Praseodymium	60 Nd 144.24 Neodymium	61 Pm (145) Promethium	62 Sm 150.35 Samarium	63 Eu 167.26 Europium	64 Gd 157.25 Gadolinium	65 Tb 158.925 Terbium	66 Dy 162.50 Dysprosium	67 Ho 164.930 Holmium	68 Er 167.26 Erbium	69 Tm 168.934 Thulium	70 Yb 173.04 Ytterbium	71 Lu 174.967 Lutetium
7 5f	90 Th 232.038 Thorium	91 Pa (231) Protactinium	92 U 238.029 Uranium	93 Np (237) Neptunium	94 Pu (244) Plutonium	95 Am (243) Americium	96 Cm (247) Curium	97 Bk (247) Berkelium	98 Cf (251) Californium	99 Es (252) Einsteinium	100 Fm (257) Fermium	101 Md (258) Mendelevium	102 No (259) Nobelium	103 Lr (262) Lawrencium

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